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Part I: The Simulation of Effective Transport Coefficients in Composite Materials II: Electron Localization: Quantum Molecular Dynamics presented by

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has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

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PART I

THE SIMULATION OF EFFECTIVE TRANSPORT COEFFICIENTS IN COMPOSITE MATERIALS

PART II

ELECTRON LOCALIZATION : QUANTUM MOLECULAR DYNAMICS

BY

SHEH-YI SHEU

A DISSERTATION

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ABSTRACT

PART I

THE SIMULATION OF EFFECTIVE TRANSPORT COEFFICIENTS IN COMPOSITE MATERIALS

PART II

ELECTRON LOCALIZATION : QUANTUM MOLECULAR DYNAMICS

BY

SHEH-YI SHEU

PART I

Simulation methods for the investigation of effective transport coefficients in composite materials are an extremely important technique in science. We study composite materials consisting of spherical impenetrable inclusions embedded in a homogeneous matrix. The method is referred to as an analytic-simulation method. The effective transport properties can be: diffusion, dielectric behavior, elastic and viscous constants, electric and thermal conductivity, and magnetic susceptibility. For a given configuration of inclusions, a set of coupled algebraic linear equations written in terms of the t-operators and the propagators between inclusions is solved to obtain the multipole moments of the inclusions. The minimum image convention, a spherical interaction cutoff, is used to evaluate the multipole moments for each inclusion. The resulting total sample polarization is related by macroscopic electrostatics to the sample's effective dielectric constant. We simulate two classes of properties of a composite material: the static and frequency dependent dielectric

constant. For the static dielectric constant, we investigate how the effective dielectric constant, ϵ_{μ} , is controlled by multipolar effects. The investigated systems are conducting inclusions in an insulating matrix, the inverse case, and coated inclusions (composite-composites). Due to the difficulty of obtaining converged results for ε_{a} , for conducting inclusions in an insulating matrix, at volume fractions above 0.5, we evaluate ϵ_{ρ} by a random walk method. The random walk method permits an accurate evalution of ϵ_{μ} up to volume fractions corresponding to near to close packing of the inclusions. We also consider the frequency dependent effective dielectric constant, $\varepsilon_{a}(\omega)$, of composites with metallic inclusions, modelled as Drude oscillators, in an insulating matrix such as a glass. The optical properties such as line-broadening and line-shift of the dielectric constant lineshape of these composites have been studied. We find that the lineshape of $\varepsilon_{a}(\omega)$ is greatly broadened by the allowance for the electrostatic interactions the inclusions in comparison with among the Maxwell-Garnett results. We consider different types of disordered configurations for this problem. Comparison is made between results based on the minimum image convention and the lattice-sum approach. The former method is more efficient than the customary lattice sum approach, which employs Ewald sums, and yields results in good agreement with the latter method.

PART II

Quantum molecular dynamics (an Adiabatic Simulation Method) has been used to discuss an excess quantum electron which interacts through pseudopotentials with a fluid of classical molecules. A detailed algorithm for the investigation of the equilibrium and dynamical properties of this coupled quantum-classical system is described. This study focuses on the localization, dynamics, and mode of transport of an excess electron in condensed helium. Properties investigated include the correlation functions and electronic energy of the ground and lowest excited states, and the diffusion coefficient of the ground state electron. Copyright by SHEH-YI SHEU 1990

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TO MY FAMILY

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PART I

CHAPTER 1 INTRODUCTION	1
CHAPTER 2 HISTORY	8
2.1 DEVELOPMENT OF THE STATIC ϵ_{e}	8
2.2 DEVELOPMENT OF THE FREQUENCY DEPENDENT $\epsilon_{e}^{(\omega)}$	13
2.2.1 DRUDE FUNCTION FOR METALLIC INCLUSION	13
2.2.2 THE QUANTUM SIZE EFFECT OF $\epsilon_{e}^{(\omega)}$	17
CHAPTER 3 ANALYTIC DEVELOPMENT	20
3.1 THE PRINCIPAL EQUATION	21
3.2 DIPOLE TENSOR $\nabla \nabla (\mathbf{r}^{-1})$	29
CHAPTER 4 NUMERICAL METHOD	38
4.1 METHODS OF GENERATING CONFIGURATIONS	38
4.1.1 IMMEDIATE METHOD	38
4.1.2 METROPOLIS METHOD	40
4.1.3 THE DISORDER OF CONFIGURATIONS	42
a) RANDOMIZED LATTICE	42
b) VACANCY LATTICE	44
4.1.4 MINIMUM IMAGE METHOD	45
4.2 COMPUTATIONAL ALGORITHM	45

CHAPTER 5 RESULTS AND DISCUSSION	51
5.1 THE STATIC DIELECTRIC CONSTANT	52
5.1.1 CONDUCTING INCLUSIONS	52
5.1.2 AN INVERSE CASE	55
5.1.3 A SPECIAL CASE	57
5.1.4 COATED INCLUSIONS	58
5.1.5 CONCLUSION	6 3
5.2 THE FREQUENCY DEPENDENT $\epsilon_{e}^{}(\omega)$	6 6
5.2.1 RANDOMIZED LATTICE	68
5.2.2 VACANCY LATTICE	70
5.2.3 RANDOM SIZE-DISTRIBUTED EFFECT	73
5.2.4 SILVER IN GLASS	78
5.2.5 COMPARISON OF MINIMUM IMAGE AND	
LATTICE SUM METHODS	80
CHAPTER 6 CONCLUSION	84
APPENDIX A DERIVATION OF THE LATTICE SUM FOR	
INDUCED DIPOLAR SYSTEM	8 8
APPENDIX B IRREDUCIBLE CARTESIAN TENSORS	97
APPENDIX C LIST OF COMPUTER PROGRAMS	101
REFERENCES	133
PART II	
CHAPTER 1 INTRODUCTION	138
CHAPTER 2 COMPUTATIONAL METHODS	145
2.1 MOLECULAR DYNAMICS	145
2.2 SCHRODINGER EQUATION	155
2.3 THE ADIABATIC SIMULATION METHOD	164

.

2.4 THE 1	MOVING GRID TECHNIQUE	167
CHAPTER 3	RESULTS AND DISCUSSIONS	169
CHAPTER 4	CONCLUSIONS	18 2
APPENDIX A	LIST OF REFERENCE PARAMETERS	184
APPENDIX B	LIST OF COMPUTER PROGRAMS	185
REFERENCES		218

•

.

.

LIST OF TABLES

PART I

.

Table	1	Comparison of	ε _e /ε ₂	for	a special case.	59
Table	2	Comparison of	ε _e /ε _m	fo r	composite-composites case.	61

PART II

Table 2.1	List of the diffusion coefficient of helium.	154
Table A.1	List of the reference parameters.	184

LIST OF FIGURES

•

PART I

Figure 3.1	Supercells.	31
Figure 4.1	Comparison of the radial distribution functions.	43
Figure 5.1	Plots of $\epsilon_{e}^{\prime}/\epsilon_{2}^{\prime}$ for conductors-in-insulating matrix	
	versus ϕ .	54
Figure 5.2	Plots of $\epsilon_e^{\ell}/\epsilon_2^2$ for insulators in conducting matrix	
	versus ϕ .	56
Figure 5.3	Plots of $\epsilon_{e}^{2}/\epsilon_{2}$ for composite-composites versus ϕ .	62
Figure 5.4	Plots of CPU time versus the dimension of matrix.	64
Figure 5.5	The $\epsilon_{e}^{2}/\epsilon_{2}^{2}$ versus ϕ for the different types of	
	configurations.	65
Figure 5.6	Im $\varepsilon_{e}(\omega)$ for fluid and randomized lattice.	6 9
Figure 5.7a	Im $\varepsilon_{e}(\omega)$ for vacancy lattice.	71
Figure 5.7b	Im $\varepsilon_{e}(\omega)$ for vacancy lattice.	72
Figure 5.8	The log-normal distribution.	74
Figure 5.9	Comparison of Im $\epsilon_{e}(\omega)$ for equal-sized and	
	size-distributed fluid.	76
Figure 5.10	Im $\varepsilon_{e}(\omega)$ for size-distributed fluid.	77
Figure 5.11	Im $\varepsilon_{\theta}(\omega)$ for Ag in a glass.	79
Figure 5.12	Cole-Cole plot of silver spheres in glass.	82
Figure 5.13	Im $\epsilon_{e}(\omega)$ for silver spheres in glass.	83

PART II

Figure 2.1	The helium-helium radial distribution function.	150
Figure 2.2	Plot of <r<sup>2> versus time.</r<sup>	153
Figure 3.1	Plot of the electron radial distribution function.	170
Figure 3.2	Contours of the excess electron density.	171
Figure 3.3	The radial distribution function of helium	
	measured from the center of mass of the electron.	173
Figure 3.4	Plots of the electronic energy versus	
	the number of quench steps.	174
Figure 3.5	Contours of the electronic configurations for	
	ground and lowest excited states.	176
Figure 3.6	Plots of the fluctuation of the energy in the	
	molecular dynamics adiabatic simulation.	177
Figure 3.7	The electron mean-square displacement versus	
	time in helium.	1 81

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PART I

THE SIMULATION OF EFFECTIVE TRANSPORT COEFFICIENTS

IN COMPOSITE MATERIALS

1. INTRODUCTION

Many composite materials are of great scientific and technological interest. The concept of the dielectric constant is of considerable importance in the description of the macroscopic electric behavior of composite materials. Based on the electrostatic point of view, when an electric field is imposed on a perfect conductor, there is no difference between microscopic and macroscopic fields. In contrast, when we apply the same field on a dielectric system, the dielectric will respond to the field and a polarization will develop at a molecular level, and dipoles will reorient in response to the field. If the constituents of the composite are sufficiently large that they can be assigned a spatially-dependent dielectric constant $\epsilon(\mathbf{r})^{1}$, then the electric displacement $D(\mathbf{r})$ in the system is related to the electric

field E(r) as

$$D(\mathbf{r}) = \varepsilon(\mathbf{r}) E(\mathbf{r}). \tag{1.1}$$

The electric field E(r) is given in terms of the potential field as

$$\mathbf{E}(\mathbf{r}) = - \nabla \psi(\mathbf{r}). \tag{1.2}$$

Let us combine Eqs. (1.1) and (1.2) to obtain a first order

differential equation, which can be applied equally well to similar phenomenologies such as diffusion, electric and thermal conduction, elasticity, viscosity and magnetization². In order to calculate the dielectric constant of a composite material, we must solve Maxwell's equation

$$\nabla \cdot \mathbf{D}(\mathbf{r}) = \mathbf{S}(\mathbf{r}). \tag{1.3}$$

where S(r) is the source term.

Many composite materials are heterogeneous on a scale such that at each space point the material properties obey the macroscopic constitutive equations. Thus, for a macroscopic sample of the material the ensemble average obeys

which gives a definition for the effective dielectric constant ε_{e} of the composite. The concept for this description of phenomena must be on a length scale that is large compared to the typical scale of the inhomogeneities, or the microscopic correlation lengths. The average means a configuration average over many realizations of the material distribution functions, a so-called statistically ensemble average.

In order to evaluate the effective dielectric constant ε_{e} , the composite material's structure must be prescribed; this is done

statistically. Then an averaging procedure must be carried out over the prescribed distribution of configurations.

We study materials consisting of spherical non-overlapping inclusions, which are assumed to be statistically distributed with a probability distribution independent of the position of the external applied field, embedded in a homogeneous matrix.

Simulations for the investigation of effective transport coefficients in composite materials have become an extremely powerful technique in science. The properties of diffusion, dielectric, elastic, and viscous constants, electric and thermal conductivity, and magnetic susceptibility can be studied by analogous methods. There are two steps in the study of effective transport properties by this technique: First, an expression for the transport property must be given in terms of some microscopic quantities, which can be obtained from the simulation method. For example, the effective dielectric constant $\boldsymbol{\varepsilon}_{a}$ of a composite material is obtained via the polarization of sample and the electric field. The polarization is defined as the total dipole moment per unit volume. Here the microscopic quantity is the dipole moment on each inclusion. Second, a simulation method must be developed to evaluate these microscopic quantities.

The method we present is a combination of an analytic calculation and a numerical simulation, which we will refer to as an analytic-simulation method. It is exact in principle. For the given dielectric constants of the inclusion and matrix, the sizes, shapes,

volume fraction ϕ and distribution in space of the inclusions it will yield ε_{e} to the accuracy implied by a finite size simulation of an infinite material.

In order to evaluate an accurate ε_{a} , we employ a technique similar to the method used by Lebenhaft and Kapral in their study of diffusion-controlled reactions³. For a given configuration of inclusions, a set of coupled linear equations for the multipole moments of the polarization of the inclusions can be written in terms of the t-operators of each inclusion and the propagator between pairs of the inclusions. The total polarization of the sample is obtained by matrix algebra. The multipole expansion for the polarization is required to convert the coupled integral equations for the inclusion polarizations to linear algebraic equations. The t-operator gives the response of the ith inclusion to an "arbitrary field", which arises from the external field and all the inclusions excluding the ith inclusion. Correlations among the inclusions are exactly accounted for with this method. For high volume fractions of the inclusions it is necessary to be concerned with the higher multipole contributions for the calculation of an accurate effective dielectric constant. A systematic and direct method is used to solve these linear coupled equations, Eq. In the following, numerical results for some special models (3.19). will illustrate the importance of multipole contributions to the effective dielectric constant.

The simulations will be carried out by generating the inclusions in a primary cell (typically using a Monte Carlo method) and

periodically imaging the cell. We use a minimum image method to evaluate the dipole moment and higher order multipoles of a given inclusion inside the primary cell.

As the multipole moments are defined in terms of the propagator tensors, the dipole field involves the dipole tensor $\nabla (\frac{1}{r})$. This is a long-ranged interaction and leads to conditional convergence of dipole sums. Due to the long-ranged behavior of the dipole tensor, the dielectric constant is not well-defined i.e. it is sample shape-dependent in the thermodynamic limit. The lattice sum approach, which employs a large number of periodic images of the primary cell and involves an Ewald-summation method⁴, has been used to represent the dipole propagator in an efficient and rapidly convergent form. Comparison is made between results based on the minimum image method and the lattice-sum approach.

In the investigation of the optical properties of composite materials, it is the frequency dependent effective dielectric constant $\varepsilon_{e}(\omega)$ that is experimentally probed. The absorption lineshape-broadening and line-shift of the frequency dependent dielectric constant for composite materials can also be studied by the analytic-simulation method. The types of the configurations we investigate include: randomized lattice, vacancy lattice, and mono- and poly-disperse liquid-like structure.

The frequency dependent dielectric constant of the inclusions is given by a Drude model, as appropriate to metallic inclusions. We find

that the lineshape of the imaginary part of the effective dielectric constant is greatly broadened by the allowance for the electrostatic interactions among the inclusions in comparison with the Maxwell-Garnett results.

The rest of our work is outlined as follows. In Chapter 2 we review some methods for calculating the effective dielectric constant of composite materials. The first section discusses the historical development of the methods of calculation of the static dielectric constant in random media. The second section contains an introduction of the concept of the Drude model for a metallic inclusion and the development of the frequency dependent dielectric constant in composite materials. We also discuss the Quantum size effect that becomes important for small particles. In Chapter 3 the analytic development of analytic-simulation method is presented in terms of the t-operator or the polarizability of the inclusion and the propagator tensor $G^{\mathcal{U}}$. The relation between the microscopic dipole moments and the macroscopic averaged polarization is discussed. The other part in this Chapter discusses the properties of the dipolar tensors including the basic idea of the lattice sum approach. In Chapter 4 we describe the numerical simulation methods and introduce the different methods to generate the different types of configurations. We extend the minimum image method to calculate the dipole moments and higher order multipoles for each inclusion. The rest of this Chapter demonstrates the intent of the computer programs and lists the algorithm for computations. In Chapter 5 we present the results for the different physical models. First, in the static dielectric problem we use the

analytic-simulation method to discuss the conducting case, the inverse case and a composite-composite case. Then, the results from the random walk method are compared with those of the analytic-simulation method for the conducting case. The second section contains the calculation of the frequency dependent dielectric constant for the different types of configurations for a hypothetical and more realistic model of silver in glass. Finally, we compare the results of the analytic-simulation method using the minimum image method with the results of the lattice-sum approach. Chapter 6 contains the conclusions and outlines future applications of the method to composites with non-spherical electromagnetic versus inclusions. electrostatic effects and wavevector-dependent effective transport coefficients.

2. HISTORY

2.1 DEVELOPMENT OF THE STATIC ϵ_{e}

Theories about the static dielectric constants of composite materials have a long history. For this field there is a great deal of literature reviewed by Landauer¹. In the following we will briefly summarize some approaches to these problems.

A general expression for the dielectric virial coefficient for the one inclusion problem was derived by Maxwell⁵ in 1873. He considered a spherical inclusion of dielectric constant ε_1 embedded in a matrix of dielectric constant ε_2 . The dielectric constant ε_e of a macroscopic sample of the material depends on the ratio $\varepsilon_1/\varepsilon_2$ and the volume fraction of inclusions, 4. His formula takes into account the induced dipole moments of the inclusions, and the ε_e is calculated by taking the result from one inclusion and multiplying by the number density of inclusions. This can be applied to obtain an accurate ε_e for small volume fractions. For the dilute inclusion problem ε_e is given by

 $\varepsilon_{\phi}/\varepsilon_2 = 1 + 3 \alpha \phi \tag{2.1}$

where $\alpha = \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}$ and $\phi = \frac{4\pi}{3V} a^3 N$. V is the volume of the system, • a is the radius of inclusion, and N is the number of inclusions.

Maxwell-Garnett⁶ presented an effective medium theory for the calculation of $\varepsilon_{\rm e}$. The $\varepsilon_{\rm e}$ evaluated by this theory is identical to a result from the Clausius-Mossotti formula^{7,8}. In effective medium theory the effective field applied on a given inclusion is defined as the sum of an applied field and a field due to the polarizations induced on the other inclusions. The matrix is thought of as a homogeneous polarized medium surrounding the inclusions. This leads to an expression

$$\frac{(\varepsilon_{e} - \varepsilon_{2})}{(\varepsilon_{e} + 2\varepsilon_{2})} = \frac{(\varepsilon_{1} - \varepsilon_{2})}{(\varepsilon_{1} + 2\varepsilon_{2})} \phi.$$
(2.2)

called the Maxwell-Garnett or Clausius-Mossotti formula.

A similar expression was also obtained by $Bruggeman^9$. He iterated the polarization of the inclusions and the matrix until the average net polarization vanishes. It is a self-consistent field calculation. He employed this method to improve the Clausius-Mossotti result. The formal expression is

$$\left[\begin{array}{c} (\varepsilon_{1} - \varepsilon_{e}) \\ \hline (\varepsilon_{1} + 2\varepsilon_{e}) \end{array}\right] \phi + \left[\begin{array}{c} (\varepsilon_{2} - \varepsilon_{e}) \\ \hline (\varepsilon_{2} + 2\varepsilon_{e}) \end{array}\right] (1 - \phi) = 0 \quad (2.3)$$

This treats the two phases in a symmetric fashion.

These mean field theories neglect the correlations among the inclusions, which become important at high volume fractions of inclusions. Certainly, these theories have the virture of simplicity and give physically meaningful results over the entire range of volume fractions. However, it is necessary to ascertain whether ε_{e} can be calculated accurately by these theories.

 ε can be expressed as an expansion in the volume fractions of inclusions. It is a virial series :

$$\varepsilon_{\phi}/\varepsilon_2 = 1 + A_1\phi + A_2\phi^2 + \dots$$
 (2.4)

Batchelor¹⁰ discussed the calculation of the second virial coefficient. The second virial coefficient involves the two-body distribution function and reflects the local structure of the system. In 1968, Levine and McQuarrie¹¹ obtained the polarizability of metallic spheres embedded in insulating medium by solving Laplace's equation in bispherical coordinates to get an exact second dielectric virial coefficient. In 1973 Jeffrey¹² expanded the work of Maxwell to second order by using Batchelor's¹⁰ method, which reduced the problem to a consideration of interactions between pairs of spheres, in order to avoid the convergence difficulties. He used a twin spherical harmonics expansion due to Ross¹³ to solve the two-spheres Laplace problem. In Jeffrey's work the second dielectric virial coefficient **ر** A corresponding to thermal conduction, is evaluated explicitly for all

values of the ratio of conductivities of the two phases.

Subsequently, Felderhof, Ford and Cohen¹⁴ developed a multiple scattering expansion in order to obtain a formal expression for the virial coefficients. They formulated an infinite system as an expansion in cluster terms, each of which is absolutely convergent. By rearrangement of the terms, corresponding to removing the depolarization effects, problems of conditional convergence never arise in their problem.

Sridharan and Cukier¹⁵ developed a t-operator multiple scattering theory for the Clausius-Mossotti function $\frac{(\epsilon_{\rm e} - \epsilon_{\rm 2})}{(\epsilon_{\rm e} + 2\epsilon_{\rm 2})}$ as a virial expansion in terms of a reference medium dielectric constant $\epsilon_{\rm m}$. There are several results obtained from their expressions. When they neglect the correlations among the inclusions and $\epsilon_{\rm m}$ is set to be equal to the medium dielectric constant $\epsilon_{\rm 2}$, they get the Clausius-Mossotti formula. When $\epsilon_{\rm m}$ is set to the effective dielectric constant $\epsilon_{\rm e}$, the Bruggeman result is established. As the correlations among inclusions are considered, the second virial coefficient is able to be calculated exactly when we set $\epsilon_{\rm m}=\epsilon_{\rm 2}$. Another result also can be obtained with $\epsilon_{\rm m}=\epsilon_{\rm e}$ called pair order effective medium theory. It is not possible to get results without an approximate evaluation of the formal expression. This theory generalizes Bruggeman's self-consistent lowest order theory. However, the shortcoming of this theory is the difficulty of evaluating the results even at pair order. Because the virial diagrammatic expansion has not been carried out beyond the second virial coefficient, it is restricted to low volume fractions. Meanwhile, the self-consistent expansion is not well controlled. This theory is limited to spherical inclusions and to static material properties. The evaluation of this theory for arbitrarily shaped inclusions and frequency dependent material properties has not been carried out.

A variational approach leading to upper and lower bounds for the effective material properties was developed by Hashin and Shtrikman¹⁶. For a two-phase problem the bounds for ε_{e} are in terms of the ratio $\varepsilon_{1}/\varepsilon_{2}$ and ϕ . When the ratio, $\varepsilon_{1}/\varepsilon_{2}$, is extremely large or small, the bounds are far apart for moderate volume fractions. The variational approach is summarized in the literature¹⁷.

In 1892 Rayleigh¹⁸ solved the partial differential equation to second order for periodically arranged conductors and provided results for a wide range of conductivity and the entire range of volume fraction. McPhedran and McKenzie¹⁹ extended his method to calculate the conductivity of periodic lattices consisting of conducting spheres in an insulating matrix. They solved the problem by a potential and field expansion on each sphere and obtained the expansion coefficients of the fields. They were able to include multipolar effects to very high order. Their results for the conductivity of a regular array of spheres yield good agreement between theory and experimental measurements²⁰, even when the volume fraction approaches a lattice close packed value. 2.2 DEVELOPMENT OF THE FREQUENCY DEPENDENT $\boldsymbol{\varepsilon}_{\boldsymbol{\omega}}(\boldsymbol{\omega})$

2.2.1 DRUDE FUNCTION FOR METALLIC INCLUSION

The development of frequency dependent dielectric properties starts from the assumption of the Drude²¹ model for the dielectric constant of metallic inclusions. If the inclusions are so small that the quantum size effect comes out, then Drude model can no longer be used. Let us consider a system consisting of spherical inclusions of radius "a" embedded in a homogeneous medium with dielectric constant $\varepsilon_1(\omega)$. If the absorption of the medium can be neglected ε_2 is frequency independent and therefore real. For example, the medium could be a ceramic^{22,25}, glass^{23,24}, KCl²⁵, gelatin²⁵ and so on. The definition of the Drude model for the dielectric constant of metallic inclusions is

$$\varepsilon_{1}(\omega) = \varepsilon_{1\infty} - \frac{\omega_{p}^{2}}{\omega (\omega + i \Gamma)}$$
(2.5)

where $\varepsilon_{1\infty}$ is the (complex) high-frequency dielectric constant, ($\varepsilon_{1\infty} = \varepsilon_{1\infty}' \pm i \varepsilon_{1\infty}''$), ω_p is the plasma frequency, which is the natural frequency of the density fluctuation for the free electron in bulk metal, and Γ is the damping constant or width, defined as

$$\Gamma = \gamma_{a} + \Gamma_{ib} = \gamma_{a} + \varepsilon_{1\infty}'' \frac{\omega_{s}^{3}}{\omega_{p}^{2}}.$$
 (2.6)

14

where ω_{a} is the resonant frequency and γ_{a} is the damping constant for a radius "a" of inclusion given by²⁶

$$\gamma_{\mathbf{a}} = \gamma_{\infty} + V_{\mathbf{F}}/\mathbf{a}, \qquad (2.7)$$

where γ_{∞} is the bulk damping constant, $V_{\rm F}$ is the Fermi velocity, and $\Gamma_{\rm ib}$ is the interband contribution. The Drude model provides that the dielectric constant of metal inclusion is a function of the frequency and the damping constant Γ . The dielectric constant can also be written in terms of the frequency dependent conductivity $\sigma(\omega)$

$$\epsilon_1(\omega) = \epsilon_{1\infty} - \frac{i \sigma(\omega)}{\omega}$$
 (2.8)

For one inclusion effect, the frequency independent ε_{e} is replaced by $\varepsilon_{e}(\omega)$ in Eq. (2.1). By combining Eqs. (2.1) and (2.5), the effective dielectric constant $\varepsilon_{e}(\omega)$ has an absorption peak of width Γ centered at the approximate resonant frequency

$$\omega_{g} = \frac{\omega_{p}}{\left(\varepsilon_{10}' + 2\varepsilon_{2}\right)^{1/2}}$$
(2.9)

When the Clausius-Mossotti (CM) or Maxwell-Garnett (MG) expression is applied for $\varepsilon_{E}(\omega)$, we can write the CM formula as

$$\frac{(\epsilon_{e}(\omega) - \epsilon_{2})}{(\epsilon_{e}(\omega) + 2\epsilon_{2})} = \frac{(\epsilon_{1}(\omega) - \epsilon_{2})}{(\epsilon_{1}(\omega) + 2\epsilon_{2})} \phi \qquad (2.10)$$

Eqs. (2.5) and (2.10) show that the lineshape is similar to a Lorentzian distribution with its absorption peak centered around

$$\bar{\omega} = \omega_{\rm p} \left\{ \frac{(1-\phi)}{\epsilon_{1\omega}' (1-\phi) + (2+\phi) \epsilon_2} \right\}^{1/2}$$
(2.11)

The width is independent of the volume fraction of inclusions. These approximate expressions result from the conditions $\Gamma \ll \omega_p$ and $\omega_s \gg \frac{\Gamma}{2}$. The CM results predict that there is a shift of the line to lower frequency due to increasing ϕ and no line broadening since the width does not change.

The description of electromagnetic propagation and the investigation of the optical properties of composite materials in terms of the properties of the dielectric constants of the components and the volume fraction of the inclusions have been done both experimentally and theoretically^{1,27}. One of the key issues involves the broadening of the spectrum due to the effect of interactions among the inclusions.

Kreibig²⁸ calculated $\varepsilon_{e}(\omega)$ for silver in gelatin by using the average-t-matrix approximation (ATA)⁶. The ATA is also a Maxwell-Garnett approximation, corresponding to obtaining an accurate result at low ϕ . Another approach is the Coherent Potential

Approximation (CPA). The CPA corresponds to Bruggeman's effective medium theory⁹. These approximations have the common properties : 1) They are long-wavelength approximations. 2) The scattering process is only dipole, because this is one sphere problem and the response is to a constant applied field. 3) The structural information is only the volume fraction of inclusions.

The interesting problems are related to the strong scattering properties and the higher volume fractions of inclusions. Davis and Schwartz^{25a} employed multiple scattering theory to evaluate $\varepsilon_{e}(\omega)$ for a disordered system with spherical inclusions at quite high ϕ . They used Lax's quasicrystalline approximation (QCA)²⁹, which is known as the Maxwell-Garnett approximation, and compared with the application of Roth's effective medium approximation (EMA)^{30,31}. The EMA provides a complete description of the spatial correlations of the inclusions but not the electromagnetic correlations, and an accurate description of the plasma resonance in composite problems. They found that the EMA is better than the QCA.

Felderhof and Jones²³ calculated $\varepsilon_{e}(\omega)$ for silver in glass or water by a cluster expansion technique, which is combined with a spectral representation analysis based on the work by Bergman³². The $\varepsilon_{e}(\omega)$ in Bergman representation is an integral of Hilbert type with a spectral density determined by the statistical geometry of the configurations, and is accurate to second order in ϕ . The results obtained by them assume dipolar intersphere interactions, and neglect higher multipolar interactions. From section 2.1, note that it is necessary to include the higher order multipolar effects during the calculation of the static dielectric quantities at high ϕ . For example, the contributions from all multipoles to the second dielectric virial coefficient are roughly double that of the dipole contributions. Meanwhile, they²³ found that around the resonance peak the dipolar interaction term dominates the multipolar contributions. They predict that when the distance between the pairs of inclusions is roughly equal to the mean pair separation, d = $(1-\phi)^{1/3}$ a $\phi^{-1/3}$, (a is the radius of inclusions) only pairs of inclusions dominate the line-broadening and line-shift of resonance. The dipolar approximation is quite accurate for $\varepsilon_{e}(\omega)$ at large pair separation or at low ϕ .

Kantor and Bergman² also used Bergman's spectral representation and an expansion in spherical harmonics in order to describe the interactions among the inclusions. They derived an exact theory for calculating $\varepsilon_{e}(\omega)$ for composites. Their theory is not restricted to lower order interactions between inclusions.

2.2.2 THE QUANTUM SIZE EFFECT OF $\epsilon_{\theta}(\omega)$

What is the quantum size effect? Quantum size effects^{33,34} (QSE) occur when the inclusion size is so small that the material properties (e.g. $\varepsilon_1(\omega)$) do depend on size because of the discreteness of the energy levels, yet it is still useful to describe the inclusion in terms of a macroscopic material property.

From the expression Eq. (2.6), γ_a is larger than γ_{∞} due to the finite size of inclusion or the term $\frac{V_F}{a}$. The size of inclusion controls the value of γ_a . Consequently, the width Γ is dominated by γ_a . Therefore, the Drude model of $\varepsilon_1(\omega)$ is size dependent and $\varepsilon_e(\omega)$ is too. The interesting problem is how $\varepsilon_e(\omega)$ is affected as the inclusion size decreases.

"As the particle size continues to decrease to the tens of phenomena involving angstrom range. new quantum physics. electromagnetics, and hydrodynamics are still to be explored." 35 For very small inclusions of equal size and shape, the plasma resonance absorption shifts and broadens, and shows fine structure corresponding to transitions between discrete conduction band energy levels. Two main effects on optical properties may occur as a function of size: a shift of the peak and a change in the width. There are two expressions for the dielectric constant: the classical Drude model used with a size limited mean free path and the quantum mechanical theory of Kawabata and Kubo³⁹ accounting for quantum size effects. If the inclusions are so small that the Drude model can no longer be used, the dielectric constant should take quantum size effects into account.

Fröhlich³⁷ pointed out in 1937 that the continuous electronic conduction band of a metal should break up into observable discrete states when the dimension of the metal become small enough. Kubo³⁵

formulated this problem quantitatively in 1962 and observed these quantum size effects. Both theoretical and experimental results on these problems have been reviewed by Kreibig and Genzel³⁸. There are quantum mechanical and classical models used to explain the changes in the optical properties as the size of particle decreases. In the classical model, the damping constant in the Drude free electron theory, which is the inverse of the collision time for conduction electrons, is increased due to increasing collisions with the boundary of the particles. In quantum mechanical model, Kawabata and Kubo³⁹ have argued that the optical spectrum should be discrete with the spacing increasing as the particle size decreases. The width of the resonance should be described as due to the plasma mode damping which resultes from the excitation of one-particle modes. The peak width predicted by the quantum mechanical model is in better agreement with experiment³³ than that predicted from the size-dependent Drude model, where the size dependence arises from the classical limitation of the electrons' mean free paths.
3. ANALYTIC DEVELOPMENT

We study the problem of the effective transport properties of small material inclusions dispersed in a dielectric host. We use a method similar to that used by Lebenhaft and Kapral in a reaction-diffusion problem³. Let us consider a system consisting of N non-overlapping spherical inclusions of dielectric constant ε_1 and radius "a" embedded in a composite medium of the dielectric constant ε_2 all within a volume V.

If one attempts to impose an external electric field on such a heterogeneous material, it is important to understand the response of the system and that of the inclusions due to an external field. For instance, in rather dilute media, since the inclusion separation is quite large, there is little difference between the macroscopic electric field of the system and that incident on every inclusion. But in dense media due to the closeness of the inclusions, the polarization of neighboring inclusions induces an internal field E_i at any given inclusion in addition to the average macroscopic electric field of the system. The induced dipole moment is proportional to the electric field acting on the inclusions. The polarizability of an inclusion, α , is defined as the ratio of the average polarization to the total applied field on the inclusions. Thus, the inclusion's polarizability

characterizes the capacities of the response to an applied field for inclusions.

The approach is: First, the microscopic induced dipole moments of the inclusions must be addressed by an analytic method. Then, the effective dielectric constant has to be obtained by relating the ensemble average of the total polarization and the macroscopic electric field.

3.1 THE PRINCIPAL EQUATION

According to the electrostatic problem, the material equation for the electric potential, $\psi(\mathbf{r})$, is

$$\nabla \cdot (\varepsilon(\mathbf{r}) \nabla \psi(\mathbf{r})) = S(\mathbf{r})$$
(3.1)

where $\varepsilon(\mathbf{r}) = \varepsilon_1 \ (\varepsilon_2)$ for \mathbf{r} inside (outside) any of inclusions, and S(r) is a source term, which is independent of the positions of the inclusions. For convenience, let $\delta\varepsilon(\mathbf{r}) = \varepsilon(\mathbf{r}) - \varepsilon_2$. If \mathbf{r} is inside an inclusion, $\delta\varepsilon(\mathbf{r})$ equals $\varepsilon_1 - \varepsilon_2$; otherwise it is zero. Rewriting Eq. (3.1) by using the definition $\delta\varepsilon(\mathbf{r})$ yields

$$\varepsilon_2 \nabla^2 \psi(\mathbf{r}) = - \nabla \cdot [\delta \varepsilon(\mathbf{r}) \nabla \psi(\mathbf{r})] + S(\mathbf{r})$$
(3.2)

This alternative permits us to introduce the medium propagator, corresponding to the inverse of the operator $\varepsilon_2 \nabla^2$. Let us take the gradient of Eq. (3.2) and solve it formally to get

$$E(\mathbf{r}) = \int d\mathbf{r}' g(|\mathbf{r} - \mathbf{r}'|) \nabla \nabla \cdot [\delta \varepsilon(\mathbf{r}') E(\mathbf{r}')] + E_0(\mathbf{r})$$
(3.3)

The electric field in Eq. (3.3) has been defined as

$$E(\mathbf{r}) = -\nabla \psi(\mathbf{r}), \qquad (3.4)$$

the propagator in the medium is

$$\mathbf{g}(\mathbf{r}) = (4\pi\epsilon_2 \mathbf{r})^{-1}, \qquad (3.5)$$

and the external source field $\mathop{\mathrm{E}}_{\sim 0}(\mathbf{r})$ is

$$E_{\gamma 0}(\mathbf{r}) = \nabla \int d\mathbf{r}' \mathbf{g}(|\mathbf{r}-\mathbf{r}'|) S(\mathbf{r}')$$
(3.6)

Then, integrating Eq. (3.3) by parts, we have

$$E(\mathbf{r}) = \int d\mathbf{r}' \underline{G}(|\mathbf{r}-\mathbf{r}'|) \cdot \delta \varepsilon(\mathbf{r}') E(\mathbf{r}') + E_0(\mathbf{r})$$
(3.7)

.

where

$$\underline{G}(|\mathbf{r}|) = \nabla \nabla \mathbf{g}(\mathbf{r}) = \underline{H}(\mathbf{r}) - \frac{1}{3\varepsilon_2} \underline{1} \delta(\mathbf{r})$$
(3.8)

$$\underline{\mathbf{H}}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_2 \mathbf{r}^3} (\underline{1} - 3 \hat{\mathbf{r}} \hat{\mathbf{r}}).$$
(3.9)

 $\underline{\underline{H}}(\mathbf{r})$ is a dipole propagator for $\mathbf{r} \neq 0$. $\mathbf{\hat{r}}$ is a unit vector of \mathbf{r} . We only need $\underline{G}(|\mathbf{r}|)$ for $\mathbf{r} \neq 0$, so that the δ -function in Eq. (3.8) is dropped. Therefore, the electric field is given in terms of dipole propagators and $\delta \varepsilon(\mathbf{r})$, the response of the inclusion due to $\underline{E}_0(\mathbf{r})$.

In order to get an expression for the effective dielectric constant, ε_{e} or $\varepsilon_{e}(\omega)$, we define a polarization related to the electric field by $\delta \varepsilon(\mathbf{r})$

$$P = \delta \varepsilon(\mathbf{r}) \quad E(\mathbf{r}) = \sum_{i=1}^{N} \mu_i(\mathbf{r}), \qquad (3.10)$$

where we anticipate that in isotropic media the polarization and field are parallel. The last equality is the sum of the polarization of the inclusions over the N inclusions. Because $\delta \epsilon(\mathbf{r})$ is zero outside the inclusion, the $\mu_i(\mathbf{r})$ is non-zero only inside the ith inclusion.

We review the theory developed by Sridharan and Cukier¹⁵. It is an application of the t-operator method expressed as a multipole expansion. First, we express the { $\mu_i(\mathbf{r})$ } in terms of the one-inclusion scattering operator $\underline{t}_i(\mathbf{r},\mathbf{r}')$, then we write $\mu_i(\mathbf{r})$ to be

$$\mu_{i}(\mathbf{r}) = \int d\mathbf{r}' \, \underline{t}_{i}(\mathbf{r},\mathbf{r}') \cdot \underline{E}_{i,\text{eff}}(\mathbf{r}')$$
(3.11)

Here $E_{i,eff}(\mathbf{r})$ is the "effective "field at r that arises from the presence of all the inclusions excluding the ith. From the perspective of the ith inclusion, all the other inclusions serve to produce a field $E_{i,eff}(\mathbf{r})$, which acts on the ith inclusion. Hence, the field $E_{i,eff}(\mathbf{r})$ is given by

$$E_{\text{ri,eff}}(\mathbf{r}) = E_{0}(\mathbf{r}) + \sum_{j \neq i}^{N} \int d\mathbf{r}' \quad \underline{G}(|\mathbf{r} - \mathbf{r}'|) \cdot \mu_{j}(\mathbf{r}')$$
(3.12)

We use the solution of the electrostatic problem of one inclusion's response to an external field $\mathop{\rm E}_{\sim 0}(r)$ to obtain an expression for $\mathop{\rm t_i}(r,r')$ as a multipole expansion and we have 15,*

$$\underline{t}_{i}(\mathbf{r},\mathbf{r}') = 4\pi\epsilon_{2} \underbrace{1}_{\ell=0}^{\infty} t_{i}^{\ell\ell} (\nabla)^{\ell} \delta(\mathbf{r}-\mathbf{R}_{i}) \odot (\nabla')^{\ell} \delta(\mathbf{r}'-\mathbf{R}_{i})$$
(3.13)

* The multipole expansion for the t-operator is defined as: $\underline{t}_{i}(\mathbf{r}, \mathbf{r}') = \sum_{\ell\ell'}^{\infty} (-1)^{\ell+\ell'} (\ell!\ell'!)^{-1} \underline{t}^{\ell\ell'} \odot [\nabla^{\ell} \delta(\mathbf{r}-\mathbf{R}_{i})][(\nabla')^{\ell'} \delta(\mathbf{r}'-\mathbf{R}_{i})],$ where $\underline{t}^{\ell\ell'}$ is a tensor of rank $(\ell+\ell'+2)$. As $\underline{t}^{\ell\ell'}$ is constructed as: $t_{\alpha\beta,\mu_{1}\mu_{2}}^{\ell\ell'} \cdots \mu_{\ell}\nu_{1}\nu_{2} \cdots \nu_{\ell'} = t_{\beta\ell\ell'}^{\ell\ell} \delta_{\ell\ell'} \delta_{\mu_{1}\nu_{1}} \cdots \delta_{\mu_{\ell}\nu_{\ell}} \delta_{\alpha\beta}$ this yields Eq. (3.13). where $\underset{\sim}{R_{i}}$ is the center of the ith inclusion relative to an arbitrary origin. The term $(\bigtriangledown \bigtriangledown)^{\ell} \delta(r-R_{i}) \odot (\bigtriangledown \bigtriangledown)^{\ell} \delta(r'-R_{i})$ involves the ℓ th order gradient with respect to r of a δ -function centered at $\underset{\sim}{R_{i}}$ fully contracted with the corresponding ℓ th order gradient with respect to r'to give a scalar. The operator \odot means the contraction of two tensors.

For a spherical inclusion, $t_i^{\mathcal{U}}$ is given in terms of the polarizability of inclusion, α_{ℓ} , to be

$$t_{i}^{\ell\ell} = \frac{\alpha_{\ell+1}}{[(\ell+1)! (2\ell+1)!!]}$$
(3.14)

and

$$\alpha_{\ell} = \frac{\ell \left(\epsilon_{2} - \epsilon_{1} \right)}{\epsilon_{1} \ell + \epsilon_{2} \left(\ell + 1 \right)} a^{(2\ell+1)}$$
(3.15)

 $\underline{t}_{i}(\mathbf{r},\mathbf{r}')$ is proportional to the unit tensor $\underline{1}$ and only the terms $t_{i}^{\ell\ell}$ exist in Eq. (3.13), as $t_{i}^{\ell\ell'} = 0$ for $\ell \neq \ell'$. This simplification is only obtained for the spherical inclusion problem and since the Eq. (3.1) is a scalar Maxwell equation.

By combining Eqs. (3.11) and (3.12), an important equation can be produced as

$$\mu_{i}(\mathbf{r}) = \int d\mathbf{r}' \, \underline{t}_{i}(\mathbf{r},\mathbf{r}') \cdot \underline{E}_{o}(\mathbf{r}') + \sum_{j \neq i}^{N} \int d\mathbf{r}' \, \int d\mathbf{r}'' \, \underline{t}_{i}(\mathbf{r},\mathbf{r}') \cdot \underline{G}(|\mathbf{r}'-\mathbf{r}''|) \cdot \mu_{j}(\mathbf{r}''). \qquad (3.16)$$

The first term of the right hand side in Eq. (3.16) describes the single inclusion's polarization induced by the applied field $\underset{\sim}{E_0(r)}$. The second terms imply that the modification of the { $\mu_i(r)$ } arises from the interaction among the inclusions. As an important issue, let us consider the effects on the ith inclusion, as arising from an external field due to the other inclusion. In other words, the inclusions $j \neq i$ set up some field that the ith inclusion feels. The $\underline{t_i(r,r')}$ operator gives the response of the ith inclusion to this field.

Eq. (3.16) is an integral representation for the { $\mu_i(\mathbf{r})$ }; given in terms of the one-inclusion t operator, the dipole propagator \underline{G} and the external applied field. In order to obtain { $\mu_i(\mathbf{r})$ }, if we assume $\underline{t}_i(\mathbf{r},\mathbf{r}')$ is known as a multipole expansion such as Eq. (3.13) and if we express $\mu_i(\mathbf{r})$ as a multipole expansion,

$$\mu_{i}(\mathbf{r}) = \sum_{\ell=0}^{\infty} (-1)^{\ell} (\ell!)^{-1} \mu_{i}^{\ell} \odot \nabla^{\ell} \delta(\mathbf{r} - \mathbf{R}_{i}), \qquad (3.17)$$

then we might be able to obtain a set of coupled algebraic equations for the multipole moments of the $\mu_i(\mathbf{r})$. Here the multipole moment μ_i^{ℓ} is an $(\ell+1)$ th rank tensor for each Cartesian component $(\mu)_{\nu i \nu}$ ($\nu = x, y, z$) of the vector $\mu_i(r)$. It is defined by

$$\mu_{i,\nu_{1},\nu_{2},\nu_{3}}^{\ell}, \dots, \nu_{\ell} = \int d\mathbf{r} \ \mu_{i}(\mathbf{r}) \ \mathbf{r}_{\nu_{1}} \mathbf{r}_{\nu_{2}} \cdots \mathbf{r}_{\nu_{\ell}}$$
(3.18)

Where $\nu_1 \cdots \nu_{\ell}$ each run on the cartesian indices x, y, z and we have set $\underset{\sim}{R_i} = 0$. Note that μ_{i}^{ℓ} is independent of r and it is a constant.

Substituting the multipole expansion of Eqs. (3.13) and (3.18) in Eq. (3.16), and equating terms of equal orders in $(\nabla)^{\zeta} \delta(r-R)$ yields the main analytic equation

$$\mu_{i}^{\ell} = 4\pi\epsilon_{2} \left[t_{i}^{00} \delta_{\ell 0} \underset{\sim}{E}_{0} + \sum_{\ell'=0}^{\infty} t_{i}^{\ell \ell} \sum_{j\neq i}^{N} \underline{G}^{\ell \ell'}(|\mathbf{R}_{ij}|) \circ \mu_{j}^{\ell'} \right]$$
(3.19)

The first term on the right hand side involves the assumption that $E_{\sim 0}(\mathbf{r})$ is a constant external field, $E_{\sim 0}$. This is to correspond to the standard experimental situation. The quantity $\underline{G}^{\ell\ell'}(|\mathbf{R}_{\sim ij}|)$ depends only on the center to center distance $|\mathbf{R}_{\sim ij}| = |\mathbf{R}_{\sim i} - \mathbf{R}_{\sim j}|$ between the ith and jth inclusions and is defined as

$$\underline{G}^{\ell\ell'}(|\underline{R}_{ij}|) = \nabla^{\ell} \nabla^{\ell'} \underline{G}(|\underline{r}-\underline{r}'|) | |\underline{r}-\underline{r}'| = |\underline{R}_{ij}|.$$
(3.20)

It is a rank ($\ell + \ell' + 2$) propagator tensor.

The reason that we use the multipole expansion in this problem is to reduce the coupled integral equations to coupled algebraic equations which can be solved easily. In practice, the problem becomes numerically large, since for N inclusions, we have to solve the linear algebraic equations, and to get convergence ℓ may have to be quite large.

In order to relate { μ_{i}^{0} } to the $\varepsilon_{e}^{}$, we need to define a macroscopic parameter, \underline{Q} , called the average polarizability tensor, which connects the mean polarization to the external electric field.

The mean polarization is written as

$$\frac{1}{\epsilon_2 V} \left\langle \sum_{i=1}^{N} \mu_i^{\circ} \right\rangle = \mathbf{Q} \cdot \mathbf{E}_{\mathbf{v}}$$
(3.21)

Due to the dipole propagator's $\frac{1}{r^3}$ range, the polarization depends on the macroscopic system's shape. \underline{Q} is a shape-dependent polarizability tensor, but $\varepsilon_{\underline{Q}}$ cannot be shape dependent¹⁶. Macroscopic electrostatics provides the connection between \underline{Q} and $\varepsilon_{\underline{Q}}^{40}$. Fixman⁴¹ has provided a clear discussion of this connection. For a spherical macroscopic system, the relation is given as

$$\frac{(\epsilon_{e} - \epsilon_{2})}{(\epsilon_{e} + 2\epsilon_{2})} = \frac{Q}{3}$$
(3.22)

where $Q = \frac{1}{3}$ Tr(\underline{Q}).

Other macroscopic geometries lead to other functional dependences of ε_{e} on \underline{Q} , but \underline{Q} also changes and the result will always be that ε_{e} is independent of the shape of the macroscopic sample. The value of ε_{e} is determined as well by this relation, since we can evaluate \underline{Q} from Eqs. (3.17), (3.19) and (3.21).

3.2 DIPOLE TENSOR
$$\nabla \nabla$$
 (r⁻¹)

When we attempt to calculate the effective dielectric constant of a system, we must solve the set of equations Eq. (3.19), which includes the dipole propagator \underline{G}^{00} acting between the inclusions. A source of difficulty is the long-ranged nature of the dipole field. Since these equations involve the long-ranged dipole-dipole interaction operator, $\frac{1}{r}$), summation over the inclusion separations leads to a conditionally convergent, sample shape-dependent sum. Qualitatively, if a divergence can be subtracted from the given conditionally convergent integral to get another conditionally convergent integral whose integrand has the same asymptotic behavior as the integrand of the original integral, then the ensemble average of the given integral is unchanged, but the divergent behavior of the integrand is removed. The result is well-defined.

For a finite system the dipole tensor is well defined. However,

in order to coincide with the thermodynamic limit, $N \rightarrow \infty V \rightarrow \infty$ and N/V = constant, the present consideration must apply to an infinite system. To include the long range interactions, we calculate the interactions of the dipoles and higher-order multipoles under periodic boundary conditions, where a primary cell is periodically imaged to form a large spherical (or ellipsoidal) supercell surrounded by vacuum (see Figure 3.1). Macroscopic electrostatics can be applied to the supercell. We proceed to sum the interactions by the Ewald method⁴, and to obtain the effective dipole propagators by the lattice sum approach⁴².

The dipole propagator evaluated at the positions i and j is

$$\underline{\mathbf{T}} = - \nabla \nabla \left\{ \frac{1}{|\mathbf{r}_{ij}|} \right\}$$
(3.23)

with $|\mathbf{r}_{ij}| = |\mathbf{r}_j - \mathbf{r}_i|$.

As we develop the dipole propagator over all the images, we can express the dipole propagator as the following

$$\underline{\mathbf{T}} = \sum_{\mathbf{n}} \left\{ - \nabla \nabla \left\{ \frac{1}{|\mathbf{R}_{ij}|} \right\} \right\}$$
(3.24)

Here, $|\underset{ij}{R}_{ij}| = |\underset{j}{r}_{j} - \underset{i}{r}_{i} + n|$, and $n = n_x \hat{i} + n_y \hat{j} + n_z \hat{k}$. Here n_x, n_y , n_z are arbitary integers, and n = 0 corresponds to the primary cell.



Figure 3.1 Spheroidal macroscopic sample consists of supercells and the center heavy line is the primary cell.

.

The prime on the sum indicates that if i = j, the n = 0 should be omitted.

By applying the two grads on
$$\frac{1}{|R_{ij}|}$$
 in Eq. (3.24), we obtain

$$\underline{\mathbf{T}} = \sum_{n}^{\prime} \left\{ \frac{\frac{1}{\mathbf{r}_{ij}}}{||\mathbf{r}_{ij}|^{2} + n||^{3}} - \frac{\frac{3(|\mathbf{r}_{ij}|^{2} + n|)(|\mathbf{r}_{ij}|^{2} + n|)}{||\mathbf{r}_{ij}|^{2} + n||^{5}} \right\}$$
(3.25)

In such circumstances, there are two issues: (1) The existence of the sum and (2) The shape-dependent effects of the thermodynamic limit. As we can see, \underline{T} has a singularity at $\underset{ij}{R} = 0$ and the integrand $\frac{1}{\left|\underset{ij}{R}_{ij}\right|^3}$

is shape-dependent at $R_{ij} \rightarrow the$ boundary.

The lattice sum of the dipole propagator in Eq. (3.25) is conditionally convergent. Both sums in Eq. (3.25) diverge independently. So it is important to use a summation method to adjust the cancellation of the divergences^{4,42}.

Let us multiply the terms of the conditionally convergent series by a convergence factor $\exp(-s|n|^2)$. We may write Eq. (3.25) as

$$\underline{\mathbf{T}} = \sum_{n}^{\prime} \left\{ \frac{\frac{1}{2}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_{ij}}{|\frac{\mathbf{r}_$$

Then we expand these sums as power series in s and subsequently take the limit $s \rightarrow 0$ to obtain convergent results.

We start with a general form

\$1

$$\phi (\mathbf{r}_{ij}, \mathbf{x}) = \sum_{n}' |\mathbf{r}_{ij} + n|^{-2\mathbf{x}}.$$
 (3.27)

Then Eq. (3.27) multiplied by $\exp(-s|n|^2)$ is

.

$$\phi'(r_{ij}, x) = \sum_{n}' |r_{ij}+n|^{-2x} e^{-s|n|^2}.$$
 (3.28)

Henceforth,
$$\lim_{s\to 0} \phi'(r_{ij}, n, x) = \phi(r_{ij}, n, x).$$
 (3.29)

We introduce the identities^{43a} :

$$R^{-2Z} = \frac{1}{\Gamma(Z)} \int_{0}^{\infty} dt \ t^{Z-1} \ e^{-R^{2}t}.$$
 (3.30)

By using Eq. (3.30), we express Eq. (3.28) as the integral representation

$$\phi'(\mathbf{r}_{ij}, \mathbf{x}) = \sum_{n}' \frac{1}{\Gamma(\mathbf{x})} \int_{0}^{\infty} dt \ t^{\mathbf{x}-1} \ e^{-|\mathbf{r}_{ij}+n|^{2}t} \ e^{-\mathbf{s}|n|^{2}}$$
(3.31)

Another important identity is the Jacobi transformation^{43b}. This

transformation serves to invert the lattice space sum from the coordinate space to the reciprocal space, wherein the lattice vectors are $k = 2\pi$ n.

$$\sum_{n=-\infty}^{\infty} e^{-\left|\frac{r}{t}+n\right|^{2}t} = \left(\frac{\pi}{t}\right)^{3/2} \sum_{n=-\infty}^{\infty} e^{\left(-\pi^{2}n^{2}/t + i 2\pi n \cdot r\right)}.$$
 (3.32)

Applying the Jacobi transformation, we rewrite the integral of Eq. (3.31) (assuming $r \neq 0$) as

$$\phi'(\mathbf{r}_{ij}, \mathbf{n}, \mathbf{x}) = \sum_{n} \frac{1}{\Gamma(\mathbf{x})} \int_{0}^{\infty} dt t^{n-1} \left[\left(\frac{\pi}{t} \right)^{3/2} e^{(-\pi^{2}n^{2}/t + i 2\pi \mathbf{n} \cdot \mathbf{r}_{ij})} \right] e^{-s|n|^{2}}$$
(3.33)

In Eq. (3.33) the integral of $t^{x-5/2}$ is an analytic function for x > 3/2. For $x \le 3/2$, there is a singularity as $t \rightarrow 0$. We split the integral in Eq. (3.33) into two parts. The integral of the first part is from α^2 to ∞ , with α^2 an arbitrary value. The second one is over the range (0, α^2).

Now, we are able to integrate Eq. (3.33) over (α^2, ∞) and take the limit $s \rightarrow 0$ without difficulty. The divergence is due to the second integral at t = 0 so that in k space we subtract this term at k = 0 (n = 0) from the integrand and add it on again as a separate term. In other words, the divergent behavior is due to the lattice sum over the whole r space at large r, $k \rightarrow 0$ in reciprocal space, which causes the shape-dependent effect of the problem. At n = 0 (k = 0) the transformed sum yields the shape-dependent term. For instance, for a spherical supercell, the shape-dependent term is $\frac{4\pi}{3}$ 1, as $r \rightarrow \infty$.

For $r_{ij} = 0$, then n must have a nonzero value. But it is necessary to include n = 0 term during a Jacobi transformation, and to do that we add a contribution from n = 0 in r space in the second part, and subtract again the same term, which can been evaluated to produce the self-term operator of the inclusion, $\frac{4 \alpha^3}{3 \sqrt{\pi}} = 1$, at r = 0.

From Appendix A we obtain the two different dipole propagators: (1) \underline{T}_{-} diff is the dipole propagator for the different dipoles, $\underline{r}_{-,ij} \neq 0$. and (2) \underline{T}_{-} self is the self-dipole propagator for the dipole and the image dipole, $\underline{r}_{-,ij} = 0$.

$$\frac{\mathbf{T}}{\mathbf{I}} \operatorname{diff} = \sum_{n} \left\{ \frac{\frac{1}{|\mathbf{r}_{ij} + n|^{3}} \mathbf{B}(\alpha |\mathbf{r}_{ij} + n|)}{|\mathbf{r}_{ij} + n|^{3} \mathbf{B}(\alpha |\mathbf{r}_{ij} + n|)} - \frac{3 (|\mathbf{r}_{ij} + n|) (|\mathbf{r}_{ij} + n|)}{||\mathbf{r}_{ij} + n||^{5}} \mathbf{C}(\alpha |\mathbf{r}_{ij} + n|) \right\}$$

+
$$\sum_{n \neq 0} \frac{4\pi nn}{|n|^2} e^{\left(-\frac{\pi^2 n^2}{\alpha^2}\right)} e^{\left(i2\pi n \cdot r_{ij}\right)} + \frac{4\pi}{3} \frac{1}{2}$$
. (3.34)

 $\quad \text{and} \quad$

$$\frac{T}{2} \operatorname{self} = \sum_{n \neq 0} \left\{ \frac{\frac{1}{|n|^3} B(\alpha|n|) - \frac{3 nn}{|n|^5} C(\alpha|n|)}{|n|^5} \right\} + \sum_{n \neq 0} \frac{4\pi nn}{|n|^2} e^{\left(-\frac{\pi^2 n^2}{\alpha^2}\right)} + \left(\frac{4\pi}{3} - \frac{4\alpha^3}{3\sqrt{\pi}}\right) \frac{1}{2}.$$
(3.35)

Here, B(x) = erfc(x) +
$$\frac{2}{\sqrt{\pi}}$$
 x e^{-x²}

$$C(x) = B(x) + \frac{4}{3\pi} x^3 e^{-x^2}$$

where erfc(x) is the complementary error function.

The Jacobi transformations of the calculations have exponentials which decay as fast as $\exp(-n^2\pi)$ to produce rapid convergence compared with that in r space. By means of the integrand splitting and the transformation, it has been shown that the integrals are quickly convergent as $\operatorname{erfc}(x)$ in r space and $\exp(-n^2\pi)$ in k space.

In practice, the rate of convergence of the sum depends upon the

choice of the α value. We choose α to be 5 or π .

When we increase the number of supercells in r space, the dielectric constant does not change significantly, because $\operatorname{erfc}(x)$ decays quickly in the primary cell. Relatively, $\operatorname{erfc}(x)$ decays faster than $\exp(-n^2\pi)$, such that it is important to add enough supercells in k space to get an accurate result. When the n value in k space is increased to 4 the results are quite stable and convergent.

4. NUMERICAL METHOD

We summarize the techniques of the simulations in the following. The different methods of generating the configurations and the boundary conditions on the system will be discussed.

4.1 METHODS OF GENERATING CONFIGURATIONS

Conventionally, there are several ways to generate the relevant fluid-like configurations for these calculations. In this section, the methods which we use are listed as follows. Generally speaking, when the volume fraction of the system is less than 0.1, the immediate method (see below) is more efficient; when the volume fraction is greater than 0.1, the Metropolis method⁴⁴ is a good candidate. Some methods for generating configurations with other types of disorders also are developed.

4.1.1 IMMEDIATE METHOD

Let us consider either a spherical system with volume $\frac{4\pi}{3} R^3$ where R is the radius of system, and the center point of the spherical system is at (R, R, R), or a cubic system with the side of length 2R.

A sequence of random numbers between one and zero have to be assigned as the coordinates of the centers for N inclusions of radius "a" inside the given system. The configurations must satisfy the conditions: (1) no inclusion is outside the system. That is, if the minimum distance, D, between the center of spherical system and the center of the generated inclusion is equal or less than the radius of spherical system, R, we accept it. Otherwise, we reject it and generate a new inclusion repeatly until $D \leq R$. (2) inclusions cannot overlap with each other. A new inclusion can not overlap with any other inclusions which are already in the system; otherwise we will reject it and try a new one.

An important feature of this method is that a boundary effect appears when the volume fraction increases. Because the excluded volume effects have most of the inclusions generated on the edge of system, about 50% of the inclusions gather on the surface. This is due to a small finite volume system. When we employ these configurations to evaluate any quantities, the statistical error becomes large. This is not true for a real system, because for a real system the inclusions do not gather on the edge of the system at low ϕ .

At lower volume fractions $\phi \leq 0.1$ we can directly generate the inclusions in an empty spherical or cubic system without difficulties. This immediate method is efficient.

4.1.2 METROPOLIS METHOD

In contrast, for a higher volume fraction configuration, it becomes gradually more difficult to throw these inclusions one by one into a system, because the rate of overlapping is rising. In addition, at higher volume fractions $\phi > 0.1$, periodic boundary condition must be used to minimize boundary effects. We must: (1) set up a cell with length. L. containing N inclusions. (2) duplicate such a cell ---called the primary cell — in all directions to provide the conventional periodic boundary conditions. The initial configuration is established by placing the inclusions randomly inside the primary choosing lattice cell or a structure. i.e. simple cubic or face-centered cubic, and then equilibrating such a configuration by using the Metropolis algorithm⁴⁴ to correspond to a hard sphere fluid.

The Metropolis procedure consists of moving an inclusion to a new position at random. The new position is accepted only if the ith inclusion does not overlap with any other inclusions already placed in the primary cell and its periodic images. The density is conserved because when an inclusion moves out across the surface of the cell, then another will move into the cell from the opposite surface. Thus if the position of an inclusion's center is outside the primary cell, it is brought inside the primary cell by translating it by \pm L, where L is the length of the cell. This procedure of randomly moving, checking overlap and translating into the primary cell is repeated for each inclusion inside the primary cell. One attempt to move each inclusion is called one Monte Carlo step (MCS).

In order to provide equilibration, the acceptance rate for the Monte Carlo moves is chosen to be about 50% and the maximum step size for one Monte Carlo step is determined. If after such a move an inclusion happens to overlap with another inclusion, we place it in its original position.

For higher volume fractions $\phi \ge 0.3$ the configurations are started from a lattice structure, and run for several million configurations (typically 10^6 x N MCS) to equilibrate. For the volume fractions between 0.1 and 0.2 the configurations are started as generated from the immediate method, and equilibrated for 10^3 x N MCS initially. After such an initial equilibration, these configurations have been selected at intervals of 10^2 x N MCS apart. This is in order to establish a Markov chain of configurations, thereby eliminating correlations among the configurations.

To check that these configurations correspond to a fluid, the pair distribution functions for these configurations have been calculated. A similar case, the pair distribution function for a hard sphere fluid has been evaluated by Alder et al.⁴⁵ in 1954, and by Henderson⁴⁶ to higher precision.

The following outline describes how to measure the pair distribution function by the Monte Carlo method:

(1) In a generated configuration we choose each inclusion as the central inclusion and evaluate, $n_i(r,dr)$, the density of the inclusions in the ith shell of radius r and r+dr centered around the central inclusion, normalized by the total number of inclusions in the bulk.

(2) The pair distribution function is defined as

$$g(r) = -\frac{1}{m} - \sum_{i=1}^{m} n_i(r, dr)$$
 (4.1)

where m is the number of configurations.

- (3) The number of configurations must be rather large in order to reduce the statistical error. Repeat step (1) m times, and sum n_i(r,dr).
- (4) Average the sums over m to obtain g(r).

The comparison of our configurations with Henderson's result⁴⁶ is shown in Figure 4.1. This shows that our configurations are correct.

4.1.3 THE DISORDER OF CONFIGURATIONS

The effects on ε_{e} of other types of disordered configurations have been investigated (see section 5.2). We will consider:

a) RANDOMIZED LATTICE

At volume fractions below $\phi_c = 0.524$ (simple cubic lattice close packed volume fraction), the inclusions are initially placed on a



Figure 4.1 Comparison of the hard-sphere radial distribution functions between our liquid-like structure and Henderson's results.

simple cubic lattice and are then displaced randomly within the Wigner-Seitz primitive cell⁴⁷ centered on their respective lattice cells. Here, a DS parameter is defined to control the degree of randomness of a configuration. In a unit cell of side 1 let max = 0.5 - a, where a is the radius of inclusion. DS is the actual displacement allowed in the randomization around the lattice position divided by max. DS = 0 corresponds to the periodic lattice and DS = 1 the maximum randomness.

When the volume fraction is above 0.524, we replace the simple cubic lattice by a face-centered cubic lattice (fcc) and use the same procedures. Note that the Wigner-Seitz primitive cell of the fcc lattice is a rhombohedron. For convenience, we choose the biggest sphere with $\phi_c = 0.74$ (fcc close-packed volume fraction) instead of the rhombohedral cell.

b) VACANCY LATTICE

Here we start with a lattice structure as in a). The inclusions are deleted randomly and the size of the remaining inclusions is expanded to regain the original volume fraction. The original volume fractions must be smaller than the close packed volume fractions of the lattice structures.

4.1.4 MINIMUM IMAGE METHOD

In the previous sections, the system has either a spherical boundary condition or a periodic boundary condition. In our calculations, we have extended the periodic boundary condition by using a minimum image method to evaluate the induced multipole moments for each inclusion in the primary cell.

This method is to generate the inclusions in a primary cell and duplicate its identical replicas throughout space. Then, the mutual interaction between ith inclusion and jth is not restricted to be within the primary cell. The ith inclusion is only allowed to interact with those inclusions in the primary cell or the periodic replicas, which are inside a radius $R \ge L/2$ of a sphere centered on the ith inclusion — image sphere. This method corresponds to setting a spherical cutoff, R, for the pair interaction range. We have measured the effective dielectric constant followed by changing the size of this image sphere: 0.5L, L, and 1.5L. The results show that the effective dielectric constants seem very stable with any size of image sphere. This method provides accurate values for the induced multipole moments.

4.2 COMPUTATIONAL ALGORITHM

Now, we have to evaluate the induced dipole moment and higher multipole moments for each inclusion in the primary cell by using the minimum image method. We repeat this method for each inclusion inside

the primary cell to yield a set of 3ⁿ N linear algebraic equations for the induced multipole moments μ_{-i}^{ℓ} on each inclusion. Here $n = \ell + 1$ is the nth multipole moment, and N is the number of inclusions inside the primary cell.

The solution of the linear equations, Eq. (3.19), for the multipole moments depends on the shape of the system, due to the dipole-dipole interactions. That is, the second term on the right hand side of Eq. (3.19) is conditionally convergent when the summation is extended to an infinite system, for example, by using periodic boundary condition. We have discused this problem in Chapter 3 and Appendix A.

We have evaluated the dielectric constants of a composite material at the dipole level approximation using our minimum image method and compared the results with those of Cichocki and Felderhof⁴⁸, who used a version of the lattice sum method, and found that the results are in excellent agreement. We will show this comparison of our results with those of Felderhof and Cichocki⁴⁸ for the frequency dependent dielectric constants of a composite composed of metallic inclusions in insulating matrix evaluated the dipole an at approximation level in Chapter 5. The minimum image method is considerably faster than lattice sum method; results for the system in Chapter 5 are in accord with the minimum image method. We use it for the simulations presented in our work.

In order to get dipole moments and higher multipoles, the

propagators, $\underline{G}^{\ell\ell'}(|\mathbf{r}|)$, must be determined. We discuss the construction of these tensors in Appendix B.

Now we must relate the microscopic dipole moments to the macroscopic polarization of the sample. To do so we inscribe a sphere of radius L/2 in the primary cell. The polarization of this sphere is defined by the volume average of the sum of the dipole moments of the inclusions inside the sphere. The macroscopic polarization is then obtained by averaging the polarization over a suitable number of configurations. Then, the effective dielectric constant can be evaluated with the use of Eqs. (3.21) and (3.22).

We have tested the convergence of the simulations by changing the number of inclusions in the primary cell. The dielectric constants from three sets of numbers of inclusions: 25, 125 and 256 are nearly independent of the number of inclusions. The spatial distribution of the polarization was also monitored. The fluctuation of the polarization is quite small throughout the space, even up to the edge of the cell, indicating that the boundary effects are under control.

Computer programs have been written for the numerical simulations. A listing of the programs is in Appendix C. These programs are written in FORTRAN.

The program STDIEL is used to compute the static effective dielectric constants (used in section 5.1). This program is written at

the multipole level, expanding n up to 5. The multipole moments on the inclusions are evaluated by the minimum image method. The matrix equations are solved by using the LINPACK facilities. It is essential to have sufficient memory space for storing the large matrices generated by the multipolar expansion method.

The program FRQDIEL was written for the calculations of the frequency dependent effective dielectric constants (used in section 5.2). This program is constructed at the dipole level. There are two subroutines called LSMATRIX and MIMATRIX. LSMATRIX is used to compute the dipole moments by the lattice sum approach. MIMATRIX uses the minimum image method to compute the dipole moments. In the program FRQDIEL complex matrices are created. Therefore, we solve these linear complex equations by calling CSOLVQ, which is one of the routines in the mathematical library (IMSL) of the FPS-164 Floating Point Systems Attached Processor.

The statistical error analysis is addressed in both of programs. The principle of the error analysis is the application of the statistical standard deviation. For instance, if the measured quantity and the number of measurements are respectively x and m, the statistical error is defined by⁶⁴

$$\delta_{\mathbf{X}} = \left[\begin{array}{c} ABS\left(\sum_{i=1}^{m} \mathbf{x}^{2} - \mathbf{m} \langle \mathbf{x} \rangle^{2}\right) \\ \frac{\mathbf{i} = 1}{\mathbf{m} (\mathbf{m} - 1)} \end{array} \right]^{1/2}$$
(4.2)

Here $\langle x \rangle = \sum_{i=1}^{m} x_i / m$. The larger the m value the smaller the error. In our calculations m is chosen between 100 and 200, and our results are quite stable.

The algorithm of the simulation procedures is summarized below:

- (1) The configurations must be generated with the information on the number of inclusions, the number of configurations, the volume fraction, the radius of the system, the radius of the inclusions and the positions of the inclusions in x, y, z stored in "TININP".
- (2) The parameters must be set: the number of inclusions, the number of configurations, the radius of the inclusions, the radius of the system, the volume fraction, the dielectric constants : ε_1 , ε_2 and ε_m , the magnitude of the applied electric field, the convergence factor α , the frequency scanning range (from BF to EF), and so on stored in "TININ2".
- (3) Data from (1) and (2) is read.
- (4) The <u>G</u> matrix and the constant parts, B, are created, i.e. <u>G</u> $\cdot \mu = B$ and the matrix equations are solved to obtain all the multipole moments on the inclusions.
- (5) For each run all of the dipole moments of the inclusions are summed. The above steps from (3) to (5) are repeated m times to accumulate the total dipole moments, then the average of the total dipole moments for each run is

taken.

(6) ε_{e} is calculated according to Eqs. (3.21) and (3.22), then the error analysis is performed.

For convenience, we set the side of the system to be unity, and fix the number of inclusions to vary the radius of inclusion in accord with the desired volume fractions. In these programs the radius of image sphere is set to be half of the side length. The x-component of applied field is a constant, and the others are 0. The parameters have been set in Chapter 5 according to these considerations.

5. RESULTS AND DISCUSSION

In this chapter, we will present results on the effective dielectric constant of a composite material that are obtained by use of the analytic-simulation method.

We simulate two properties of a composite material, the static and frequency dependent dielectric constant. To address the former problem, a multipole simulation of the static effective dielectric constant ε_{e} is carried out. We study the effects of multipole moments on the effective dielectric constant for a uniformly-conducting inclusion case, the inverse case of insulating inclusions, and for coated inclusions. Then we compare the results obtained from the analytic-simulation of the uniformly conducting case with a random walk method^{49,50}.

Another problem is the calculation of the frequency dependent effective dielectric constant, $\varepsilon_{e}(\omega)$. Here, we will investigate the effect of disordered configurations on the frequency dependent effective dielectric constant. Thus, we consider systems, including a randomized lattice, a vacancy lattice, random size-distributed fluids, and real silver in glass. Finally we will compare the effective dielectric constants, $\varepsilon_{e}(\omega)$ which result from both of the methods,

the minimum image method and the lattice sum approach, discussed in section 3.2. The results presented below demonstrate the use of these different models.

5.1 THE STATIC DIELECTRIC CONSTANT

We consider a system of N non-overlapping, spherical inclusions of radius "a" and dielectric constant ε_1 embedded in a matrix phase of dielectric constant ε_2 all within a volume V. In the current problem, we attempt to calculate the effective dielectric constants of composite materials accurately, discuss the effects of multipoles on the $\varepsilon_{\rm e}$, and determine how the convergence of the effective dielectric constant depends upon the various physical models.

5.1.1 CONDUCTING INCLUSIONS

We first study perfectly conducting inclusions embedded in an insulating matrix. In other words, the dielectric constant of the inclusions is much larger than that of the matrix. A typical case, for example, is a cermet, a ceramic matrix with metallic inclusions. Analytic results of a similar multipole expansion method for ε_{e} have been obtained by Dukhin⁵¹ and McPhedran¹⁹ for lattices. The computer simulation of the conductivity of the simple cubic lattice by McPhedran^{19b} has a good convergence. Their calculation is restricted for m = 0 component among the ($2\ell+1$) moments for order ℓ . McPhedran shows by direct comparision that the $m\neq 0$ components do not contribute to the dielectric constant for cubic lattices, though no proof of this observation is available. For a random structure we find that the $m \neq$ 0 components must be included. Since our interests are focused on random systems with liquid-like volume fractions we must consider many multipoles with all the m values included.

We choose the dielectric constant of the inclusions, ϵ_1 , to be 10⁸ and set the dielectric constant of the insulating matrix, ϵ_2 , equal to 1. The volume fractions are chosen to produce fluid structure. The range of the fluid structure is defined from a extremely dilute gas to a liquid-solid compatible state, where the volume fraction is about 0.45. We have implemented the calculations for multipole moments ℓ from 0 up to 4. For convenience, we set $\ell + 1 = n$ so that, for example, n = 1 corresponds to the dipole term.

We carried out the simulations at seven volume fractions: $\phi = 0.001$, 0.01, 0.1, 0.2, 0.3, 0.4, and 0.45. The results for ε_{0} as a function of the number, n, of multipole moments versus the volume fraction ϕ are shown in Figure 5.1. These have been compared with the convergent results, corresponding to $n \rightarrow \infty$ for a simple cubic lattice, calculated by McPhedran and McKenzie^{19b}, which are indicated by the solid curve in Figure 5.1.

As can be seen from Figure 5.1, for ϕ below 0.3, the interaction among inclusions can be treated with dipole-dipole interactions only. Thus, the calculation at the dipole level is enough to obtain an



Figure 5.1 The effective dielectric constant $\varepsilon_{\rm e}/\varepsilon_2$ for conducting inclusions ($\varepsilon_1=10^8$) embedded in an insulating matrix ($\varepsilon_2=1$) as a function of the volume fraction ϕ for n=1(o), n=2(\Delta), n=3(\Box), n=4(ϕ), and n=5(∇). The error bar is indicated. These results have been compared with the exact results, indicated by the solid curve, for the simple cubic lattice (n= ∞) calculated by McKenzie and McPhedran^{19b}.

accurate effective dielectric constant. As ϕ increases above 0.3, the higher order interactions must be included. The results show that multipole effects are important at high volume fractions. At ϕ higher than 0.45, the n = 5 results do not converge. This conductor in insulator case is the most difficult to converge as the electric field in the gap between a pair of nearly touching inclusions has a very rapid spatial variation.

5.1.2 AN INVERSE CASE

Figure 5.2 shows the inverse case of the previous uniform case, where the system consists of poorly conducting inclusions in a conducting medium.

The ratio of the effective dielectric constant to the dielectric constant of metallic matrix, $\varepsilon_e/\varepsilon_2$ versus the volume fraction ϕ from 0.05 to 0.7 has been presented. The reason we can calculate the ε_e at higher volume fractions in this case is that these insulating inclusions avoid a divergence of ε_e . Physical models include impurities in metals.

Comparison of the variation of $\varepsilon_e^{\epsilon_2}$ with increasing n indicates that for n = 5, even when $\varepsilon_2^{\epsilon_1} \rightarrow \infty$, quite good convergence is obtained even for ϕ near to the hexagonal close packed volume fraction $\phi_c = 0.74$. In our calculation the highest ϕ is chosen to be 0.7, which is between the random close packed $\phi_c = 0.63$ and the hexagonal close


Figure 5.2 The effective dielectric constant $\varepsilon_e/\varepsilon_2$ of a system with poorly-conducting inclusions (ε_1 =1) surrounded by conducting medium (ε_2 =10⁸) as a function of the volume fraction ϕ from 0.05 to 0.7 for n=1(o), n=2(Δ), n=3(\Box), n=4(\Diamond), and n=5(∇).

packed $\phi_c = 0.74$. The difference between the results with n = 4 and n = 5 is very small, and cannot be resolved in Figure 5.2. From Figure 5.1 and Figure 5.2, explicitly, the effective dielectric constants of the inverse case converge faster than those of the conducting case.

The rate of convergence of ε_{e} with n exhibits an even-odd pattern at high ϕ . It is important to realize that, in principle, the high density liquid structure is quite symmetric, and therefore most of the contribution to the polarization is from the odd n multipoles. For example, in a simple cubic lattice, due to the symmetrical structure, the dipole moment at a given inclusion will have equal in magnitude but opposite in sign contributions from symmetrically located pairs of inclusions when n is even.

5.1.3 A SPECIAL CASE

From the results of the uniform case, when $\varepsilon_1/\varepsilon_2 \rightarrow \infty$, the effective dielectric constant will diverge at high ϕ . It is interesting to study how the closeness of the inclusions affects the effective dielectric constant. We generate two sets of configurations: one set at volume fraction $\phi = 0.4$ and 0.6, and the other initially at $\phi = 0.5$ and 0.7, but then the inclusions are shrunk sufficiently to adjust the volume fraction to be $\phi = 0.4$ and 0.6. A characteristic feature of these two sets of configurations is the different value of the closest distance between inclusions.

We compare the results from these two different sets of configurations in Table 1 with ϵ_1 = 100 and ϵ_2 = 1. Clearly, by directly generating configurations (the former method), the inclusions can get closer than in the latter method. Thus, the effective dielectric constant ϵ_{e} evaluated from the former configurations should be higher than that from the latter configurations, as is borne out by the data. Also, note that at the higher ϕ value, the difference between n and n+1 is much larger than low 4, illustrating the non-convergence of the multipole method at very high volume fractions. This is similar to the case of oxide-coated metallic inclusion in insulating matrix which we consider in the next section. The conclusion there is that a thin layer (i.e. oxide-coated or insulating material) is capable of preventing the divergence of the effective dielectric constant arising from touching inclusions.

5.1.4 COATED INCLUSIONS

An interesting extension of our methodology is to consider a problem of composite composites. In this section, we investigate the effect on the ε_{e} of a coated-metal inclusion with an arbitrary thickness of coating material.

That is, we consider spherical inclusions which are composed of spherical layers. For example we consider the modification of the effective dielectric constant by coating an inclusion with a thin layer of material. The conductivity of the coating material is relatively

Table 1 $\varepsilon_{\rm e}^{\prime}\varepsilon_{2}^{\prime}$ for two sets of configurations: The 0.4/0.4 and 0.6/0.6 set is generated as for Figure 5.1. The 0.4/0.5 and 0.6/0.7 sets are generated at ϕ = 0.5 and 0.7 and the inclusions are then shrunk to correspond to ϕ = 0.4 and 0.6, respectively.

	n=1	n=2	n=3	n=4	n=5
0.4/0.4	2.9848	3.0705	3.1527	3.2069	3.2333
0.4/0.5	2 . 956 2	3.0107	3.0631	3 .0969	3.1121
0.6/0.6	5.4109	5.4764	5.6676	5.7692	6.1042
0.6/0.7	5.4121	5.4350	5.5822	5 . 5899	5.8884

.

small compared with that of the medium, and the interior of the inclusion is a good conductor. For parameter values we choose $\varepsilon_1 = 10^8$, $\varepsilon_2 = 1$, and $\varepsilon_m = 10^3$, where ε_1 , ε_2 , ε_m refer, respectively, to the dielectric constant of the metal inclusion, coating and medium. Now, if the multipole polarizability for this composite inclusion is known, then we can solve the problem. Let us define that the inner radius of the composite as a, corresponding to a metal inclusion, and the outer is R, for the metal inclusion and coating. The expression for the multipolar polarizabilities of a composite inclusion has been given by Maxwell⁵ as

$$\alpha_{\ell} = \frac{\ell(\nu-1) \{\nu(\ell+1) + \mu\ell\} R^{2\ell+1} + \ell(\mu-\nu) \{\ell+\nu(\ell+1)\} a^{2\ell+1}}{\{\nu(\ell+1) + \mu\ell\} \{\nu(\ell+1) + \nu\ell\} + \ell(\ell+1) (\nu-\mu) (1-\nu) (a/R)^{2\ell+1}}$$
(5.1)

Here $\mu = \epsilon_1/\epsilon_m$ and $\nu = \epsilon_2/\epsilon_m$. In Table 2 we list the data from the simulations, the parameter values, and the volume fraction ϕ_i and ϕ_o corresponding to the inner and outer sphere volume fractions. The first three data sets are for a/R ~ 0.9999, a thin coating. Comparison of Figure 5.1 (uniformly-conducting inclusion) and Figure 5.3 (this case) shows that a thin, protective layer rapidly reduces the dielectric constant relative to the uniform inclusion case. These simulations also describe the effective thermal conductivity of This simulation method can be used to predict the composites. metal-insulating by oxidative coating of matrix degeneration Meanwhile, note that the multipole expansion for the composites. composite-composites converges at much higher volume fraction than those for the uniform composite.

Table 2 $\varepsilon_{\rm e}^{\prime}\varepsilon_{\rm m}^{\prime}$ for composite-composites. The first three data sets are for a thin insulating coating; the final two are for a thick insulating coating, as discussed in the text ($\mu = 10^5$, $\nu = 10^{-3}$).

Φ _i /Φ _o	n=1	n=2	n=3	n=4	n=5
0.3999/0.4	2.4004	2.4263	2.4446	2.4538	2.4569
0.4499/0.45	2.7490	2.7838	2.8138	2.8315	2.8384
0.4999/0.5	3.1615	3.2067	3.2531	3.2844	3.2998
0.3/0.45	0.4567	0.4545	0.4510	0.4487	0.4475
0.4/0.45	0.4695	0.4666	0.4633	0.4611	0.4602



Figure 5.3 The effective dielectric constant $\epsilon_{\rm e}/\epsilon_2$ of metal inclusions coated with an insulator as a function of the volume fraction ϕ for n=1(o), n=2(Δ), n=3(\Box), n=4(ϕ), and n=5(∇). See Table 2 for the chosen parameters.

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The last two data sets in Table 2 correspond to thicker coatings a/R = 0.9615 and 0.8735, respectively, where the composite-composites are now clearly acting as insulators in the sense that $\epsilon_{e}/\epsilon_{m} < 1$. Conditions on the values of μ , ν , and a/R were previously obtained by Sridharan and Cukier¹⁵ which indicate which regime $(\epsilon_{e}/\epsilon_{m} < 1 \text{ or } > 1)$ composite-composites would fall in for the second virial coefficient. The results presented here obey those conditions. The results displayed in Figure 5.3 show that a thinly coated inclusion permits the multipole expansion to converge quickly in comparison with a uniform inclusion. The thickness of the coating controls the composite-composites behavior as insulator or conductor-like.

5.1.5 CONCLUSION

For the static case, if we know the expression of the n rank tensor and the analytic form of the multipole polarizabilities, then the analytic simulation of the higher order multipole contributions to the effective dielectric constants of a composite material can be carried out straightforwardly. By adding as many multipoles as we can, we can obtain more accurate results for the effective dielectric constant. However, the application of the multipole simulation method runs into the following problem.

In Appendix B we have represented an n rank tensor as a power series in the reciprocal distance between inclusion pairs and summarized it into a general expression to arbitrary n value $(n \ge 0)$.



Figure 5.4 Plot of the dimension of the matrix versus the total CPU time.



Figure 5.5 The effective dielectric constant ϵ_e/ϵ_2 versus a function of the volume fraction ϕ for the different types of configurations. The solid line is generated by the multipole method of Ref. 19b for the simple cubic lattice. For the Metropolis (randomized lattice) configurations the random walk method is denoted by Δ (x). For the face-centered cubic lattice the random walk method is denoted by \Box The o's are generated for the Metropolis configurations by the multipole simulation method (see section 5.1.1) for a conducting case.

Thus, it is not difficult to figure out. But, because the computation involves complicated matrix algebra, the computing time and computing space of the computer system must be of concern. Figure 5.4 shows the total CPU (Central Proceeding Unit) time versus the dimension of the matrix of these calculations with 25 inclusions and 100 configurations. It demonstrates that if the higher multipoles are included, the CPU time increases parabolically.

Due to the non-convergence of $\varepsilon_{\rm e}$ for the conducting case, the comparison of Figure 5.1 and the $\varepsilon_{\rm e}$ resulting from a random walk method ⁵² has been shown in Figure 5.5. The benefit of the random walk method is that it can be applied to higher ϕ than a multipole simulation. As can be seen from the above, the multipole simulation of the conducting case is difficult to converge at ϕ higher than 0.45. From Figure 5.5, at low ϕ (~ 0.3) the multipole simulation (n = 5) and random walk method results are in quite good agreement with each other. It also shows that a multipole simulation is sufficient to obtain an accurate result. Thus, at high ϕ the use of the random walk can supply the data not available from the multipole simulation.

5.2 THE FREQUENCY DEPENDENT $\varepsilon_{\alpha}(\omega)$

We have studied $\varepsilon_{e}(\omega)$ of a composite material consisting of inclusions of dielectric constant $\varepsilon_{1}(\omega)$, which have a Drude model resonant form, embedded in a background medium of frequency-independent dielectric constant ε_{2} . Our interest is to find how the optical properties of such materials are affected due to the electrostatic interactions among the inclusions. The frequency dependence of the effective dielectric constant as a function of the inclusions' geometry, size-distribution, spatial distribution and concentration is explored. Our method is the analytic simulation method described in Chapter 4.

We assume that the quasi-static Maxwell equations are valid. Because the wavelength of the applied field (~ 3600 A) that we choose is long compared with the inclusions' size (~ 100 A) and the mean distance between inclusions, the electrostatic approximation with $\varepsilon_1(\omega)$ can be used here. The multipolar effects on $\varepsilon_e(\omega)$ at high volume fractions of inclusions have been investigated in several hypothetical cases. From the previous static multipole simulation, at low volume fraction the dipole approximation is enough to obtain ε_e quite accurately. Thus, a comparision with the Clausius-Mossotti formula, which applies to dilute inclusions, is shown in the Figures.

In the following, we have set the plasma frequency $\omega_p = 9.4 \times 10^{15} \text{s}^{-1}$, the damping constant $\Gamma = 10^{14} \text{s}^{-1}$, $\varepsilon_{1\infty} = 1$ and $\varepsilon_2 = 1$ for a hypothetical case. Only the resonant, imaginary part of $\varepsilon_e(\omega)$ is displayed in the Figures. All of the parameters are defined in Chapter 2.

5.2.1 RANDOMIZED LATTICE

In Figure 5.6, $\varepsilon_{e}^{(\omega)}$ of the randomized lattice is compared with $\varepsilon_{e}^{(\omega)}$ of the fluid structure at volume fraction $\phi = 0.03$. The parameter DS is chosen to be 1 or 3/4. DS = 1 corresponds to the maximum randomness for this method of randomization. Each curve corresponds to an average over 200 configurations. They demonstrate that the fluid structure broadens the spectrum. That is, each inclusion is presented with a different local environment. Since the Clausius-Mossotti theory predicts that the plasma resonant peak position $\bar{\omega}$ depends on ϕ (see Chapter 2), the local environments associated with slightly different local densities lead to a broadening of the resonance.

An important feature of the definition of $\bar{\omega}$ is that as ϕ increases, the resonant peak has a redshift. Similarly, this is the case for a randomized lattice. DS = 0 for the randomized lattice corresponds to the periodic case. We then certainly obtain the Clausius-Mossotti result. With some randomization of the configurations the resonant absorption peak is broadened. The reason has been explained previously. The broadening increases with increasing randomization, i.e., increasing DS value of the configurations. From Figure 5.6, for the maximum possible excursion, DS = 1, the broadening is still considerably less than that of the fluid. The broadening for the randomized lattice is very symmetric, which indicates that on average the local fluctuations in $\bar{\omega}$ are themselves symmetric.



Figure 5.6 Im $\varepsilon_{e}(\omega)$ for fluid (Δ) and randomized lattice (o, \blacksquare). The solid line is the Clausius-Mossotti expression. See text for the definition of DS.

5.2.2 VACANCY LATTICE

In the following, we apply the same parameters to a vacancy lattice. Figure 5.7a and 5.7b presents the $\varepsilon_{e}(\omega)$ for a vacancy lattice. There are four cases we will discuss. First, we start with 125 inclusions on a simple cubic lattice and randomly delete inclusions until there are the number remaining indicated on the figures. The remaining inclusions in the cubic box are expanded to obtain the original ϕ . A second run starts with 343 inclusions with 63 remaining. As the system becomes more dilute in terms of the number of inclusions, the spectra develop a bimodal distribution, with the weight of the higher frequency part growing at the expense of the lower frequency part.

In principle, at high ϕ the Clausius-Mossotti formula for the effective dielectric constant of composite material predicts a redshift of the resonant peak. In other words, the lower ω peak corresponds to more dense regions. Hence, it appears that such systems consist of low and high density regions, and this is responsible for the development of the bimodal distribution. The notation in the Figure, 40/125, indicates that 125 inclusions were present initially in a cubic box and then inclusions were randomly removed until 40 were left. All results have been compared with the Clausius-Mossotti formula with the same parameters. Each curve corresponds to an average over 200 configurations.



Figure 5.7a Im $\varepsilon_{e}(\omega)$ for vacancy lattices. The notation 75/125 indicates that of 125 inclusions on a cubic lattice, all but 75 were randomly removed.



Figure 5.7b Im $\varepsilon_{0}(\omega)$ for vacancy lattices.

5.2.3 RANDOM SIZE-DISTRIBUTED EFFECT

Experimental results⁵³ on the size-distribution of inclusions has been fitted to a log normal distribution

$$f(x) = \frac{1}{\sqrt{2\pi} x \ln \sigma} \exp \left[-\frac{\left[\ln \frac{x}{u} \right]^2}{2 \left(\ln \sigma \right)^2} \right]$$
(5.2)

where f(x) is a normalized distribution in the inclusion radius, a(x) = xa, u is the mean inclusion size, and σ is the standard deviation of the distribution. The expression for the volume fraction due to the size-distribution of inclusions is given as

$$\phi = (\frac{4\pi}{3}) n a^3 u^3 exp(\frac{9}{4\lambda})$$
 (5.3)

where n is the number density of the inclusions and λ is defined as

$$\lambda = \frac{1}{2} \left(\ln \sigma \right)^2. \tag{5.4}$$

The log normal distributions with different standard deviation values σ and with u = 3.3 have been plotted in Figure 5.8. The σ = 0 corresponds to equal size inclusions. We consider fluid configurations which are generated by throwing inclusions into a cubic box, while avoiding overlap, and choosing each new inclusion's size from the log normal distribution until the desired volume fraction ϕ is obtained by adjusting the parameter, fac, defined as



Figure 5.8 The log-normal distribution for different standard deviation values σ .

fac =
$$\begin{bmatrix} \frac{\phi}{\frac{4 \pi}{3} u^3 n \exp\left(\frac{9}{4 \lambda}\right)} \end{bmatrix}^{1/3}$$
. (5.5)

In practice, it is difficult to generate fluid configurations with large σ , because overlap occurs frequently with increasing σ . The maximum σ in our present work is 2.72. In Figure 5.9 the results for equal size and three sets of the different size distributions of inclusions are compared. For the equal size and the $\sigma = 1.4$ fluids, the results are not significantly different. This σ is chosen because the size distributed data were fitted with this σ in the experimental work⁵³. If we increase the width to $\sigma = 2.02$, there occurs a low frequency shoulder relative to the equal size case. It appears that high density regions occur because of large size inclusions. All the results correspond to an average over 200 configurations.

In order to investigate the effects of the spatial distribution of these inclusions, we exhibit two different runs at $\sigma = 2.02$ in Figure 5.10. Each run has 200 configurations averaged. The difference between the random-size distributed and equal-size results is not an artifact of the choice of configurations. There is no background contribution to the imaginary part of $\varepsilon_{\mu}(\omega)$ from the matrix absorption.

There are several mechanisms which will lead to such additional lineshift and line broadening provided by the size distribution: (1) The local density fluctuates and results in line-broadening. (2) The



Figure 5.9 Im $\varepsilon_{e}(\omega)$ for equal-sized (σ =0.00) and size-distributed fluids.



Figure 5.10 Im $\varepsilon_{e}(\omega)$ for size-distributed fluids with the same width, but different sets of configurations.

large size of inclusions causes local high density compared with the average density and a red lineshift occurs. Under the condition of such a low volume fraction as we have chosen, the red lineshift is not obvious.

5.2.4 SILVER IN GLASS

Now, let us consider a system with a suspension of silver spheres in glass, which is a more realistic model for a experimental investigation^{23,24}. Because bulk silver has a low damping constant, it is used for studying optical spectra. According to the values used in Felderhof's work²³, we choose the plasma frequency for silver as $\omega = p$ 1.46x10¹⁶s⁻¹, the bulk damping constant as $\gamma_{\infty} = 0.24x10^{14}s^{-1}$, the interband contribution as $\Gamma_{ib} = 0.87 \times 10^{14} \text{s}^{-1}$, the Fermi velocity as V_F = 1.44x10⁸ cm/s, $\epsilon'_{1\infty}$ = 4.5, and the dielectric constant of glass as ϵ_2 = Then the damping constant γ_{a} of Drude form for a sphere of 2.25. radius, 100Å, is equal to $1.68 \times 10^{14} \text{ s}^{-1}$, the width is $\Gamma = 2.55 \times 10^{14} \text{ s}^{-1}$, the resonance frequency is $\omega_s = 4.87 \times 10^{15} s^{-1}$, and $\varepsilon''_{1\infty} = 0.16$. The results are presented in Figure 5.11. The width parameter of the Drude form we use is larger relative to ω_{a} than in the preceding hypothetical case (section 5.2). Thus, the peak of the Clausius-Mossotti formula is Even at $\phi = 0.1$, the broadening is less than in a sharper. hypothetical case at ϕ = 0.03. In such a circumstance when the spheres are size distributed with the narrower distribution, σ = 1.40, the results are indistinguishable from those with equal size. Even for the wider distribution, $\sigma = 2.02$, the results are not resolved.



Figure 5.11 Im $\varepsilon_{e}(\omega)$ for parameters chosen to represent Ag in a glass matrix. Equal-sized and two size-distributed configurations are compared. Note that Γ depends on the inclusion's size.

We found that for the volume fractions considered here the dipole approximation is accurate. We have probed this in $\varepsilon_{e}(\omega)$ by including the quadrupolar effects, where they are expected to be greatest, and have found minimal changes with respect to the dipole simulations.

5.2.5 COMPARISON OF MINIMUM IMAGE AND LATTICE SUM METHODS

In this section we compare $\varepsilon_{e}(\omega)$ evaluated by using the minimum image and lattice sum approaches. Our computational technique used in the previous calculations of the effective dielectric constant $\varepsilon_{e}(\omega)$ is based on the minimum image method. In addition, we have extended the calculation of the frequency dependent effective dielectric constant by using the lattice sum approach.

It is worthwhile to note that the speed of calculation using the minimum image method is considerably faster than a lattice sum approach. We have performed our calculations of $\varepsilon_{e}(\omega)$ for silver in glass case at volume fraction $\phi = 0.2$ using both techniques, shown in Figure 5.12, in the dipole approximation. Here we exclude the interband contribution to the width parameter. Because we want to compare with the simulation results by Felderhof and Cichocki⁴⁸, we choose the same parameters as their values. Felderhof and Cichocki used the lattice sum approach with 500 inclusions in the primary box, but we use only 75 inclusions. The Cole-Cole plot of the imaginary part of $\varepsilon_{e}(\omega)$, $Im(\varepsilon_{e}(\omega))$, versus the real part $Re(\varepsilon_{e}(\omega))$ clearly shows differences between the results from the Clausius-Mossotti expression

and those of the various simulations. In Figure 5.12 the large circle follows from the Clausius-Mosstti expression. The small solid curve is a result of the analytic-simulation technique using 75 inclusions; solid dots resulted from the lattice sum approach using 75 inclusions; pluses are points excerpted from Figure 5 in reference 48.

The Cole-Cole plot shows that the results from both techniques nearly agree with each other. The spectral shape of the imaginary part $Im(\epsilon_{e}(\omega))$ using both techniques has also been plotted in Figure 5.13. We find that the analytic-simulation technique yields results that agree quantitatively with those of the lattice sum calculations. Hence, we have demonstrated that the effective dielectric constant can be accurately, directly, and quickly obtained by using the analytic-simulation technique. Similar conclusions have been reached, in a somewhat different context; by Gales et al.⁵⁴, who studied Coulomb and dipole effects in disordered solids.

Finally, we note that at $\phi = 0.2$, dipole level approximations are not sufficient to describe correctly $\varepsilon_{e}(\omega)$, or ε_{e} . However, the sums of higher multipole terms do not exhibit conditional convergence due to their much shorter range interaction. Hence the special techniques associated with the analytic-simulation method or lattice sum approach need not be used to obtain accurate results for higher multipole interactions.



Figure 5.12 Cole-Cole plot of the dielectric constant of silver spheres in glass (neglecting interband transitions), at volume fraction ϕ =0.2, in the dipole approximation. The large circle follows from the Clausius-Mossotti expression. The small solid curve is a result of the analytic-simulation technique using 75 inclusions; solid dots result from the lattice-sum approach using 75 inclusions; pluses are points excerpted from Figure 5 of Ref. 48.



Figure 5.13 Im $\epsilon_{e}(\omega)$ for monodisperse silver spheres in glass (neglecting interband transitions). Solid curve, Clausius-Mossotti expression; dashed curve, analytic-simulation technique, 75 inclusions; dots, lattice-sum approach, 75 inclusions.

6. CONCLUSION

The use of computer simulations provides the ability to look at detailed microscopic properties which are difficult to probe theoretically and experimentally, and permits the use of more realistic models in order to make comparison with experiments. Therefore, as long as the analytic formalism is known, then the computer simulation can give practical results.

In the present study we have shown that the effective dielectric and optical properties of composite materials or nonpolar polarizable systems can be obtained by the analytic-simulation method. As long as the multipolar polarizabilities α_{ρ} of the inclusions are known, the analytic-simulation method can be employed routinely to obtain the effective dielectric constant and optical properties of a macroscopic sample. In the static case, we were able to deal with any ratio of $\varepsilon_1/\varepsilon_2$, as well as composite-composites. The drawbacks of the analytic-simulation method are the difficulty of convergence at high volume fraction ϕ , and the requirement of obtaining α_{ℓ} analytically. For the most difficult case of infinitely conductive inclusions in an insulating matrix, higher-order multipoles than we have used are required for convergence at volume fractions beyond $\phi=0.45$. In other words, when the average electric field varies rapidly in space it becomes necessary to include more multipoles to describe this rapid spatial variation.

For the frequency-dependent dielectric constant, the interactions among the inclusions lead to the following strong deviations from the Clausius-Mossotti result. The lineshape broadens and shifts to lower frequency. The broadening arises from the distribution of peak frequencies in the slightly different local environments.

In our work, the applied field is limited to long wavelengths relative to the size of inclusions, so the electromagnetic interactions among the inclusions can be replaced by electrostatic interactions. It is important to investigate systems with the wavelength of the applied field comparable to the size of inclusions, as this is a common experimental situation. Therefore, in addition to electric effects, magnetic effects should be considered^{27,25,34}. About the calculation of optical properties under this circumstance, one may go back to Mie^{36} . He first found the color variation of colloidal metal inclusions and he derived a theory to calculate the optical properties when the inclusion size is comparable to the wavelength of the applied field. Mie provided the solution to the problem of the interaction of a plane electromagnetic wave with a sphere of arbitrary size. Α depolarization effect associated with the inclusion boundary usually causes an apparent size-dependent optical constant because electrons are confined by the surfaces of inclusion and produce large depolarization effects; these effects cause the electron cloud to resonate at a quite different frequency than in the bulk.

The problem of the conditional convergence of the dipolar tensors for an infinite system was handled via the Ewald summation method. In our work, the long-ranged interaction of the dipolar field has been overcome by using a minimum image method to evaluate the induced multipole moments on each inclusion. We found that this latter method gave the same results as the former, and it is much faster computationally.

Another application of simulation methods is to non-spherical inclusions, which could be shaped like ellipsoids, slabs, needles, etc. For ellipsoids the generation of Metropolis configurations can be developed via a contact function⁵⁵. Although the generation of any geometrical distribution of inclusions is not hard, the problem is the difficulty in deriving the multipolar polarizabilities for these non-spherically shaped inclusions. In these cases, the random walk simulation method is more powerful because it does not require simple inclusion geometries.

We have evaluated the static and frequency-dependent dielectric constant in our present work. For wavevector dependent applied fields and the resulting wavevector dependent dielectric constant, Felderhof et al.^{56,57,58} used a diagrammatic expansion to analyze the optical properties of a random medium. The direct use of the analytic simulation method to study this problem is quite promising. A similar problem is to investigate the localization of an electromagnetic wave in a dielectric medium. Arya et al.⁵⁹ have discussed the localization of classical waves in a dielectric medium of randomly distributed metal particles. The localization of one electron in a random medium can also be addressed.

Finally, chemical reaction problems⁶⁰ can be equally well solved by the analytic-simulation method. APPENDICES

APPENDIX A

A. DERIVATION OF THE LATTICE SUM FOR INDUCED DIPOLAR SYSTEMS

$$\underline{\mathbf{T}} = \sum_{n}^{\prime} \left\{ \frac{1}{|\mathbf{r} + \mathbf{n}|^{3}} - \frac{3(|\mathbf{r} + \mathbf{n}|)(|\mathbf{r} + \mathbf{n}|)}{||\mathbf{r} + \mathbf{n}|^{5}} \right\} e^{-\mathbf{s}|\mathbf{n}|^{2}}$$
(A.1)

where the prime on the sum indicates that if r = 0, the term with n = 0should be omitted. Let us separate \underline{T} into two parts, A and B.

$$A = \sum_{n} \frac{\frac{1}{|r + n|^{3}}}{|r + n|^{3}} e^{-s|n|^{2}}$$
(A.2)

Applying Eq. (3.30), the integral representation, gives

$$A = \sum_{n}^{\prime} \frac{1}{2} \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} dt t^{1/2} e^{-|t_{z}^{*} + n|^{2} t_{e}^{-s|n|^{2}}} e^{-s|n|^{2}}$$
$$= \sum_{n}^{\prime} \frac{1}{2} \frac{2}{\sqrt{\pi}} \left\{ \left(\int_{\alpha^{2}}^{\infty} + \int_{0}^{\alpha^{2}} \right) dt t^{1/2} e^{-|t_{z}^{*} + n|^{2} t} \right\} e^{-s|n|^{2}}$$
$$= (A1) + (A2)$$
(A.3)

There are two situations considered: (1) If $r \neq 0$, then the sum over n includes 0 and the prime is removed. (2) If r = 0, then n = 0 is

excluded. (Here $n = (n_x, n_y, n_z)$ with n_x, n_y, n_z from $-\infty$ to ∞ in 3-dimensions).

IN CASE (1) :

(A1) =
$$\sum_{n} \frac{1}{\sqrt{\pi}} \left\{ \int_{\alpha^{2}}^{\infty} dt t^{1/2} e^{-|r+n|^{2}t} \right\} e^{-s|n|^{2}}$$
 (A.4)

We substitute $u = t^{1/2} |r+n|$,

(A1) =
$$\sum_{n} \frac{1}{\sqrt{\pi}} \left\{ \int_{\alpha|r+n|}^{\infty} du \ 2 \frac{u^2}{|r+n|^3} e^{-u^2} \right\} e^{-s|n|^2}$$
 (A.5)

and then integrate by parts, subsequently taking the limit $s \rightarrow 0$,

$$(A1) = \sum_{n} \frac{1}{\sqrt{\pi}} \frac{2}{|r+n|^{3}} \left\{ \alpha |r+n| e^{-(\alpha |r+n|)^{2}} + \frac{\sqrt{\pi}}{2} \operatorname{erfc}(\alpha |r+n|) \right\}.$$
(A.6)

(A2) =
$$\sum_{n} \frac{1}{4} \frac{2}{\sqrt{\pi}} \left\{ \int_{0}^{\alpha} dt t^{1/2} e^{-|r+n|^{2}t} \right\} e^{-s|n|^{2}}$$
 (A.7)

We combine the exponential terms and rearrange as shown

$$-|\underline{r} + n|^{2}t - s|n|^{2} = -(s + t)|n + \frac{t\underline{r}}{s + t}| - \frac{st|\underline{r}|^{2}}{s + t}.$$
 (A.8)

We can directly apply Jacobi's transformation (in k space) because 0 is included in \sum_{n} . Thus, we obtain

(A2) =
$$\sum_{n} \frac{1}{\sqrt{\pi}} \int_{0}^{\alpha^{2}} dt t^{1/2} \left(\frac{\pi}{s+t}\right)^{3/2} e^{\left(-\frac{\pi^{2}n^{2}}{s+t} + \frac{i2\pi(n\cdot r)t}{s+t}\right)} e^{\left(-\frac{st|r|^{2}}{s+t}\right)}$$

(A.9)

For n = 0 and $s \rightarrow 0$, there is divergence in part (A2). We extract n = 0 from \sum_{n}^{∞} (in k space) and add it on again. Now, (A2) = (A2.1) + (A2.2)

$$\underset{s \to 0}{(A2.1)} = \sum_{n \neq 0} \frac{1}{1 - \frac{2}{\sqrt{\pi}}} \int_{0}^{\alpha^{2}} dt \ t^{-1} \ \pi^{3/2} \ e^{\left(-\frac{\pi^{2}n^{2}}{t} + i2\pi \ n \cdot r\right)}$$
(A.10)

We substitute $u = t^{-1}$ to get

(A2.1) =
$$\sum_{n \neq 0} \frac{1}{2} 2 \pi e^{i2\pi n \cdot r} \int_{1/\alpha^2}^{\infty} du u^{-1} e^{-\pi^2 n^2 u}$$
. (A.11)

$$(A2.2) = \frac{1}{2} \frac{2}{\sqrt{\pi}} \int_{0}^{\alpha^{2}} dt t^{1/2} \left(\frac{\pi}{s+t} \right)^{3/2} e^{\left(-\frac{\pi^{2}n^{2}}{s+t} + \frac{i2\pi(n\cdot r)t}{s+t} \right)} e^{\left(-\frac{st|r|^{2}}{s+t} \right)} \left|_{n = 0}$$
$$= \frac{1}{2} \int_{0}^{\alpha^{2}} dt t^{1/2} \left(\frac{\pi}{s+t} \right)_{0}^{3/2} \left(\frac{-\frac{st|\mathbf{r}|^{2}}{s+t}}{s+t} \right)$$
(A.12)

Expanding in powers of s yields

$$(\lambda 2.2) = \frac{1}{2} \frac{2}{\sqrt{\pi}} \int_{0}^{\alpha^{2}} dt \ t^{1/2} \ \left(\frac{\pi}{s+t} \right)^{3/2} + O(s)$$
(A.13)

Setting $t^{1/2} = s^{1/2} \tan \theta$ and using the trigonometric method leads to

$$(A2.2) = \frac{1}{2} 2\pi \left\{ \ln(\frac{2\alpha^2}{s}) + \ln\left(\frac{s}{2\alpha^2} + 1 + \sqrt{1 + \frac{s}{2\alpha^2}}\right) - 2\left(\frac{\alpha^2}{s + \alpha^2}\right)^{1/2} \right\} + O(s)$$

$$s \rightarrow 0$$

$$= (-2\pi \ln(s/2\alpha^2) + 2\pi \ln(2) - 4\pi) \frac{1}{2}.$$
(A.14)

Now, we pull out the divergent part, $\ln(s/2\alpha^2)$, and keep it separate.

IN CASE (2) : The term (A1) is equal to (A1) from case (1), evaluated with r = 0.

Due to the application of Jacobi's transformation, we need to include the n = 0 term in the summation over n (in r space) and then subtract it separately.

$$(A2) = (A2.1)|_{\tilde{r}} = 0 + (A2.2)|_{\tilde{r}} = 0 - (A2.3)$$
(A.15)

$$(A2.3) = \frac{1}{2} \frac{2}{\sqrt{\pi}} \left\{ \int_{0}^{\alpha} dt \ t^{1/2} \ e^{-|t|^{2}t} \right\} e^{-s|n|^{2}} \left|_{t} = 0, \ n = 0$$

$$= \frac{4}{2} \frac{4 \ \alpha^{3}}{3(\pi)^{1/2}}$$
(A.16)

We follow an analogous derivation for ${\boldsymbol B}$:

$$B = \sum_{n}^{\prime} \frac{3 (r + n)(r + n)}{|r + n|^{5}} e^{-s|n|^{2}}$$

= $\sum_{n}^{\prime} 3 (r + n)(r + n) \left\{ \frac{4}{3\sqrt{\pi}} \int_{0}^{\infty} dt t^{3/2} e^{-|r + n|^{2}t} \right\} e^{-s|n|^{2}}$
(A.17)

Applying the identity,

$$\begin{array}{c} \mathbf{R} \quad \mathbf{R} \quad \mathbf{R} \quad \mathbf{z} \quad \mathbf{z} \quad \mathbf{z} \quad \mathbf{e}^{\mathbf{i}\boldsymbol{\xi}\cdot\mathbf{R}} \\ \mathbf{z} \quad \mathbf{z} \quad \mathbf{z} \quad \mathbf{e}^{\mathbf{i}\boldsymbol{\xi}\cdot\mathbf{R}} \quad \mathbf{e}^{\mathbf{i}\boldsymbol{\xi}\cdot\mathbf{R}} \quad \mathbf{z}^{\mathbf{z}} \end{array}$$
 (A.18)

let us write

$$\mathbf{B} = -\frac{4}{\sqrt{\pi}} \sum_{n}^{\prime} \nabla_{\xi} \nabla_{\xi} e^{-i\xi \cdot (r+n)} \int_{0}^{\infty} dt t^{3/2} e^{-|r+n|^{2}t} e^{-s|n|^{2}} \left| \xi = 0 \right|$$

B = (B1) + (B2) (A.19)

IN CASE (1):

$$(B1) = \frac{4}{\sqrt{\pi}} \sum_{n} (|\mathbf{r} + \mathbf{n}|) (|\mathbf{r} + \mathbf{n}|) \int_{\alpha^{2}}^{\infty} dt \ t^{3/2} \ e^{-|\mathbf{r} + \mathbf{n}|^{2}t} \ e^{-\mathbf{s}|\mathbf{n}|^{2}}$$

$$= \frac{4\alpha^{3}}{\sqrt{\pi}} \sum_{n} (|\mathbf{r} + \mathbf{n}|) (|\mathbf{r} + \mathbf{n}|) \frac{e^{-(\alpha|\mathbf{r} + \mathbf{n}|)^{2}}}{||\mathbf{r} + \mathbf{n}|^{2}}$$

$$+ \frac{6\alpha}{\sqrt{\pi}} \sum_{n} (|\mathbf{r} + \mathbf{n}|) (|\mathbf{r} + \mathbf{n}|) \frac{e^{-(\alpha|\mathbf{r} + \mathbf{n}|)^{2}}}{||\mathbf{r} + \mathbf{n}|^{4}}$$

$$+ 3 \sum_{n} (|\mathbf{r} + \mathbf{n}|) (|\mathbf{r} + \mathbf{n}|) \frac{\operatorname{erfc}(|\alpha||\mathbf{r} + \mathbf{n}|)}{||\mathbf{r} + \mathbf{n}|^{5}} \qquad (A.20)$$

$$(B2) = -\frac{4}{\sqrt{\pi}} \sum_{n} \nabla_{\xi} \nabla_{\xi} e^{-i\xi \cdot (r+n)} \int_{0}^{\alpha^{2}} dt t^{3/2} e^{-|r+n|^{2}t}.$$

$$e^{-s|n|^{2}} |\xi| = 0 \qquad (A.21)$$

Rearranging the exponential parts gives :

Taking Jacobi's transformation for (B2) yields

$$(B2) = -\frac{4}{\sqrt{\pi}} \sum_{n}^{\infty} \nabla_{\xi} \nabla_{\xi} \int_{0}^{\alpha^{2}} dt t^{3/2} \left(\frac{\pi}{s+t}\right)^{3/2} \\ e^{\left(-\frac{\pi^{2}n^{2}}{s+t} + \frac{i2\pi n \cdot rt}{s+t} - \frac{\pi\xi \cdot n}{s+t}\right)} e^{-P} \left|\xi = 0 \right|$$
(A.23)

(B2) = (B2.1) + (B2.2)

.

$$\frac{(B2.1)}{s \to 0} = -\frac{4}{\sqrt{\pi}} \sum_{n \neq 0} \nabla_{\xi} \nabla_{\xi} \int_{0}^{\alpha^{2}} dt \ t^{3/2} \ (\frac{\pi}{t})^{3/2}$$

$$= \left(-\frac{\pi^{2}n^{2}}{t} + i2\pi \ n \cdot r - \frac{\pi\xi \cdot n}{t} \right) e^{\left(-\frac{\xi^{2}}{4t} \right)} \left| \xi = 0 \right|$$

$$= -\sum_{n \neq 0} \frac{4\pi nn}{|n|^2} e^{\left(-\frac{\pi^2 n^2}{\alpha^2}\right)} e^{\left(i2\pi n \cdot r\right)}$$

+ $2\pi \frac{1}{2} \sum_{n \neq 0} \int_{0}^{\alpha^2} dt t^{-1} e^{\left(-\frac{\pi^2 n^2}{t} + i2\pi n \cdot r\right)}$ (A.24)

$$(B2.2) = -\frac{4}{\sqrt{\pi}} \nabla_{\xi} \nabla_{\xi} \int_{0}^{\alpha^{2}} dt t^{3/2} \left(\frac{\pi}{s+t}\right)^{3/2} e^{-P} \left| \xi = 0, n = 0 \right|$$
$$= 2 \pi \frac{1}{2} \int_{0}^{\alpha^{2}} dt t^{3/2} \left(\frac{1}{s+t}\right)^{5/2} e^{\left(-\frac{st|r|^{2}}{s+t}\right)}$$
$$+ 4 \pi s^{2} r r \int_{0}^{\alpha^{2}} dt t^{3/2} \left(\frac{1}{s+t}\right)^{7/2} e^{\left(-\frac{st|r|^{2}}{s+t}\right)}$$
$$s \to 0$$
$$= 4 \pi \frac{1}{2} \left[-\frac{4}{3} + \frac{1}{2} \ln(2) - \frac{1}{2} \ln(s/\alpha^{2}) \right]$$
(A.25)

IN CASE (2) :
(B1) = (B1) from case (1), evaluated at
$$r = 0$$
. (A.26)
(B2.1) = (B2.1) from case (1), evaluated at $r = 0$. (A.27)
(B2.2) = (B2.2) from case (1), evaluated at $r = 0$. (A.28)
(B2) $|_{r=0,n=0} = 0$ (A.29)

Summarizing,

$$\frac{T}{2} \left(\operatorname{case} (1) \right) = A - B = \sum_{n} \frac{1}{2} \frac{2}{\sqrt{\pi}} \frac{1}{|\underline{r}+n|^{3}} \left\{ \alpha |\underline{r}+n| e^{-(\alpha |\underline{r}+n|)^{2}} + \frac{\sqrt{\pi}}{2} \operatorname{erfc}(\alpha |\underline{r}+n|) \right\} - \sum_{n} \frac{(\underline{r}+n)(\underline{r}+n)}{|\underline{r}+n|^{2}} \left\{ \frac{4\alpha^{3}}{\sqrt{\pi}} e^{-(\alpha |\underline{r}+n|)^{2}} + \frac{6\alpha}{\sqrt{\pi}} \frac{e^{-(\alpha |\underline{r}+n|)^{2}}}{|\underline{r}+n|^{2}} + 3 \frac{\operatorname{erfc}(\alpha |\underline{r}+n|)}{|\underline{r}+n|^{3}} \right\} + \sum_{n\neq 0} \frac{4\pi nn}{|n|^{2}} e^{\left(-\frac{\pi^{2}n^{2}}{\alpha^{2}}\right)} e^{(i2\pi n \cdot \underline{r})} + \frac{4\pi}{3} \frac{1}{2}.$$
(A.30)

$$\frac{\underline{T}}{\underline{r}} (case (2))$$

$$= A - B$$

$$= \sum_{n \neq 0} \frac{1}{2} \frac{2}{\sqrt{\pi}} \frac{1}{|n|^3} \left\{ \alpha |n| e^{-(\alpha |n|)^2} + \frac{\sqrt{\pi}}{2} \operatorname{erfc}(\alpha |n|) \right\}$$

$$-\sum_{\substack{n\neq 0\\n\neq 0}} \frac{nn}{|n|^{2}} \left\{ \frac{4\alpha^{3}}{\sqrt{\pi}} e^{-(\alpha|n|)^{2}} + \frac{6\alpha}{\sqrt{\pi}} \frac{e^{-(\alpha|n|)^{2}}}{|n|^{2}} + 3 \frac{\operatorname{erfc}(\alpha|n|)}{|n|^{3}} \right\}$$
$$+\sum_{\substack{n\neq 0\\n\neq 0}} \frac{4\pi nn}{|n|^{2}} e^{\left(-\frac{\pi^{2}n^{2}}{\alpha^{2}}\right)} + \left(\frac{4\pi}{3} - \frac{4\alpha^{3}}{3\sqrt{\pi}}\right) \frac{1}{2}.$$
(A.31)

The divergent terms in (A2) and (B2) cancel each other; thus, the divergence is removed.

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APPENDIX B

B. IRREDUCIBLE CARTESIAN TENSORS

The study of tensors is important in electrostatics, electromagnetics, and hydrodynamics. The analysis and properties of tensors are detailes in textbooks⁶¹ and the literature⁶². Here, in order to determine $\underline{G}^{\ell\ell'}(\mathbf{r})$ defined in Eq. (3.20), we use a potential-theory approach⁶³ to the construction of irreducible cartesian tensors and focus on the technical development of these tensors.

The definition of an irreducible tensor $\begin{bmatrix} n \\ r \end{bmatrix}$, of rank n, is

$$\mathbf{r}^{n} = (-1)^{n} \frac{\mathbf{r}^{2n+1}}{(2n-1)!!} \frac{\partial}{\partial \mathbf{r}} \frac{1}{(\mathbf{r})}$$
(B.1)

The means irreducible. An irreducible tensor of rank n is characterized by being: (1) traceless and (2) symmetric. A tensor is traceless if it vanishes on contraction on any pair of indices, i.e. $\sum_{r \to \infty} \cdots \left(\nabla^2 \frac{1}{r} \right) = 0$, $r \neq 0$. For a symmetric tensor it is arbitrary as to which indices are used to make the contraction.

As we differentiate in Eq. (B.1) to order n, we can represent the

expansion of r^n in terms of the sum of rr(n-2m)...11(m) factors. Here n is the rank of the tensor, and m is the number of unit tensors, 1. The definition of rr(n-2m)...11(m) is, for example, for n = 1, 2 and m = 1, 2

$$\begin{bmatrix} \mathbf{r}_{\mathbf{1}} \\ \mathbf{r}_{\mathbf{2}} \end{bmatrix} = \mathbf{r}_{\alpha}\delta_{\beta\gamma} + \mathbf{r}_{\beta}\delta_{\alpha\gamma} + \mathbf{r}_{\gamma}\delta_{\alpha\beta}$$

$$\begin{bmatrix} \mathbf{r}_{\mathbf{1}} \\ \mathbf{r}_{\mathbf{2}} \end{bmatrix} = \mathbf{r}_{\alpha}\mathbf{r}_{\beta}\delta_{\gamma\phi} + \mathbf{r}_{\alpha}\mathbf{r}_{\gamma}\delta_{\beta\phi} + \mathbf{r}_{\alpha}\mathbf{r}_{\phi}\delta_{\beta\gamma} + \mathbf{r}_{\beta}\mathbf{r}_{\gamma}\delta_{\alpha\phi} + \mathbf{r}_{\beta}\mathbf{r}_{\phi}\delta_{\alpha\gamma} + \mathbf{r}_{\gamma}\mathbf{r}_{\phi}\delta_{\alpha\beta}$$

$$\begin{bmatrix} \mathbf{1} \\ \mathbf{1} \end{bmatrix} = \delta_{\alpha\beta}\delta_{\gamma\phi} + \delta_{\alpha\gamma}\delta_{\beta\phi} + \delta_{\beta\gamma}\delta_{\alpha\phi}$$

$$\vdots$$
and so on.

where $\delta_{\alpha\beta} = \nabla_{\alpha} r_{\beta} = \frac{\partial r_{\beta}}{\partial r_{\alpha}}$. $\alpha, \beta, \gamma, \phi$ each run on the cartesian indices x, y, z.

$$C_{2m}^{n}(2m-1)!! = \frac{n(n-1)...(n-2m+1)}{(2m)!}$$
 (2m-1)!! terms.

The coefficient of each term is determined by the condition that r^{n} must be traceless. For example, the coefficient for rr(n-2m)..11(m) is $\frac{(-1)^{m}r^{2m}}{(2n-1)(2n-3)...(2n-2m+1)}$ A formal expression then is:

$$\begin{bmatrix} r^{n} \\ r^{n} \end{bmatrix} = r_{1} r_{2} r_{3} \cdots r_{n} - \frac{r^{2}}{(2n-1)} \begin{bmatrix} rr(n-2)\underline{1} \\ r^{2} \\ (2n-1)(2n-3) \end{bmatrix} + \frac{r^{4}}{(2n-1)(2n-3)} \begin{bmatrix} rr(n-4)\underline{1}\underline{1} \\ r^{2} \\ r^{2} \\ r^{2} \\ (2n-1)(2n-3) \\ r^{2} \\$$

Since $\underline{G}^{\ell\ell'}(\underline{r})$ is a $\ell+\ell'+2$ rank tensor, for convenience, we let $\ell+\ell'+2 = n$, and thus:

$$\underline{G}^{\ell\ell'}(\underline{r}) = (\frac{1}{4\pi\epsilon_2}) \ (-1)^n \ \frac{(2n-1)!!}{r^{2n+1}} \ [r^n].$$
(B.3)

Since \mathbf{r}^n is an irreducible tensor, $\mathbf{G}^{\ell\ell'}(\mathbf{r})$ is symmetric in all pairs of its indices. For instance, for the 3-rank tensor, $\mathbf{G}^{01}(\mathbf{r})$, there are the equalities: $\mathbf{G}_{\alpha\alpha\beta}(\mathbf{r}) = \mathbf{G}_{\beta\alpha\alpha}(\mathbf{r}) = \mathbf{G}_{\alpha\beta\alpha}(\mathbf{r})$. Generally speaking, for the tensor of rank n, $\mathbf{G}^{\ell\ell'}(\mathbf{r})$, there are $\mathbf{3}^n$ ($n \ge 1$) components. By using this symmetric point of view, we can reduce the $\mathbf{3}^n$ components to a smaller number. In the following table, we have reduced the first five n. Here, Nc is the reduced number.

n	1	2	3	4	วี
3 ⁿ	3	9	27	81	243
Nc	3	6	10	15	21

Each reduced set of components must be accompanied by a suitable coefficient indicating the number of times it occurs in the its expression. This coefficient is determined by the number of permutations. For example, with n = 5, there are the equalities: $G_{\alpha\alpha\beta\gamma\gamma}(\mathbf{r}) = G_{\alpha\beta\alpha\gamma\gamma}(\mathbf{r}) = G_{\gamma\gamma\beta\alpha\alpha}(\mathbf{r}) = \cdots \cdots$. The total number of permutations for indices $\alpha\alpha$, β , and $\gamma\gamma$ is 30. Also, we can reduce the dimension of the $(\ell+1)$ th rank tensor, $\mu_j^{\ell}(\mathbf{r})$, by using the same reduced numbers.

The dimension of the $\underline{G}^{\ell\ell'}(\underline{r})$ matrix array not only depends on the number of components, it also depends on the number of inclusions in the primary cell. The use of the above described reduction method permits us to incorporate a relatively large number of multipole moments in the simulation.

APPENDIX C

C. LIST OF COMPUTER PROGRAMS

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This section presents the programs used for the calculation of the static and frequency-dependent effective dielectric constants in the simulations of Chapter 5.

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102

C***	**********
č	PROCRAM TITLE : STDIEL *
Ċ	PURPOSE : THE MULTIPOLE MOMENTS EFFECTS ON THE
Č	STATIC DIFLECTRIC CONSTANT OF COMPOSITE *
Č	MATERIALS FOR UNIFORM OR COATED INCLUSIONS *
č	THE CONTRIBUTIONS OF MULTIPOLES ARE UP TO #
c	
Ċ	METHOD · BY THE MINIMEM IMAGE METHOD *
C	CONTAINS · ONE MAIN PROCEAM THREE SUBBOUTINES AND *
ĉ	ONE CALLING MATHILIB/LINDACK OP EDS-164) *
č	EOP SOLVING LINEAD FOLIATIONS
Č	DATE · 1990
C***	
C+++	
Č	DI · DIFIETTOIC CONSTANT OF INCLUSION *
Ċ	D2 · DIELECTRIC CONSTANT OF INCLUSION +
C	E1 · V_COMPONENT OF ADDITED FIETD *
C	E1. A-COMPONENT OF APPLIED FIELD *
Č	E2 . I - CONDONENT OF APPLIED FIELD +
C	ES . 2-CONFONENT OF APPLIED FIELD *
	NA(MAA) AND NS . NUMBER OF INCLUSIONS *
C	NCELL : INTEGER NOMBER FOR IMAGE CELL *
	NUM : NUMBER OF CONFIGURATIONS *
	NIVE : FINAL VOLUME FRACTION TO REACH
	NP(MAX) AND NPOLE : DIMENSIONS OF MULTIPOLES *
C	NPL: FINAL NPOLE IO REACH
C	NSINK : NUMBER OF INCLUSIONS
C	RADSINK : RADIUS OF INCLUSION
C	RALSIS : RADIUS OF SISTEM
	VFRAC : VOLUME FRACTION *
0	TATE TARABANA A TATABANA
C	
C	OUIPUI ; IINOUI *
0+++	• • • • • • • • • • • • • • • • • • • •
	DOCTOAN STIDIET
	THE TABLE $A = A = A = A = A = A = A = A = A = A $
	$\frac{1}{1} \frac{1}{1} \frac{1}$
	INFLICII INIEUER+4 (I-N)
	DADAMETER (NA - 75 ND - 3)
	$\frac{1}{2} \frac{1}{2} \frac{1}$
	$\frac{1}{2} \frac{1}{2} \frac{1}$
	$DPAT, WV(ND \pm NA \pm 1) \wedge TNV(ND \pm NA ND \pm NA)$
	COMMON /ST/T/10)
	COMMON (SD / NOTI , DD DD DD DADOTT)
	$(\mathbf{Y} \mathbf{M} \mathbf{M} \mathbf{N} \mathbf{M} \mathbf{M} \mathbf{N} \mathbf{M} \mathbf{A} \mathbf{N} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} A$
	WING / INTRY AL JAU JAI JAIO JAIO JAIO JAIO JAIO
	OPEN(1, FILE = 'TININP')
	OPEN(2, FILE = 'TININ2')
	OPEN(7, FILE = 'TINOIT')

- PI = 4.0* ATAN(1.0) PI2 = 2.0*PI ANCUT=1.0 A7=105. A9=-A7*9. A11=-A9*11. A13=-A11*13. A15=-A13*15. A17=-A15*17. A19=-A17*19.
- C GET INFORMATION FROM CONFIGURATION DATA SET READ(1,*) NSINK, NCONG, VFRAC, RADSYS, RADSINK
- C GET VARIABLES FROM INPUT DATA READ(2,*) NSINK, NCON, RADSYS, NPL, NIVL READ(2,*) D2, D1, E1, E2, E3, NCELL
- C SCAN N-POLE; FROM 3,9,19,34,55 DO 200 IPL = 1, NPL IF(IPL.EQ.1) NPOLE=3 IF(IPL.EQ.2) NPOLE=9 IF(IPL.EQ.3) NPOLE=19 IF(IPL.EQ.4) NPOLE=34 IF(IPL.EQ.5) NPOLE=55
- C SCAN VOLUME FRACTION DO 100 IVOL = 1, NIVL C GET VOLUME FRACTION FROM INPUT DATA READ(2,*) VFRAC RADSINK=(3.0*VFRAC/(4.0*PI*NSINK))**(1.0/3.0)

RADCUT = ANCUT * RADSYS RADCUT2 = RADCUT * RADCUT TDIST = RADCUT + RADSYS PRD = 2.0*RADSYS PRD2 = PRD*PRD RADSYS2 = RADSYS*RADSYS FACT = 4.0*PI*D2

- C CREATE T(MP) VECTOR D1D2=D1-D2 MP=7 DO 30 L=0,MP-1 A=1. BB=1. DO 35 I=1,L BB=FLOAT(I)*BB 35 CONTINUE
 - IF(BB.EQ.0.) BB=1.

```
DO 33 I=1,L
      A=FLOAT(2*I+1)*A
33
      CONTINUE
      T(L+1) = (D1D2)*(RADSINK**(2*L+3))/(A*BB*((L+1)*D1+(L+2)*D2))
30
      CONTINUE
      WRITE(6,20)
20
      FORMAT(2X,//,40X,' RANDOM SINK CONFIGURATION ',//)
      WRITE(6,*) ' NUMBER OF SINKS = ',NSINK
      wRITE(6,*) ' RADIUS OF SINK = ',RADSINK
      wRITE(6,*) ' RADIUS OF SYSTEM = ',RADSYS
      wRITE(6,*) ' VOLUME FRACTION = ',VFRAC
      WRITE(6, *) ' NUMBER OF CONFIGURATIONS = ', NCON
      wRITE(6,*) ' NPOLE=',NPOLE
      wRITE(6,*) ' DIELECTRIC CONSTANT OF SINK: D1 = ',D1
      wRITE(6,*) ' DIELECTRIC CONSTANT OF BACKGROUND: D2 = ', D2
      WRITE(6,*) ' T-OPERATOR FOR SINK: TZZ&t11&T22 = ',TZZ,T11,T22
      wRITE(6,*) ' X-COMPONENT OF APPLIED FIELD = ',E1
      wRITE(6,*) ' Y-COMPONENT OF APPLIED FIELD = ',E2
      WRITE(6,*) ' Z-COMPONENT OF APPLIED FIELD = ',E3
С
      SET INITIAL VALUE
      SSMPX = 0.0
      SSMPX2 = 0.0
С
      BEGINNING CONFIGURATION AVERAGE
      DO 1000 ICON = 1, NCON
С
      GET NEW CONFIGURATION
      READ(1, *) ICI
      NS = 0
      DO 888 I = 1, NSINK
      NS = NS + 1
      READ(1,\star) PX(I), PY(I), PZ(I)
888
      CONTINUE
      NDIM=NS*NPOLE
С
      CREATE B VECTOR (CONSTANT PARTS)
      DO 51 I = 1, NS
      IP1 = (I-1) \times NPOLE + 1
      IP2 = (I-1) \times NPOLE + 2
      DO 52 IA = 1. NPOLE
      ID = (I-1) * NPOLE + IA
      IF(ID. EQ. IP1) THEN
      B(ID) = FACT * B1
      ELSE IF(ID.EQ.IP2) THEN
      B(ID) = FACT * E2
      ELSE
      B(ID) = FACT \neq E3
      ENDIF
```

52 CONTINUE 51 CONTINUE С FOLLOWING CALL FOR CREATING THE MATRIX ELEMENTS CALL POLEALL(PX, PY, PZ, NS, NDIM, TT, NPOLE) С FOLLOWING CALL FOR SOLVING THE LINEAR EQUATIONS С FROM FPS-164 MATH-LIB CALL PFINV(NDIM, TT, WV, AINV, IERR) DO 81 I=1,NDIM SUM=0. DO 82 J=1,NDIM SUM=SUM+AINV(I,J)*B(J) 82 CONTINUE DP(I) = SUM81 CONTINUE С FOLLOWING CALL FOR SOLVING THE LINEAR EQUATIONS С FROM LINPACK MATH-LIB С CALL SGEFA(TT, NDIM, NDIM, IPVT, IERR) CALL SGESL(TT, NDIM, NDIM, IPVT, B, 0) С С DO 81 I=1,NDIM DP(I)=B(I)С C81 CONTINUE THIS SECTION EVALUATES THE EFFECTIVE DIELECTRIC CONSTANT С NK = 0DO 333 I = 1, NDIM, NPOLE NK = NK + 1CC(NK) = DP(I)/D2333 CONTINUE SMPX = 0.0DO 151 I = 1, ns SMPX = SMPX + CC(I)151 CONTINUE SSMPX = SSMPX + SMPX SSMPX2 = SSMPX2 + SMPX*SMPX 1000 CONTINUE SSMPX = SSMPX/FLOAT(NOON)IF(NCON.GT.1) THEN TEMP = ABS((SSMPX2 - FLOAT(NCON)*(SSMPX**2))/* FLOAT(NCON*(NCON-1)))SDSMPX = SQRT(TEMP)

```
WRITE(6,501) SSMPX, SDSMPX
     ENDIF
     FORMAT(2X, ' X-COMPONENT OF DIPOLE MOMENT = '
501
     *,F14.8,' (',F14.8,')',/)
      PTSH = SSMPX/((4.D0*PI/3.D0)*RADSYS**3)
С
     PTSH=SSMPX/1.0
     TOPDE = 1.0 + 2.0 \neq PTSH/(3.0 \neq E1)
     BOTDE = 1.0 - PTSH/(3.0 \times E1)
     DED2 = TOPDE/BOTDE
     BOT2 = BOTDE * 2
     SDDE = ABS((SDSMPX/((2.0*PI*E1)*RADSYS**3)))
    Ż
            * (BOTDE+0.50*TOPDE)/BOT2)
     WRITE(6,66)DED2,SDDE
      WRITE(7,43)VFRAC, DED2
С
     FORMAT(2X,/,3X,' EFFECTIVE DIELECTRIC CONSTANT: DE = ',
66
    *F20.13,' (',F20.13,')',/)
      format(2x, 2f15.8)
c43
100
     CONTINUE
200
     CONTINUE
     STOP
     END
THIS SUBROUTINE CREATE THE MATRIX ELEMENTS
C
····
     SUBROUTINE POLEALL(PX, PY, PZ, NS, NDIM, TT, NN)
     IMPLICIT REAL*4 (A-H.O-Z)
      IMPLICIT INTEGER*4(I-N)
     DIMENSION AK(55),G(55,55)
     DIMENSION PX(NS), PY(NS), PZ(NS), TT(NDIM, NDIM)
     COMMON /ST/ T(10)
     COMMON /SP/ NCELL, PRD, PRD2, RADCUT2
     COMMON /MR/ R(11)
     DATA (AK(I), I=1, 55) / 1., 1., -1., -1., -1.
     * ,-2.,-2.,-2.,1.,1.,1.,3.,3.,3.,3.,3.,3.,3.
     * ,6.,-1.,-1.,-1.,-4.,-4.,-4.,-4.,-4.,-4.,-4.
    * ,-6.,-6.,-6.,-12.,-12.,-12.,1.,1.,1.,5.
    * ,5.,5.,5.,5.,5.,10.,10.,10.,10.,10.,10.
    * ,20.,20.,20.,30.,30.,30./
С
     FOLLOWING CALL FOR CREATING t COEFFICIENTS
     CALL CREATET (NDIM, NN, NS, TT)
С
     START TO CONSTRUCTE THE MATRIX ELEMENTS
     DO 6 I = 1, NS
     DO 3 J = 1, NS
     DO 100 K = -NCELL, NCELL
     DO 110 L = -NCELL, NCELL
     DO 120 M = -NCELL, NCELL
```

```
DIST2 = (K*K+L*L+M*M)*PRD*PRD
     IF(I.EQ.J.AND.DIST2.EQ.0.D0) GO TO 130
     XJ = PX(J) + K PRD
     YJ = PY(J) + L * PRD
     ZJ = PZ(J) + M \neq PRD
     R2 = (PX(I)-XJ) * *2 + (PY(I)-YJ) * *2 + (PZ(I)-ZJ) * *2
     IF(R2.EQ.0.) GO TO 130
     IF(R2.GT.RADCUT2) GO TO 130
     R1 = SQRT(R2)
     R(1)=R1
     R(2)=R2
     DO 21 II = 3,11
     R(II) = 1.0/(R(1)**II)
21
     CONTINUE
     RX = (PX(I) - XJ)/R(1)
     RY = (PY(I) - YJ)/R(1)
     RZ = (PZ(I) - ZJ)/R(1)
     DO 16 ID=1,NN
     DO 13 JD=1,NN
     KN=NN*(I-1)+ID
     JN=NN*(J-1)+JD
     IF(ID.LE.JD) THEN
     CALL ELEMENT(ID, JD, H, RX, RY, RZ)
     G(ID, JD)=H
     ENDIF
     IF(ID.GT.JD) THEN
     G(ID, JD) = G(JD, ID)
     ENDIF
     TT(KN, JN) = TT(KN, JN) - ABS(AK(ID)) * G(ID, JD) * AK(JD)
13
     CONTINUE
     CONTINUE
16
130
     CONTINUE
120
     CONTINUE
110
     CONTINUE
100
     CONTINUE
     CONTINUE
3
6
     CONTINUE
     RETURN
     END
THIS SUBROUTINE CREATE THE t COEFFICIENTS
С
SUBROUTINE CREATET (NDIM, NN, NS, TT)
     IMPLICIT REAL*4(A-H,O-Z)
     IMPLICIT INTEGER*4(I-N)
```

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107
```

DIMENSION TT(NDIM, NDIM) COMMON /ST/ T(10) DO 1 I = 1,NSDO 3 IS = 1,NNID = (I-1)*NN+ISDO 2 J = 1,NSDO 4 JS = 1.NNJD = (J-1)*NN+JSIF(ID.EQ.JD) THEN IF(IS.LE.3) TT(ID, JD) = 1./T(1)IF(IS.GT.3.AND.IS.LE.6) TT(ID, JD) = 1. /T(2)IF(IS.GT.6.AND.IS.LE.9) TT(ID, JD) = 2. /T(2)IF(IS.GT.9.AND.IS.LE.12) TT(ID.JD) = 1. /T(3)IF(IS.GT.12.AND.IS.LE.18) TT(ID,JD) = 3. /T(3)IF(IS.EQ.19) TT(ID,JD) = 6./T(3)IF(IS.GT.19.AND.IS.LE.22) TT(ID,JD) = 1. /T(4)IF(IS.GT.22.AND.IS.LE.28) TT(ID.JD) = 4. /T(4)IF(IS.GT.28.AND.IS.LE.31) TT(ID,JD) = 6. /T(4)IF(IS.GT.31.AND.IS.LE.34) TT(ID, JD) = 12./T(4)IF(IS.GT.34.AND.IS.LE.37) TT(ID,JD) = 1. /T(5)IF(IS.GT.37.AND.IS.LE.43) TT(ID,JD) = 5. /T(5)IF(IS.GT.43.AND.IS.LE.49) TT(ID, JD) = 10./T(5)IF(IS.GT.49.AND.IS.LE.52) TT(ID,JD) = 20./T(5)IF(IS.GT.52.AND.IS.LE.55) TT(ID, JD) = 30./T(5)ELSE TT(ID, JD)=0.ENDIF CONTINUE CONTINUE CONTINUE CONTINUE RETURN END THIS SUBROUTINE CREATE THE MATRIX ELEMENTS SUBROUTINE ELEMENT(I, J, H, RX, RY, RZ) IMPLICIT REAL*4 (A-H,O-Z) IMPLICIT INTEGER*4 (I-N) COMMON /MR/ R(11) COMMON /MAIN/ A7, A9, A11, A13, A15, A17, A19 KCX, KCY, KCZ REFER TO COUNT THE NUMBER OF X, Y, Z RX, RY, RZ ARE THE DISTANCE BETWEEN INCLUSIONS IN X,Y,Z DIRECTIONS

¥

KCX=0KCY=0 KCZ=0

4

2

3

1

С

С

С

С

DO 1 II=1,2 IF(II.EQ.1) THEN N=I ELSE N=J ENDIF IF(N.EQ.1) THEN KCX=KCX+1 KCY=KCY KCZ=KCZ ELSE IF(N.EQ.2) THEN KCX=KCX KCY=KCY+1 KCZ=KCZ ELSE IF(N.EQ.3) THEN KCX=KCX KCY=KCY KCZ=KCZ+1 ELSE IF(N.EQ.4) THEN KCX = KCX + 2KCY=KCY KCZ=KCZ ELSE IF(N.EQ.5) THEN KCX=KCX KCY=KCY+2 KCZ=KCZ ELSE IF(N.EQ.6) THEN KCX=KCX KCY=KCY KCZ=KCZ+2 ELSE IF(N.EQ.7) THEN KCX=KCX+1 KCY=KCY+1 KCZ=KCZ ELSE IF(N.EQ.8) THEN KCX=KCX+1 KCY=KCY KCZ=KCZ+1 ELSE IF(N.EQ.9) THEN KCX=KCX KCY=KCY+1 KCZ=KCZ+1 ELSE IF(N.EQ.10) THEN KCX=KCX+3 KCY=KCY KCZ=KCZ ELSE IF(N.EQ.11) THEN

KCX=KCX KCY=KCY+3 KCZ=KCZ ELSE IF(N.EQ.12) THEN KCX=KCX KCY=KCY KCZ=KCZ+3ELSE IF(N.EQ.13) THEN KCX=KCX+2 KCY=KCY+1 KCZ=KCZ ELSE IF(N.EQ.14) THEN KCX=KCX+2 KCY=KCY KCZ=KCZ+1 ELSE IF(N.EQ.15) THEN KCX=KCX+1 KCY=KCY+2 KCZ=KCZ ELSE IF(N.EQ.16) THEN KCX=KCX KCY=KCY+2 KCZ=KCZ+1 ELSE IF(N.EQ.17) THEN KCX=KCX+1 KCY=KCY KCZ=KCZ+2 ELSE IF(N.EQ.18) THEN KCX=KCX KCY=KCY+1 KCZ=KCZ+2 ELSE IF(N.EQ.19) THEN KCX=KCX+1 KCY=KCY+1 KCZ=KCZ+1ELSE IF(N.EQ.20) THEN KCX=KCX+4 KCY=KCY KCZ=KCZ ELSE IF(N.EQ.21) THEN KCX=KCX KCY=KCY+4 KCZ=KCZ ELSE IF(N.EQ.22) THEN KCX=KCX KCY=KCY KCZ=KCZ+4 ELSE IF(N.EQ.23) THEN KCX=KCX+3

KCY=KCY+1 KCZ=KCZ ELSE IF(N.EQ.24) THEN KCX=KCX+3 KCY=KCY KCZ=KCZ+1 ELSE IF(N.EQ.25) THEN KCX=KCX+1 KCY=KCY+3 KCZ=KCZ ELSE IF(N.EQ.26) THEN KCX=KCX KCY=KCY+3 KCZ=KCZ+1 ELSE IF(N.EQ.27) THEN KCX=KCX+1 KCY=KCY KCZ=KCZ+3 ELSE IF(N.EQ.28) THEN KCX=KCX KCY=KCY+1 KCZ=KCZ+3 ELSE IF(N.EQ.29) THEN KCX=KCX+2 KCY=KCY+2 KCZ=KCZ ELSE IF(N.EQ.30) THEN KCX=KCX+2 KCY=KCY KCZ=KCZ+2 ELSE IF(N.EQ.31) THEN KCX=KCX KCY=KCY+2 KCZ=KCZ+2 ELSE IF(N.EQ.32) THEN KCX=KCX+2 KCY=KCY+1 KCZ=KCZ+1 ELSE IF(N.EQ.33) THEN KCX=KCX+1 KCY=KCY+2 KCZ=KCZ+1 ELSE IF(N.EQ.34) THEN KCX=KCX+1 · KCY=KCY+1 KCZ=KCZ+2 ELSE IF(N.EQ.35) THEN KCX=KCX+5

KCY=KCY

•

KCZ=KCZ ELSE IF(N.EQ.36) THEN KCX=KCX KCY=KCY+5 KCZ=KCZ ELSE IF(N.EQ.37) THEN KCX=KCX KCY=KCY KCZ=KCZ+5 ELSE IF(N.EQ.38) THEN KCX=KCX+4 KCY=KCY+1 KCZ=KCZ ELSE IF(N.EQ.39) THEN KCX=KCX+4 KCY=KCY KCZ=KCZ+1 ELSE IF(N.EQ.40) THEN KCX=KCX+1 KCY=KCY+4 KCZ=KCZ ELSE IF(N.EQ.41) THEN KCX=KCX KCY=KCY+4 KCZ=KCZ+1 ELSE IF(N.EQ.42) THEN KCX=KCX+1 KCY=KCY KCZ=KCZ+4 ELSE IF(N.EQ.43) THEN KCX=KCX KCY=KCY+1 KCZ=KCZ+4ELSE IF(N.EQ.44) THEN KCX=KCX+3 KCY=KCY+2 KCZ=KCZ ELSE IF(N.EQ.45) THEN KCX=KCX+3 KCY=KCY KCZ=KCZ+2 ELSE IF(N.EQ.46) THEN KCX=KCX+2 KCY=KCY+3 KCZ=KCZ ELSE IF(N.EQ.47) THEN KCX=KCX KCY=KCY+3 KCZ=KCZ+2 ELSE IF(N.EQ.48) THEN

KCX=KCX+2 KCY=KCY KCZ=KCZ+3ELSE IF(N.EQ.49) THEN KCX=KCX KCY=KCY+2 KCZ=KCZ+3 ELSE IF(N.EQ.50) THEN KCX=KCX+3 KCY=KCY+1 KCZ=KCZ+1 ELSE IF(N.EQ.51) THEN KCX=KCX+1 KCY=KCY+3 KCZ=KCZ+1 ELSE IF(N.EQ.52) THEN KCX=KCX+1 KCY=KCY+1 KCZ=KCZ+3 ELSE IF(N.EQ.53) THEN KCX=KCX+2 KCY=KCY+2 KCZ=KCZ+1ELSE IF(N.EQ.54) THEN KCX = KCX + 2KCY=KCY+1 KCZ=KCZ+2ELSE IF(N.EQ.55) THEN KCX = KCX + 1KCY=KCY+2 KCZ=KCZ+2 ENDIF CONTINUE NT=KCX+KCY+KCZ KX=MAX(kCX,KCY,KCZ) KZ=MIN(KCX,KCY,KCZ) KY=NT-KX-KZ IF (KCX.EQ.KX.AND.KCY.EQ.KY.AND.KCZ.EQ.KZ) THEN X=RX Y=RY Z=RZ ELSE IF (KCX.EQ.KY.AND.KCY.EQ.KX.AND.KCZ.EQ.KZ) THEN X=RY Y=RX Z=RZ ELSE IF (KCX.EQ.KZ.AND.KCY.EQ.KY.AND.KCZ.EQ.KX) THEN X=RZ Y=RY

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1
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Z=RX ELSE IF (KCX.EQ.KX.AND.KCY.EQ.KZ.AND.KCZ.EQ.KY) THEN X=RX Y=RZ Z=RY ELSE IF (KCX.EQ.KY.AND.KCY.EQ.KZ.AND.KCZ.EQ.KX) THEN X=RY Y=RZ Z=RX ELSE IF (KCX.EQ.KZ.AND.KCY.EQ.KX.AND.KCZ.EQ.KY) THEN X=RZ Y=RX Z=RY ENDIF IF(NT.EQ.2) GO TO 2 IF(NT.EQ.3) GO TO 3 IF(NT.EQ.4) GO TO 4 IF(NT.EQ.5) GO TO 5 IF(NT.EQ.6) GO TO 6 IF(NT.EQ.7) GO TO 7 IF(NT.EQ.8) GO TO 8 IF(NT.EQ.9) GO TO 9 IF(NT.EQ.10) GO TO 10 IF(KX.EQ.2) THEN H = R(3) * (3.0 * X * * 2 - 1.0)ELSE IF(KX.EQ.1) THEN H = R(3) * (3.0 * X * Y)ENDIF GO TO 999 IF(KX.EQ.3) THEN H = -R(4) * (15.0 * X * * 3 - 9.0 * X)ELSE IF(KX.EQ.2) THEN H = -R(4) * (15.0 * Y * X * 2 - 3.0 * Y)ELSE IF(KX.EQ.1) THEN H = -R(4) * (15.0 * X * Y * Z)ENDIF GO TO 999 IF(KX.EQ.4) THEN H = -R(5) * (90.0 * X * * 2 - 105.0 * X * * 4 - 9.0)ELSE IF(KX.EQ.3) THEN H = -R(5) * (45.0 * X * Y - 105. * Y * X * 3)ELSE IF(KX.EQ.2.AND.KY.EQ.2) THEN H = -R(5)*(15.0*(X**2+Y**2)-105.0*(X*Y)**2-3.0)ELSE IF(KX.EQ.2.AND.KY.EQ.1) THEN H = -R(5)*(15.0*Y*Z-105.0*Y*Z*X**2)ENDIF

2

3

4

GO TO 999



H = R(8) * (A13 * X * 5 * Y * 2 + A11 * (10. * X * 3 * Y * 2 + X * 5) +

A9*(15.*X*Y**2+10.*X**3)+A7*15.*X)

*

```
ELSE IF(KX.EQ.5.AND.KY.EQ.1) THEN
   H = R(8) * (A13 * X * 5 * Y * Z + A11 * 10 \cdot * X * 3 * Y * Z + A9 * 15 \cdot * X * Y * Z)
 ELSE IF (KX.EQ.4.AND.KY.EQ.3) THEN
   H = R(8) * (A13 * X * 4 * Y * 3 + A11 * (6 \cdot * X * 2 * Y * 3 + 3 \cdot * X * 4 * Y) +
                            A9*(3.*Y**3+18.*X**2*Y)+A7*9.*Y)
*
 ELSE IF(KX.EQ.4.AND.KY.EQ.2) THEN
   H = R(8) * (A13 * X * 4 * Y * 2 * Z + A11 * (6 * X * 2 * Y * 2 * Z + X * 4 * Z) +
ġ.
                              A9*(3.*Y**2*Z+6.*X**2*Z)+A7*3.*Z)
 ELSE IF (KX.EQ.3.AND.KY.EQ.3) THEN
   H = R(8) * (A13 * X * 3 * Y * 3 * Z + A11 * (3 * X * Y * 3 * Z + 3 * X * 3 * Y * Z) +
Ż
                              A9*9.*X*Y*Z)
 ELSE IF(KX.EQ.3.AND.KY.EQ.2) THEN
   X**3*Z**2+X**3*Y**2)+A9*(3.*X*Z**2+3.*X*Y**2+
*
Ż
                       X**3)+A7*3.*X)
 ENDIF
 GO TO 999
 IF(KX.EQ.8) THEN
   H = R(9) * (A15 * X * * 8 + A13 * 28 * X * * 6 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * * 4 + A11 * 210 * X * X * * 4 + A11 * 210 * X * X * * 4 + A11 * 210 * X * X * * 4 + A11 * 210 * X * X * * 4 + A11 * X * X * * 4 + A11 * X * X * * 4 + A11 * X * X * * 4 + A11 *
±
                 A9*420.*X**2+A7*A7)
 ELSE IF(KX.EQ.7) THEN
   H = R(9) * (A15 * X * * 7 * Y + A13 * 21. * X * * 5 * Y + A11 * 105. * X * * 3 * Y +
×
                          A9*105.*X*Y)
 ELSE IF (KX.EQ.6.AND.KY.EQ.2) THEN
   H = R(9) * (A15 * X * * 6 * Y * 2 + A13 * (15 . * X * * 4 * Y * 2 + X * * 6) +
                   A11*(45.*X**2*Y**2+15.*X**4)+A9*(Y**2+45.*X**2)+
*
±
                   A7*15.)
 ELSE IF (KX.EQ.6.AND.KY.EQ.1) THEN
   ±
                     A9*15.*Y*Z)
 ELSE IF(KX.EQ.5.AND.KY.EQ.3) THEN
   H = R(9) * (A15 * X * 5 * Y * 3 + A13 * (10. * X * 3 * Y * 3 + 3. * X * 5 * Y) +
±
                            A11*(15.*X*Y**3+30.*X**3*Y)+A9*45.*X*Y)
 ELSE IF(KX.EQ.5.AND.KY.EQ.2) THEN
   H = R(9)*(A15*X**5*Y**2*Z+A13*(10.*X**3*Y**2*Z+X**5*Z)+
±
                              A11*(15.*X*Y**2*Z+10.*X**3*Z)+A9*15.*X*Z)
 ELSE IF(KX.EQ.4.AND.KY.EQ.3) THEN
   H = R(9) * (A15 * X * * 4 * Y * 3 * Z + A13 * (6 \cdot * X * * 2 * Y * * 3 * Z + 3 \cdot * X * * 4 * Y * Z)
±
                        +A11*(3*Y**3*Z+18.*X**2*Y*Z)+A9*9.*Y*Z)
 ELSE IF(KX.EQ.4.AND.KY.EQ.2) THEN
   Ż
                          X**4*Z**2+X**4*Y**2)+A11*(3.*Y**2*Z**2+
*
                          6.*X**2*Z**2+6.*X**2*Y**2+X**4)+A9*(3.*Z**2+
                          3.*Y**2+6.*X**2)+A7*3.)
Ż
 ELSE IF(KX.EQ.4.AND.KY.EQ.4) THEN
   H = R(9) * (A15 * X * 4 * Y * 4 + A13 * (6 * X * 2 * Y * 4 + 6 * X * 4 * Y * 2) +
                     A11*(3.*Y**4+3.*X**4+36.*X**2*Y**2)+
*
×
                     A9*(18.*Y**2+18.*X**2)+A7*9.)
 ELSE IF(KX.EQ.3.AND.KY.EQ.3) THEN
```

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±
                                 +3.*X**3*Y*Z**2
                                 +X**3*Y**3)+A11*(9.*X*Y*Z**2+3.*X*Y*3+3.*X**3*Y)+
*
±
                                 A9*9.*X*Y)
  ENDIF
  GO TO 999
  IF(KX,EQ.9) THEN
      H = R(10) * (A17 * X * * 9 + A15 * 36 \cdot * X * * 7 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * 378 \cdot * X * 5 + A13 * X * 5 + A13 * X * X * 5 + A1
                                 A11*1260.*X**3+A9*9.*A7*X)
×
  ELSE IF(KX.EQ.8) THEN
     H = R(10) * (A17 * X * 8 * Y + A15 * 28 * X * 6 * Y + A13 * 210 * X * 4 * Y + A15 * 28 * X * 6 * Y + A13 * 210 * X * 4 * Y + A15 * 28 * X * 6 * Y + A13 * 210 * X * 4 * Y + A15 * 28 * X * 6 * Y + A13 * 210 * X * 4 * Y + A15 * 28 * X * 6 * Y + A13 * 210 * X * 4 * Y + A15 * 28 * X * 6 * Y + A13 * 210 * X * 4 * Y + A15 * 28 * X * 6 * Y + A13 * 210 * X * 4 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 6 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * 4 * Y + A15 * 28 * X * A15
                             A11*420.*X**2*Y+A9*A7*Y)
±
  ELSE IF(KX.EQ.7.AND.KY.EQ.2) THEN
      H = R(10) * (A17 * X * 7 * Y * 2 + A15 * (21. * X * 5 * Y * 2 + X * 7) +
                                 A13*(105.*X**3*Y**2+21.*X**5)+
±
ž.
                                 A11*(105.*X*Y**2+105.*X**3)+A9*105.*X)
  ELSE IF(KX.EQ.7.AND.KY.EQ.1) THEN
      H = R(10)*(A17*X**7*Y*Z+A15*21.*X**5*Y*Z+
±
                                 A13*105.*X**3*Y*Z+A11*105.*X*Y*Z)
  ELSE IF(KX.EQ.6.AND.KY.EQ.3) THEN
      H = R(10) * (A17 * X * * 6 * Y * * 3 + A15 * (15 * X * * 4 * Y * * 3 + 3 * X * * 6 * Y) +
                                 A13*(45.*X**2*Y**3+45.*X**4*Y)+A11*(15.*Y**3+
Ż.
                                 135.*X**2*Y)+A9*45.*Y)
  ELSE IF(KX.EQ.6.AND.KY.EQ.2) THEN
     H = R(10) * (A17 * X * * 6 * Y * * 2 * Z + A15 * (15. * X * * 4 * Y * * 2 * Z + X * * 6 * Z) +
                                    A13*(45.*X**2*Y**2*Z+15.*X**4*Z)+
±.
                                     A11*(15.*Y**2*Z+45.*X**2*Z)+A9*15.*Z)
  ELSE IF (KX.EQ.5.AND.KY.EQ.3) THEN
      H = R(10) * (A17 * X * * 5 * Y * 3 * Z + A15 * (10. * X * * 3 * Y * * 3 * Z + 3. * X * * 5 * Y * Z)
±
                                     +A13*(15.*X*Y**3*Z+30.*X**3*Y*Z)+A11*45.*X*Y*Z)
  ELSE IF(KX.EQ.5.AND.KY.EQ.2) THEN
      ×
                                       X**5*Z**2+X**5*Y**2)+A13*(15.*X*Y**2*Z**2+
*
                                        10.*X**3*Z**2+10.*X**3*Y**2+X**5)+
                                       A11*(15.*X*Z**2+15.*X*Y**2+10.*X**3)+A9*15.*X)
  ELSE IF(KX.EQ.5.AND.KY.EQ.4) THEN
      H = R(10) * (A17 * X * 5 * Y * 4 + A15 * (10. * X * 3 * Y * 4 + 6. * X * 5 * Y * 2) +
Ż
                                 A13*(15.*X*Y**4+3.*X**5+60.*X**3*Y**2)+
*
                                 A11*(90.*X*Y**2+30.*X**3)+A9*45.*X)
  ELSE IF (KX.EQ.4.AND.KY.EQ.3) THEN
     H = R(10)*(A17*X**4*Y**3*Z**2+
                                        A15*(6.*X**2*Y**3*Z**2+3.*X**4*Y*Z**2+
Ż.
*
                                       X**4*Y**3)+A13*(3.*Y**3*Z**2+18.*X**2*Y*Z**2+
*
                                        6.*X**2*Y**3+3.*X**4*Y)+A11*(9.*Y*Z**2+
                                        3.*Y**3+18.*X**2*Y)+A9*9.*Y)
  ELSE IF(KX.EQ.4.AND.KY.EQ.4) THEN
      6.*X**4*Y**2*Z)+A13*(3.*Y**4*Z+3.*X**4*Z+
*
                                     36.*X**2*Y**2*Z)+A11*(18.*Y**2*Z+18.*X**2*Z)+
*
```

9

±. A9*9.*Z) ELSE IF(KX.EQ.3.AND.KY.EQ.3) THEN 3. *X**3*Y**3*Z+3. *X**3*Y*Z**3)+A13*(9. *X*Y*Z**3) * ± +9.*X*Z*Y**3+9.*X**3*Y*Z)+A11*27.*X*Y*Z) ENDIF GO TO 999 IF(KX.EQ.10) THEN A13*3150.*X**4+A11*45.*A7*X**2-A9*A9) ELSE IF(KX.EQ.9) THEN H = R(11) * (A19 * X * * 9 * Y + A17 * 36 . * X * * 7 * Y + A15 * 378 . * X * * 5 * Y +A13*1260.*X**3*Y+A11*9.*A7*X*Y) ELSE IF(KX.EQ.8.AND.KY.EQ.2) THEN H = R(11) * (A19 * X * 8 * Y * 2 + A17 * (28 * X * 6 * Y * 2 + X * 8) +A15*(210.*X**4*Y**2+28.*X**6)+ ¥ A13*(420.*X**2*Y**2+210.*X**4)+ ± A11*(A7*Y**2+420.*X**2)+A9*A7) ±. ELSE IF(KX.EQ.8.AND.KY.EQ.1) THEN H = R(11)*(A19*X**8*Y*Z+A17*28.*X**6*Y*Z+A15*210.*X**4*Y*Z+A13*420.*X**2*Y*Z+A11*A7*Y*Z) * ELSE IF (KX.EQ.7.AND.KY.EQ.3) THEN H = R(11) * (A19 * X * 7 * Y * 3 + A17 * (21. * X * 5 * Y * 3 + 3. * X * 7 * Y) +A15*(105.*X**3*Y**3+63.*X**5*Y)+A13*(105.*X*Y**3+ * 315.*X**3*Y)+A11*315.*X*Y) ELSE IF(KX.EQ.7.AND.KY.EQ.2) THEN H = R(11)*(A19*X**7*Y**2*Z+A17*(21.*X**5*Y**2*Z+X**7*Z)+* A15*(105.*X**3*Y**2*Z+21.*X**5*Z)+ ± A13*(105.*X*Y**2*Z+105.*X**3*Z)+A11*105.*X*Z) ELSE IF(KX.EQ.6.AND.KY.EQ.4) THEN $H = R(11) * (A19 * X * * 6 * Y * * 4 + A17 * (15 \cdot * X * * 4 * Y * * 4 + 6 \cdot * X * * 6 * Y * * 2)$ +A15*(45.*X**2*Y**4+3.*X**6+90*X**4*Y**2)+ ±. * A13*(15.*Y**4+45.*X**4+270.*X**2*Y**2)+ * A11*(90.*Y**2+135.*X**2)+A9*45.)ELSE IF(KX.EQ.6.AND.KY.EQ.3) THEN H = R(11) * (A19 * X * * 6 * Y * 3 * Z + A17 * (15. * X * 4 * Y* 3.*X**6*Y*Z)+A15*(45.*X**2*Y**3*Z * +45.*X**4*Y*Z)+A13*(15.*Y**3*Z+135.*X**2*Y*Z)+ Ż A11*45.*Y*Z) ELSE IF(KX.EQ.6.AND.KY.EQ.2) THEN H = R(11)*(A19*X**6*Y**2*Z**2+A17*(15.*X**4*Y**2*Z**2+Ż X**6*Z**2+X**6*Y**2)+A15*(45.*X**2*Y**2*Z**2+ * 15.*X**4*Z**2+15.*X**4*Y**2+X**6)+ * A13*(45.*X**2*Z**2+45.*X**2*Y**2+15.*X**4+ ± 15.*Y**2*Z**2)+A11*(15.*Z**2+15.*Y**2+45.*X**2) +A9*15.) ELSE IF(KX.EQ.5.AND.KY.EQ.5) THEN H = R(11)*(A19*X**5*Y**5+A17*(10.*X**3*Y**5+10.*X**5*Y**3)+* A15*(15.*X*Y**5+15.*X**5*Y+100.*X**3*Y**3)+

10

* A13*(150.*X*Y**3+150.*X**3*Y)+A11*225.*X*Y) ELSE IF(KX.EQ.5.AND.KY.EQ.3) THEN H = R(11) * (A19 * X * 5 * Y * 3 * Z * 2 +A17*(10.*X**3*Y**3*Z**2+3.*X**5*Y*Z**2+ × * X**5*Y**3)+A15*(15.*X*Y**3*Z**2+30.*X**3*Y*Z**2+ * 10.*X**3*Y**3+3.*X**5*Y)+A13*(45.*X*Y*Z**2+ ± 15.*X*Y**3+30.*X**3*Y)+A11*45.*X*Y) ELSE IF(KX.EQ.5.AND.KY.EQ.4) THEN H = R(11) * (A19 * X * 5 * Y * 4 * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z + A17 * (10. * X * 3 * Y * A * Z * A17 * (10. * X * 3 * Y * A * Z * A17 * (10. * X * 3 * Y * A * Z * A17 * (10. * X * 3 * Y *6.*X**5*Y**2*Z)+A15*(15.*X*Y**4*Z+3.*X**5*Z+ x * 60.*X**3*Y**2*Z)+A13*(90.*X*Y**2*Z+30.*X**3*Z)+ * A11*45.*X*Z) ELSE IF(KX.EQ.4.AND.KY.EQ.3) THEN 3.*X**4*Y*Z**3+3.*X**4*Y**3*Z)+A15*(3.*Y**3 ± * *Z**3+18.*X**2*Y*Z**3+18.*X**2*Y**3*Z+ 9.*X**4*Y*Z)+A13*(9.*Y*Z**3+9.*Y**3*Z+ * * 54.*X**2*Y*Z)+A11*27.*Y*Z) ELSE IF(KX.EQ.4.AND.KY.EQ.4) THEN +6.*X**4*Y**2*Z**2+X**4*Y**4)+A15*(3.*Y**4*Z**2+ ± * 3. *X**4*Z**2+6. *X**2*Y**4+6. *X**4*Y**2+36. * * X**2*Y**2*Z**2)+A13*(18.*Y**2*Z**2+3.*Y**4+ * 3.*X**4+36.*X**2*Y**2+18.*X**2*Z**2)+± A11*(9.*Z**2+18.*Y**2+18.*X**2)+A9*9.)ENDIF

999 CONTINUE RETURN END PROGRAM TITLE : FRQDIEL С PURPOSE : SIMULATION OF THE FREQUENCY-DEPENDENT С С DIELECTRIC CONSTANT OF COMPOSITE MATERIALS * FOR UNIFORM OR COATED INCLUSION. С С METHOD : CHOOSE ONE (1) THE MINIMUM IMAGE METHOD OR (2) THE LATTICE SUM METHOD С С CONTAINS : ONE MAIN PROGRAM , THREE SUBROUTINES, С AND ONE CALLING MATH-LIB FOR SOLVING THE COMPLEX LINEAR EQUATIONS С С DATE : 1989 С DEFINITION : С ANCUT = RADCUT/RADSYSС APHA : CONVERGE PARAMETER С BF : BEGINNING FREQUENCY: 0.2D0 С CD : THE CONDUCTIVITY С D1 : DIELECTRIC CONSTANT OF PARTICLE С D2 : DIELECTRIC CONSTANT OF MEDIUM DE : THE EFFECTIVE DIELECTRIC CONSTANT С DRE1 : RE(BULK DIELECTRIC CONSTANT FOR INCLUSION) С С DIM1 : IM(BULK DIELECTRIC CONSTANT FOR INCLUSION) С E1 : X-COMPONENT OF APPLIED FIELD С E2 : Y-COMPONENT OF APPLIED FIELD E3 : Z-COMPONENT OF APPLIED FIELD С С EF : ENDING FREQUENCY: 0.55D0 С II (MAX) AND NUMW : THE NUMBER OF FREQUENCY POINTS С N2(MAX) : THE NUMBER OF INCLUSIONS IN PRIMARY CELL С NCELL : INTEGER IN k-SPACE С NOONG : NUMBER OF CONFIGURATIONS С NN : THE DIMENSIONS OF DIPOLES; NN=3 FOR L=1 NSINK : NUMBER OF INCLUSIONS С С MCELL : INTEGER IN r-SPACE С PRD : UNIT LENGTH OF CELL С RADSYS : RADIUS OF SYSTEM С RADSINK : RADIUS OF INCLUSION TAOINV : DAMPING CONSTANT С С VFRAC : VOLUME FRACTION С VF : ELECTRON FERMI VELOCITY С W(I) : FREQUENCY С WP : PLASMA FREQUENCY С WS : RESONANCE FREQUENCY INPUT : TININP, TININ2 С С OUTPUT : TINOUT, TININ2

> PROGRAM FRQDIEL IMPLICIT REAL*8 (A-H,O-Z) IMPLICIT INTEGER*4 (I-N)

```
PARAMETER (N2 = 25, II = 100, NN = 3)
      REAL PX(N2), PY(N2), PZ(N2), XC(N2), YC(N2), ZC(N2), R(N2)
      REAL W(II), SSREAL(II), SSIMAG(II), SSRE2(II), SSIM2(II)
      REAL SSREIM(II), SMPXRE(II), SMPXIM(II)
      COMPLEX*16 TMAT(NN*N2, NN*N2), B(NN*N2), C(NN*N2), CC(NN*N2)
      COMPLEX*16 TTMAT(N2*NN,N2*NN),TMT(NN*N2,NN*N2),SSMPX(II)
      COMPLEX*16 SMPX(II), D1, DIN1, DDINO, SSMPXT, TOPDE, BOTDE
      COMPLEX*16 DE, TZZ, T(10), U, V, UV, D1D2, TOPT, BOTT, V1
      INTEGER IPTT(NN*N2)
      COMMON /PP/ NCELL, MCELL, PRD, APHA, RADCUT2, PI, PI2
      OPEN(1, FILE = 'TININP')
      OPEN(2,FILE = 'TININ2')
      OPEN(7, FILE = 'TINOUT')
      OPEN(8, FILE = 'TINOU1')
      PI = 4.D0 * DATAN(1.D0)
      PI2 = 2.D0 * PI
      ANCUT = 1.D0
      CONFIGURATION DATA INPUT FROM TININP
      READ(1, *)NSINK, NCONG, VFRAC, RADSYS, RADSINK
      GET VARIABLES FROM TININ2
      READ(2, *)NSINK, NCON, VFRAC, RADSYS
      READ(2,*)D2, Dm, E1, E2, E3, NUMW, NCELL, MCELL, APHA, BF, EF
      RADSINK = (3.D0*VFRAC/(4.D0*PI*NSINK))**(1.D0/3.D0)
      RAD=(3.*PHI/(4.*PI*NSINK))**(1./3.)
      AR=RADSINK/RAD
      RADCUT = ANCUT * RADSYS
      RADCUT2 = RADCUT * RADCUT
      RADSYS2 = RADSYS * RADSYS
      TDIST = RADCUT + RADSYS
      PRD = 2.D0 * RADSYS
      FACT = 4.D0*PI*Dm
      WRITE(6,20)
20
      FORMAT(2X,//,40X,' RANDOM SINK CONFIGURATION ',//)
      WRITE(6,*) ' NUMBER OF SINKS = ',NSINK
      WRITE(6,*) ' RADIUS OF SINK = ', RADSINK
      WRITE(6,*) ' RADIUS OF SINK = ',RAD
      WRITE(6, *) ' RADIUS OF SYSTEM = ', RADSYS
      WRITE(6,*) ' VOLUME FRACTION = ', VFRAC
      WRITE(6,*) ' VOLUME FRACTION = ', PHI
      WRITE(6,*) ' NUMBER OF CONFIGURATIONS = ', NCON
      WRITE(6,121)
121
      FORMAT(2X,//,40X,' PARAMETERS OF THE SYSTEM ',//)
      WRITE(6,*) ' DIELECTRIC CONSTANT OF MEDIUM:D2 = ',D2
      WRITE(6,*) ' X-COMPONENT OF APPLIED FIELD = ',E1
```

С

С

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wRITE(6,*) ' Y-COMPONENT OF APPLIED FIELD = ',E2
      WRITE(6,*) ' Z-COMPONENT OF APPLIED FIELD = ',E3
С
      SET INITIAL VALUES FOR EACH FREQUENCY POINT
      DO 49 I = 1, NUMW
      SSMPX(I) = CMPLX(0.D0, 0.D0)
      SSRE2(I) = 0.D0
      SSIM2(I) = 0.D0
      SSREIM(I) = 0.D0
49
      CONTINUE
С
      FOLLOWING IS CONFIGURATION AVERAGE
      DO 1000 ICON = 1, NCON
С
      GET NEW CONFIGURATION; RANDOMLY GENERATE THE CENTER
С
      OF NON-OVERLAPPING INCLUSIONS, XC, YC, ZC BETWEEN 0 AND 1.
С
      PERIODIC BOUNDARY CONDITION USED
      READ(1,*) ICI
      DO 888 I = 1, NSINK
      READ(1, *) XC(I), YC(I), ZC(I)
888
      CONTINUE
      CHECK PARTICLES ONLY INSIDE THE SPHERE (RADCUT)
С
С
      OR PRIMARY CELL
      WRITE(6,*)'ICON=',ICON
      PRDH = PRD/2.DO
      NS = 0
      DO 555 M = 1, NSINK
      IF (ABS (XC (M)-RADSYS) .GT. PRDH ) GO TO 555
      IF( ABS(YC(M)-RADSYS) .CT. PRDH ) GO TO 555
      IF( ABS(ZC(M)-RADSYS) .GT. PRDH ) GO TO 555
      NS = NS + 1
      PX(NS) = XC(M)
      PY(NS) = YC(M)
      PZ(NS) = ZC(M)
      CONTINUE
555
      NDIM IS TOTAL DIMENSION OF MATRIX
С
      NDIM = NN*NS
С
      CONSTRUCTION OF B VECTOR (CONSTANT PARTS)
      DO 51 I = 1, NS
      IP1 = (I-1)*NN+1
      IP2 = (I-1)*NN+2
      DO 52 IA = 1, NN
      ID = (I-1)*NN+IA
      IF(ID .EQ. IP1) THEN
      B(ID) = FACT * E1
      ELSE IF(ID .EQ. IP2) THEN
```

B(ID) = FACT * E2ELSE B(ID) = FACT * E3END IF 52 CONTINUE CONTINUE 51 С MIMATRIX AND LSMATRIX ONLY DEPEND UPON THE POSITIONS С OF INCLUSIONS. С IF USE LATTICE SUM METHOD, CALL LSMATRIX С CALL LSMATRIX(TMAT, PX, PY, PZ, NN, NS, NDIM) С IF USE MINIMUM IMAGE METHOD, CALL MIMATRIX CALL MIMATRIX (TMAT, PX, PY, PZ, NN, NS, NDIM) С SCAN FREQUENCY DO 50 IN = 1, NUMW FWP = FLOAT(IN)*(EF-BF)/FLOAT(NUMW)+BFWP=1.46D+16 С GAMAI = 0.24E + 14С TAOIB=0.87E+14 С VF=1.44E+14 С GAMAA=GAMAI+VF/(RADSINK*(10.E-5)) С TAO=GAMAA+TAOIB С WS=WP/SQRT(DRE1+2.*D2) С WSWP=WS**3/(WP**2) С DIM1=(TAO-GAMAA)/WSWP TAOINV=1.68D+14 DRE1=4.5D0 DIM1=0.16D0 W(IN) = FWP*WPWWP = W(IN)/WPTAOWP = TAOINV/WP DIN1 = CMPLX(DRE1, DIM1)DDINO = CMPLX(WWP, TAOWP) D1 = DIN1 - 1.DO/(WWP*DDINO)U=D2/DmV=D1/Dm V1=V-1. UV=U-V D1D2=D1-D2 NP=2DO 30 L=0,NP-1 A=1. BB=1. DO 35 I=1,L BB=FLOAT(I+1)*BB 35 CONTINUE IF(BB.EQ.0.) BB=1. DO 33 I=1,L

A=FLOAT(2*I+1)*A33 CONTINUE L1=L+1 L2=L+2L23=2*L+3 TOPT= L1*V1*(V*L2+U*L1)*RAD**L23+L1*UV*(L1+V*L2)*RADSINK**L23 BOTT=((V*L2+U*L1)*(L2+V*L1)+L1*L2*UV*V1*AR**L23)*A*BB T(L1) = TOPT / BOTT30 CONTINUE TZZ=T(1)С MATRIX ADDS DIAGONAL PARTS (SELF TERM IN PRIMARY CELL) С ELECTRIC DO 47 I=1.NDIMDO 47 J=1,NDIM IF(I.EQ.J) TTMAT(I,J)=TMAT(I,J)+1.DO/TZZIF(I.NE.J) TTMAT(I,J)=TMAT(I,J) 47 CONTINUE С SOLVING LINEAR EQUATION (TTMAT*C=B) CALL SOLVEC(TTMAT, C, B, NN, NDIM, NS, TZZ, IPIT, TMT) С ONLY PICK DIPOLE MOMENTS AT X-COMPONENT NK = 0DO 333 I = 1, NDIM, NN NK = NK + 1CC(NK) = C(I)/Dm333 CONTINUE SUM ALL DIPOLE MOMENTS С SMPX(IN) = CMPLX(0.D0, 0.D0)DO 151 I = 1, NS SMPX(IN) = SMPX(IN) + CC(I)151 CONTINUE SMPXRE(IN) = REAL(SMPX(IN))SMPXIM(IN) = AIMAG(SMPX(IN))SSMPX(IN) = SSMPX(IN) + SMPX(IN)SSRE2(IN) = SSRE2(IN) + SMPXRE(IN) * SMPXRE(IN)SSIM2(IN) = SSIM2(IN) + SMPXIM(IN) * SMPXIM(IN)SSREIM(IN) = SSREIM(IN) + SMPXRE(IN)*SMPXIM(IN) 50 CONTINUE 1000 CONTINUE RADNE3 = (3.DO/(4.DO*PI))*(2.DO*RADSYS)**3RADNEW = RADNE3**(1.D0/3.D0)

```
AL = 1.DO/(4.DO*PI*E1*RADNEW**3)
     AL2 = AL*AL
С
     ANALYZE FREQUENCY
     DO 60 I = 1, NUMW
     SSMPXT = SSMPX(I)/NCON
     TOPDE = 1.D0 + 2.D0 * AL * SSMPXT
     BOTDE = 1.DO - AL*SSMPXT
     DE = Dm * (TOPDE/BOTDE)
     CD = W(I) * AIMAG(DE) / (4.DO*PI)
С
     SECTION FOR ERROR ANALYSIS
      IF (NCON.GT.1) THEN
     SRET = REAL(SSMPXT)
     SIMT = AIMAG(SSMPXT)
     SREIMT = SRET * SIMT
     SIGA = ABS(SSRE2(I) - NCON*SRET*SRET)/(NCON-1)
     SIGB = ABS(SSIM2(I) - NCON*SIMT*SIMT)/(NCON-1)
     SIGAB = ABS(SSREIM(I) - NCON*SRET*SIMT)/(NCON-1)
     TOP = 1.DO+ AL*SRET- 2.DO*AL2*(SRET*SRET+ SIMT*SIMT)
     BOT = 1.DO- 2.DO*AL*SRET+ AL2*(SRET*SRET+ SIMT*SIMT)
     BOT2 = BOT * BOT
     D1DA = (BOT*(AL-4.D0*AL2*SRET)-TOP*(4.D0*AL2*SRET)
            -2.D0*AL))/BOT2
     D1DB = (BOT*(-4.DO*AL2*SIMT) - TOP*(2.DO*AL2*SIMT))
            /BOT2
     T2OP = 3.D0 * AL * SIMT
     D2DA = T2OP*(-2.D0*AL2*SRET + 2.*AL)/BOT2
     D2DB = (BOT*(3.D0*AL) - T2OP*(2.*AL2*SIMT))/BOT2
     SD11 = SIGA*D1DA*D1DA
     SD12 = SIGB * D1DB * D1DB
     SD13 = SIGAB*D1DA*D1DB
     SD21 = SIGA * D2DA * D2DA
     SD22 = SIGB*D2DB*D2DB
     SD23 = SIGAB*D2DA*D2DB
     SIGD1 = SQRT((SD11 + SD12 + SD13)/NCON)
     SIGD2 = SQRT((SD21 + SD22 + SD23)/NCON)
     ENDIF
С
     PRINT OUT DATA
     WRITE(7,43) W(I)/WP,REAL(DE),SIGD1
     WRITE(8,43) W(1)/WP,AIMAG(DE),SIGD2
43
     FORMAT(2X, f10.6, 1X, F10.6, 1X, F10.6)
     CONTINUE
60
     STOP
     END
THIS SUBROUTINE CREATES A COMPLEX-MATRIX BY LATTICE SUM *
C
```

```
SUBROUTINE LSMATRIX (TMAT, PX, PY, PZ, NN, NS, NDIM)
      IMPLICIT REAL*8 (a-h,o-z)
      IMPLICIT INTEGER*4(I-N)
      COMPLEX*16 TMAT(NDIM, NDIM)
      REAL PX(NS), PY(NS), PZ(NS)
      COMMON /PP/ NCELL, MCELL, PRD, APHA, RADCUT2, PI, PI2
      EXTERNAL ERFC
      SPI = DSQRT(PI)
      TREL = 4.D0*PI/3.D0-4.D0*APHA**3/(3.D0*SPI)
С
      CREATES THE INITIAL ELEMENTS OF THE MATRIX
      DO 777 I = 1, NDIM
      DO 777 J = 1, NDIM
      IF(I.EQ.J) TMAT(I,J)=CMPLX(TREL,0.D0)
      IF(I.NE.J) TMAT(I,J)=CMPLX(0.D0,0.D0)
777
      CONTINUE
С
      START TO CREATE THE ELEMENTS OF MATRIX
      THE ELEMENT IS THE SUM OF k-SPACE AND r-SPACE
С
      DO 6 I = 1, NS
      DO 2 IS = 1,NN
      ID = (I-1)*NN + IS
      DO 3 J = 1, NS
      DO 4 JS = 1.NN
      JD = (J-1) * NN + JS
С
      THIS CHECKS A SYMMETRIC MATRIX
      IF(ID.LT.JD) GO TO 3
      THIS PART DOES THE K-SPACE SUM
С
      DO 100 K = -NCELL, NCELL
      DO 110 L = -NCELL, NCELL
      DO 120 M = -NCELL, NCELL
      DIST2 = (K*K + L*L + M*M)*PRD*PRD
      IF(DIST2.LE.REAL(NCELL*NCELL).AND.DIST2.NE.0.) THEN
      XK = REAL(K)
      YK = REAL(L)
      ZK = REAL(M)
      RRX = (PX(I) - PX(J))
      RRY = (PY(I) - PY(J))
      RRZ = (PZ(I) - PZ(J))
      RDK = (RRX * REAL(K) + RRY * REAL(L) + RRZ * REAL(M)) * PRD
      THETA = 2.00*PI*RDK
      D = 4.D0*PI*EXP(-PI*PI*DIST2/(APHA*APHA))*COS(THETA)
     *
            /DIST2
      IF(IS.EQ.1) THEN
        IF(JS .EQ. 1) THEN
         TMAT(ID, JD) = TMAT(ID, JD) + D XK XK
        ELSE IF(JS .EQ. 2) THEN
```
С

С

 $TMAT(ID, JD) = TMAT(ID, JD) + D \times XK \times YK$ ELSE IF(JS .EQ. 3) THEN TMAT(ID, JD) = TMAT(ID, JD) + D * XK * ZKENDIF ELSE IF(IS .EQ. 2) THEN IF(JS .EQ. 1) THEN TMAT(ID, JD) = TMAT(ID, JD) + D*YK*XKELSE IF(JS .EQ. 2) THEN TMAT(ID, JD) = TMAT(ID, JD) + D*YK*YKELSE IF(JS .EQ. 3) THEN TMAT(ID, JD) = TMAT(ID, JD) + D*YK*ZKENDIF ELSE IF(IS .EQ. 3) THEN IF(JS .EQ. 1) THEN TMAT(ID, JD) = TMAT(ID, JD) + D*ZK*XKELSE IF(JS .EQ. 2) THEN TMAT(ID, JD) = TMAT(ID, JD) + D*ZK*YKELSE IF(JS .EQ. 3) THEN TMAT(ID, JD) = TMAT(ID, JD) + D*ZK*ZKENDIF ENDIF ENDIF 120 CONTINUE 110 CONTINUE 100 CONTINUE THIS PART DOES THE r-SPACE SUM DO 140 K = -MCELL, MCELLDO 150 L = -MCELL, MCELLDO 160 M = -MCELL, MCELLDIST2 = REAL(K*K+L*L+M*M)*PRD*PRDIF(DIST2.GT.REAL(MCELL*MCELL)) GO TO 130 XJ = PX(J) + K * PRDYJ = PY(J)+L*PRDZJ = PZ(J) + M * PRD $RRX = (PX(I) - X_j)$ $\mathbf{RRY} = (\mathbf{PY}(\mathbf{I}) - \mathbf{Yj})$ $\mathbf{RRZ} = (\mathbf{PZ}(\mathbf{I}) - \mathbf{Z}\mathbf{j})$ R2 = RRX*RRX+RRY*RRY+RRZ*RRZ IF(R2.EQ.0.D0) GO TO 130 IF(R2.GT.RADCUT2) GO TO 130 R1 = DSQRT(R2)

127

С

С

 $R3 = 1.D0/(R1 \pm 3)$ RX = RRX/R1RY = RRY/R1RZ = RRZ/R1AR1 = APHA * R1

```
EAR1 = ERFC(AR1)
EAR2 = EXP(-APHA*APHA*R2)
B = EAR1 * R3 + 2.D0 * APHA * EAR2/(R2 * SPI)
C = 4.D0*APHA**3*EAR2/SPI+6.D0*APHA*EAR2/(R2*SPI)
±
      +3.D0*EAR1*R3
IF(IS.EQ.1) THEN
 IF(JS .EQ. 1) then
   IF(I.EQ.J) THEN
   TMAT(ID, JD) = TMAT(ID, JD) - C*RX*RX+B
  ELSE IF(I.NE.J) THEN
     IF(DIST2.NE.0.) THEN
     TMAT(ID, JD) = TMAT(ID, JD) - C*RX*RX+B
    ELSE
      TMAT(ID,JD) = TMAT(ID,JD) - C*RX*RX+B+4.D0*PI/3.D0
    ENDIF
  ENDIF
 ELSE IF(JS .EQ. 2) THEN
  TMAT(ID, JD) = TMAT(ID, JD) - C*RX*RY
 ELSE IF(JS .EQ. 3) THEN
  TMAT(ID,JD) = TMAT(ID,JD) - C*RX*RZ
 ENDIF
ENDIF
IF(IS .EQ. 2) THEN
 IF(JS .EQ. 1) THEN
  TMAT(ID, JD) = TMAT(ID, JD) - C*RY*RX
 ELSE IF(JS .EQ. 2) then
   IF(I.EQ.J) THEN
    TMAT(ID, JD) = TMAT(ID, JD) - C*RY*RY+B
   ELSE IF(I.NE.J) THEN
    IF(DIST2.NE.O.) THEN
     TMAT(ID, JD) = TMAT(ID, JD) - C*RY*RY+B
    ELSE
      TMAT(ID, JD) = TMAT(ID, JD) - C*RY*RY+B+4.DO*PI/3.DO
    ENDIF
   ENDIF
 ELSE IF(JS .EQ. 3) THEN
  TMAT(ID, JD) = TMAT(ID, JD) - C*RY*RZ
 ENDIF
ENDIF
IF(IS .EQ. 3) THEN
 IF(JS .EQ. 1) then
  TMAT(ID, JD) = TMAT(ID, JD) - C*RZ*RX
 ELSE IF(JS .EQ. 2) then
  TMAT(ID, JD) = TMAT(ID, JD) - C*RZ*RY
 ELSE IF(JS .EQ. 3) THEN
   IF(I.EQ.J) THEN
    TMAT(ID, JD) = TMAT(ID, JD) - C*RZ*RZ+B
```

ELSE IF(I.NE.J) THEN IF(DIST2.NE.O.) THEN TMAT(ID,JD) = TMAT(ID,JD) - C*RZ*RZ+B ELSE TMAT(ID, JD) = TMAT(ID, JD) - C*RZ*RZ+B+4.D0*PI/3.D0ENDIF ENDIF ENDIF ENDIF 130 CONTINUE 160 CONTINUE 150 CONTINUE 140 CONTINUE С CREATES THE REST PARTS OF MATRIX TMAT(JD, ID)=TMAT(ID, JD) 4 CONTINUE 3 CONTINUE 2 CONTINUE 6 CONTINUE С END THE SUM RETURN END THIS IS THE COMPLEMENTARY ERROR FUNCTION С FUNCTION ERFC(X) IMPLICIT REAL*8(A-H,O-Z) IMPLICIT INTEGER*4(I-N) PARAMETER(A1=0.254829592D0.A2=-0.284496736D0 * ,A3=1.421413741D0,A4=-1.453152027D0 ,A5=1.061405429D0,P=0.3275911D0) * T=1.D0/(1.D0+P*X)XSQ=X*X TP=T*(A1+T*(A2+T*(A3+T*(A4+T*A5))))ERFC=TP*EXP(-XSQ)RETURN END С THIS SUBROUTINE IS TO CREATE A COMPLEX-MATRIX BY * С MINIMUM IMAGE METHOD Ż SUBROUTINE MIMATRIX(TMAT, PX, PY, PZ, NN, NS, NDIM) IMPLICIT REAL*8 (A-H,O-Z) IMPLICIT INTEGER*4(I-N) COMPLEX*16 TMAT(NDIM,NDIM)

REAL PX(NS), PY(NS), PZ(NS) COMMON /PP/ NCELL, MCELL, PRD, APHA, RADCUT2, PI, PI2 С CREATE THE INITIAL ELEMENTS OF MATRIX DO 777 I = 1, NDIM DO 777 J = 1, NDIM TMAT(I, J) = CMPLX(0., 0.)777 CONTINUE С STARTS TO CREATE THE ELEMENTS OF MATRIX DO 6 I = 1, NS DO 2 IS = 1, NNID = (I-1)*NN + ISDO 3 J = 1, NS DO 4 JS = 1, NNJD = (J-1) * NN + JSС USE THE PERIODIC BOUNDARY CONDITION DO 100 K = -NCELL, NCELL DO 110 L = -NCELL, NCELL DO 120 M = -NCELL, NCELL DIST2 = (K*K + L*L + M*M)*PRD*PRDС CHECKS THE SELF-INTERACTION IN THE PRIMARY CELL IF(I .EQ. J .AND. DIST2 .EQ. 0.D0) go to 120 XJ = PX(J) + K*PRDYJ = PY(J) + L*PRDZJ = PZ(J) + M*PRDR2 = (PX(I)-XJ) * 2 + (PY(I)-YJ) * 2 + (PZ(I)-ZJ) * 2IF(R2.EQ.0.D0) GO TO 120 CHOSEN PARTICLE AS CENTER TAKES THE FINITE SIZE С С OF THE SYSTEM, WHICH IS MINIMUM IMAGE METHOD IF(R2.GT.RADCUT2) GO TO 120 R1 = R2 * * (0.50)R3 = 1.D0/(R1**3)XX = (PX(I)-XJ)/R1YY = (PY(I)-YJ)/R1ZZ = (PZ(I)-ZJ)/R1С THIS PART IS TO CREATE THE ELEMENTS OF MATRIX IF(IS.EQ.1) THEN IF(JS .EQ. 1) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.D0*XX**2-1.D0)ELSE IF(JS .EQ. 2) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.DO*XX*YY)ELSE IF(JS .EQ. 3) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.D0*XX*ZZ)

•

ENDIF ENDIF С IF(IS .EQ. 2) THEN IF(JS .EQ. 1) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.DO*YY*XX)ELSE IF(JS .EQ. 2) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.D0*YY*2 - 1.D0)ELSE IF(JS .EQ. 3) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.D0*YY*ZZ)ENDIF ENDIF С IF(IS .EQ. 3) THEN IF(JS .EQ. 1) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.0*ZZ*XX)ELSE IF(JS .EQ. 2) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.0*ZZ*YY)ELSE IF(JS .EQ. 3) THEN TMAT(ID, JD) = TMAT(ID, JD) - R3*(3.0*ZZ**2 - 1.0)ENDIF ENDIF 120 CONTINUE 110 CONTINUE 100 CONTINUE 4 CONTINUE 3 CONTINUE 2 CONTINUE 6 CONTINUE RETURN END С THIS SUBROUTINE SOLVE THE COMPLEX LINEAR EQUATION * SUBROUTINE SOLVEC(TMAT, C, B, NN, NDIM, NS, TZZ, IPTT, TMT) IMPLICIT REAL*8(A-H,O-Z) IMPLICIT INTEGER*4 (I-N) COMPLEX*16 C(NDIM), TMAT(NDIM, NDIM), B(NDIM) COMPLEX*16 TMT(NDIM,NDIM),TZZ INTEGER IPTT(NDIM) С RENAME MATRIX FOR SAVING THE ORIGINAL MATRIX DO 20 I = 1, NS IN=(I-1)*NNDO 3 ID=1,NN DO 21 J = 1, NS JN=(J-1)*NNDO 4 JD=1,NN

TMT(IN+ID, JN+JD) = TMAT(IN+ID, JN+JD)

- 4 CONTINUE
- 21 CONTINUE
- 3 CONTINUE
- 20 CONTINUE
- C FOLLOWING CALL FROM FPS-164 MATH-LIB CALL CSOLVQ(TMT,NDIM,B,NDIM,C,NDIM,NDIM,1, * (10.)**(-100),IPTT,IERR) RETURN END

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LIST OF REFERENCES

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PART II

.

ELECTRON LOCALIZATION : QUANTUM MOLECULAR DYNAMICS

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1. INTRODUCTION

Electron localization is one of the most fundamental quantum mechanical phenomena related to condensed matter^{1,2}. The electron dynamics is governed by the electron-molecule interaction, the molecular distribution, and the mean free path of the electron. According to Anderson¹, electron localization is caused by fluctuations in the electrons's potential due to configurational fluctuations in the medium. This is a density effect. In low density media, the electron mean free path is larger than the thermal wavelength, $\lambda_{e} = \left(\frac{\beta \hbar^2}{-m_{e}}\right)^{1/2}$ (where β is $1/k_{\rm B}$ T, $k_{\rm B}$ is the Boltzmann constant, and me is the electron mass), and the electron is quite free before scattering occurs. As the density is increased, the electron will undergo multiple scattering with backward and forward bounces off molecules and electron localization may occur.

For a well localized electron, the electronic wavefunction becomes concentrated in a finite local region typically characterized by the order of a few molecular diameters (1.5 σ to 3. σ), where σ is a molecular diameter. The envelope of the electronic wavefunction decays exponentially to zero at points which are far away from the center of mass of the electron.

138

In a microscopic description, the electron's mean free path is the basic length scale before diffusion occurs for a localized electron. When the interaction between the electron and molecules is small or the density is low, the electronic wavefunction is extended. The mean free path of the electron is large compared to the separation between a pair of molecules and the thermal de Broglie wavelength. In terms of time evolution, the localized state is defined as a finite probability of finding the electron at its initial position after an infinite time¹.

Based on the model of a particle in spherical box^3 , as the electron evolves from an extended state to localized state there is increasing kinetic energy and decreasing potential energy, since the electron localizes in a small cage. As the cage becomes smaller, the more confined electronic state must have a higher kinetic energy.

A variety of mechanisms, based on the electron-molecule interaction, can cause the electron to localize as the density is increased. If the electron-molecule interaction is mainly attractive, the electron can become localized via the configurational fluctuations in the system, e.g. in xenon^{31a}. In contrast, if the interaction is mainly replusive, the electron may be trapped in the cage created by the strong local potential fluctuation, for example, a helium system³¹. If the electron energy is near the potential barrier, it will jump over the barrier from one trap to another trap, resulting in an activated electron transition. If the electron energy is less than the potential barrier, the electron will sit in the potential well and move very slowly through the system, because it must wait for the nuclear configuration to gradually open a path. If the configurational fluctuations create another hole with equal energy near the place where the electron is sitting, then the electron can tunnel through the barrier. The actual mechanism whether the electron tunnels or diffuses by activated jumping is still not understood.

Recently, a body of theoretical and experimental work has focused on the investigation of the properties of an excess electron in ionic fluids⁴, molten salts⁵⁻⁷, polar clusters⁸⁻¹⁵, polar fluids¹⁶⁻²⁷, and inert fluids²⁸⁻³⁵. Most recent theoretical work has been done by computer simulation methods. These methods include the quantum Monte Carlo method³⁶, quantum path-integral Monte Carlo method³⁷ and quantum path-integral molecular dynamics simulation method 5,9-10,37-38 The quantum path-integral method is based on an isomorphism³⁸ between the Feynman path-integral³⁹ in quantum statistical mechanics and a classical system. The quantum electron is represented by a cyclic necklace of pseudo-points located on the discretized path³⁷. A generalized molecular dynamics was developed in accord with the density functional formalism⁴⁰. Theoretical investigations employed the quantum path-integral molecular dynamics method to study electron localization in polar molecular clusters^{9,10}, and yielded agreement with experimental results. These methods provide information about the ground state, thermal equilibrium energies, structure, stability, and excess electron localization in small cluster and bulk liquid systems.

The numerical path-integral method^{5,9-10,37-38} cannot provide

information on the dynamics of the quantum electron. A Molecular Dynamics Adiabatic Simulation Method (MDAS)^{6-7,11-12} has been developed for the study of the dynamics of a quantum electron in a medium of classical molecules.

For the use of MDASM the quantum-classical $concept^{6,11,41}$ is considered such that the electron is represented by its electronic wavefunction and the molecules by their positions. The motion of electron and molecules are described by the integration of the time-dependent Schrödinger equation and the classical equations of motion, respectively. A time-dependent self-consistent-field procedure⁴² is used so that the time evolution of the wavefunction is determined and the classical equations of motion are treated by classical molecular dynamics^{6,11,41}. With this approach we can directly obtain information on the dynamic and equilibrium properties of electrons in fluids.

The electron dynamics is analyzed by directly solving the time-dependent Schrödinger equation of the excess electron

$$i \frac{\partial \psi}{\partial t} = -\frac{\hbar}{2m} \nabla^2 \psi + \frac{V_{ep}(r, \{R_{ij}\})}{\hbar} \psi \qquad (1.1)$$

to obtain the time evolution of $\psi(\underline{r},t)$ by using the fast Fourier transform technique⁴³. Here m_e is the mass of electron, \hbar is Planck's constant, and $Vep(\underline{r}, \{\underline{R}_{ij}\})$ is the quantum-classical interaction potential.

The molecular dynamics simulation follows the motion of molecules via the coupling to the electron and their mutual interactions. Each molecule moves along its classical trajectory. The dynamics of the system is governed by the inter-molecular interactions and quantum-classical interaction, and requires the numerical integration of the classical equations of motion. Each molecule obeys the equation of motion

$$\frac{\mathrm{d}R_{i}}{\mathrm{d}t} = \frac{P_{i}}{m}$$
(1.2)

and

$$\frac{dP_{i}}{dt} = -\frac{\partial V(R_{ij})}{\partial R_{i}} - \int d^{3}r |\psi(r,t)|^{2} \frac{\partial V_{ep}(r, \{R_{ij}\})}{\partial R_{i}}$$
(1.3)

where \mathbb{R}_{i} and \mathbb{P}_{i} are, respectively, the position and the momentum of the ith molecule, m is the mass of the molecule, and $V(\mathbb{R}_{ij})$ is the molecular interaction potential. The motion of molecules is coupled with the electron by the quantum force in the second term of Eq.(1.3).

Electron localization in dense helium^{31b} has been the subject of investigation by solving the Schrödinger equation for the electron. However, the nuclear configurations were generated from an equilibrium path-integral simulation³⁷. The molecular dynamics effects on the electron localization and the electron dynamics cannot be obtained from this work. Electron localization in water clusters and NaCl^{11,12} were investigated via MDAS, and the results provided the ground state, excited state and resonance state with the various cluster sizes. The dynamics following the electronic transition of an excess electron in clusters and in bulk water has been studied by an adiabatic simulation method¹², too. The diffusion coefficient of the electron has been simulated in a molten salt^{6,7}, and in polar fluids^{20,24}.

This study focuses on the localization, dynamics, and mode of transport of an excess electron in condensed helium via MDAS. The system consists of an excess quantum electron and several hundred helium atoms. We neglect the quantum effect of helium atoms and treat them classically. The adiabatic approximation is valid, since the electron mass is much smaller than the helium mass. Molecules are distributed by the probability distribution $P\{R_1, R_2, \dots, R_j\}$, where R_j is the center of the ith molecule and $j = 1, 2, \dots N$. N is the number of molecules. The molecule-molecule and electron-molecule interactions are given by the Lennard-Jones potential⁴⁵ and a pseudopotential⁴⁴, respectively.

To do a molecular dynamics simulation we must know the equations of motion, the molecular-molecular and electron-molecular interaction, and consider a sufficiently large system. In our application, in order to simulate an infinite system with a finite system, we apply periodic boundary conditions⁴⁶.

Much of the computation time is used for handling the sums over particles in the energy and force calculations. If we summed over all the N particles, the computational time would be proportional to N^2 . There are two efficient algorithms which have developed to limit the number of particles summed over the system: 1) the minimum image method^{47,48} and 2) the nearest neighbor list method^{47,49}— the neighbor lists with infrequent update.

In Chapter 2, we will outline the computational simulation method used to generate nuclear configurations via molecular dynamics (Section 2.1) and obtain the time evolution of the electronic wavefunction $\psi(\mathbf{r},\mathbf{t})$ of the excess electron in the given nuclear configuration (Section 2.2). The methods used to obtain the ground state, excited states, the kinetic and potential energy, the spectral analysis, and transport properties of the electron are described. A more detailed account of the adiabatic simulation method is given in Section 2.3. The effective moving grid technique¹² used to monitor the migration of the electron is described in Section 2.4. The results are presented and discussed in Chapter 3. The conclusion is given in Chapter 4.

2. COMPUTATIONAL METHOD

We describe the computational algorithms which we have been developing to explore electron localization in liquids. These programs are sufficiently flexible to be linked and allow various applications.

2.1 MOLECULAR DYNAMICS

Each atom is treated as a point mass with motion which is controlled by the forces imposed on it by all the other atoms, as described by the equations of motion of classical mechanics. The numerical solution of the equations of motion is repeated iteratively to produce the total trajectory. Rahman⁵⁰ in 1964 was the first to use computer simulation to study molecular dynamics in liquid argon with a Lennard-Jones potential. There is extrusive literature giving a detailed description of molecular dynamics⁵¹. In the following we summarize the Verlet-velocity algorithm⁴⁹ (see program MD).

VERLET-VELOCITY ALGORITHM:

1). The initial positions, \mathbb{R}_{i}^{1} , of the classical molecules are given by the face-centered cubic lattice points.

2). The initial velocities, v_i^1 , of the classical molecules are determined by the Maxwellian distribution function.

145

3). The positions at the (n+1)th time step are determined by those of the nth time step according to

$$\mathcal{R}_{i}^{n+1} = \mathcal{R}_{i}^{n} + \Delta t_{\text{HD}} \mathcal{V}_{i}^{n} + \frac{1}{2 \text{ m}} \Delta t_{\text{HD}}^{2} \mathcal{F}_{i}^{n}$$
(2.1)

where

 \mathbb{R}_{i}^{n+1} , \mathbb{R}_{i}^{n} : The positions of ith molecule at the (n+1)th time step and the nth time step.

 $\boldsymbol{\vartheta}_{i}^{n}$: The velocities of ith molecule at the nth time step.

 $\Delta t_{_{\sf MD}}$: The molecular dynamics time increment.

- m : The mass of the classical molecule.
- F_{i}^{n} : The force produced by the classical molecules acting on the ith molecule at the nth time step.

4). The velocities for the ith molecule at the (n+1)th time step are given as

$$v_i^{n+1} = v_i^n + \Delta t_{MD} \left(F_i^{n+1} + F_i^n \right) / 2m$$
(2.2)

5). Force can be calculated either by the minimum image convention method or by the nearest neighbor list method. The program we used is written in the latter method⁴⁷.

The molecule-molecule potential is chosen to be a Lennard-Jones

$$V_{LJ}(\mathbf{R}) = 4 \varepsilon \left\{ \left(\frac{\sigma}{\mathbf{R}} \right)^{12} - \left(\frac{\sigma}{\mathbf{R}} \right)^{6} \right\}, \qquad (2.3)$$

where σ is the diameter of molecule and ε is the well depth of $V_{LJ}(\mathbf{R})$, with values of ε and σ selected to represent helium, argon, and xenon

	He	Ar	Хе
σ(Å)	2.556	3.4	4.055
ε(K)	10.22	120.	229.

Hence, the x component of the force is given by

$$F_{\mathbf{x}} = -\nabla_{\mathbf{x}} V_{\mathbf{LJ}}(\bar{\mathbf{R}})$$
$$= \frac{48\varepsilon}{\sigma} \left\{ \left(\frac{\sigma}{R} \right)^{14} - \frac{1}{2} \left(\frac{\sigma}{R} \right)^{8} \right\} \frac{R_{\mathbf{x}}}{\sigma}$$
(2.4)

where R_x is the x-component of the vector R_x . The molecular equation of motion is

$$m \frac{d^2 R_{i}}{dt_{HD}^2} = \sum_{j \neq i}^{N} F(R_{ij}).$$
(2.5)

To facilitate the calculation, the lengths are in units of σ , the energies are in units of ε , and the time is in units of C_{MD} defined below⁵⁰. In order to make Eq.(2.5) dimensionless, we use the relation,

$$\frac{m\sigma}{C_{MD}^2} = \frac{48\varepsilon}{\sigma}.$$
 (2.6)

Thus, C_{MD} is defined by

$$C_{\rm MD} = \left(-\frac{m \sigma^2}{48\epsilon} \right)$$
(2.7)

The scale factor is $C_{MD} = 2.54 \times 10^{-13}$ (sec) for helium and the dimensionless length and time are $R_{\sigma} = R/\sigma$ and $\overline{t}_{MD} = t_{MD}/C_{MD}$, respectively.

The system temperature T is defined by $T = \frac{m}{3 N k_B} \sum_{i=1}^{N} v_i^2$. The atomic velocities are renormalized when the temperature is far away from the desired value so that the mean kinetic energy corresponds to the desired temperature.

Therefore, we can rewrite a dimensionless Eq.(2.1)

$$R_{i\sigma}^{n+1} = R_{i\sigma}^{n} + \Delta \overline{t}_{HD} \overline{\psi}_{i}^{n} + \frac{1}{2} \Delta \overline{t}_{HD}^{2} \overline{F}_{i}^{n}$$
(2.8)

where
$$\overline{v}_{i}^{n} = C_{MD} v_{i}^{n} / \sigma$$
 (2.9)

$$\overline{F}_{i}^{n} = C_{MD}^{2} \overline{F}_{i}^{n} / m\sigma$$
(2.10)

The scaled kinetic energy and the potential energy of the classical molecules are, respectively, $\sum_{i=1}^{N} m \frac{\overline{v}_{i}^{2}}{2} = 24 \sum_{i=1}^{N} \overline{v}_{i}^{2}$ (in unit of ε), and $V_{LI}(\overline{R}) = 4 \{ \overline{R}^{-12} - \overline{R}^{-6} \}$ (in unit of ε).

The classical molecules were placed on the face-centered cubic

148

(fcc) lattice points. For each unit fcc cell, there are four molecules in each cell. For a cubic simulated box the number of fcc cells in each direction is ncell and the total number of molecules in the simulated box is N. The relation is $N = 4 \times \text{ncell}^3$. The results presented here represent N corresponding to 108 and 864, namely, the ncell values are 3 and 6.

In all calculations the number of classical molecules is between 108 to 864. The density was fixed and periodic boundary conditions⁴⁶ were used. The effect of the long-range potential interaction has to be neglected by taking a cut-off at $r_c = 2.5\sigma$, and the nearest neighbor list is cut at $r_c = 2.7\sigma^{49}$ in order to prevent multiple interactions between molecules. In all the generated configurations, the first 10^5 molecular dynamic steps were thrown away and the calculations were carried out by running for 5000 more molecular dynamics steps.

The computation time (CPU) for one molecular dynamics step with different numbers of particles on the Titan system is, respectively, 0.2, 0.68, 6.8, 210 sec. for N = 108, 256, 864, 2916.

It is important to choose an optimal time step for the molecular dynamics. The optimal Δt_{MD} should make particles move toward each other slowly when they are within a distance less than $r_{min} = 2^{1/6}\sigma$, the separation between a pair with the minimum potential energy. This can prevent them from bouncing back too quickly; otherwise, if the time step is chosen too large molecules will be bounced out of the simulation volume. A big time step results in numerical integration

error of the equations of motion, too. On the other hand, we can not choose too small a time step; otherwise the computation time is too long. At $T^* = k_B T/\epsilon = 30.23$ (k_B is the Boltzmann constant) for helium atoms the time steps, $\Delta \overline{t}_{MD}$, we used are 4.72×10^{-3} (1.198 $\times 10^{-15}$ sec) and 2.36×10^{-3} (5.994 $\times 10^{-16}$ sec). At $T^* = 0.75$ the time step is chosen to be 0.032^{50} .

Figure 2.1 shows the molecular dynamics radial distribution function g(r) of the classical molecules at reduced number density $\rho^* = N\sigma^3/V = 0.9$ and reduced temperature $T^* = 30.23$ calculated at a given configuration after 10^5 MDR. The result shows the configuration has a typical liquid structure.

The mean square displacement $\langle R^2 \rangle$ of the atoms is defined as

$$\langle R^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} [R_i^{n+1} - R_i^n]^2$$
 (2.11)

The following algorithm was written to facilitate obtaining $\langle R^2 \rangle$ in a system when periodic boundary conditions are used. For example, let us consider only the x direction.

$$rx(i) = 0.$$

...
DO 50 i = 1, N
 $rx(i) = rx(i) + (x(i)-xp(i))$



Figure 2.1 The helium-helium radial distribution function at reduced number density $\rho^*=0.9$ with T^{*}=30.23. The number of helium atoms is 107.

50 continue

Then
$$\langle R_{\sigma}^{2}(i) \rangle = rx(i)^{2} + ry(i)^{2} + rz(i)^{2}$$

where x(i) is the forward position of the ith molecule after one molecular dynamics step, and xp(i) is the previous position of the ith molecule located inside the simulation box. By using the algorithm we cumulated the difference of displacement between every step to obtain $\langle R^2 \rangle$. After we check the boundary condition of the molecules, we then renamed

$$xp(i) = x(i)$$

The diffusion coefficient is given in terms of the dimensionless $\langle R_{\sigma}^2 \rangle$ and $\overline{t}_{\rm MD}$ as

$$D = \lim_{t \to \infty} \frac{\langle R^2 \rangle}{6t} = \lim_{t \to \infty} \left(\frac{\sigma^2}{6 C_{MD} \Delta t_{MD}} \right) \frac{\langle R^2 \rangle}{\# \text{ of } MDR}$$
(2.12)

Figure 2.2 shows a plot of the mean square displacement $\langle R^2 \rangle$ of helium versus time calculated at $\rho^* = 0.9$ and $T^* = 30.23$. The number of particles is 864, $\Delta \overline{t}_{MD}$ is 9.44×10^{-4} (2.397 $\times 10^{-16}$ sec), the side



Figure 2.2 Plot of the mean square displacement $\langle R^2 \rangle$ of helium versus time at $\rho^{\ddagger}=0.901$ and $T^{\ddagger}=30.23$. The estimated diffusion constant is 4.86×10^{-4} .

Table 2.1The list of the diffusion coefficient of helium at givenreduced number density and reduced temperature.

ب *	T [‡]	D
0.5	30.23	1.09x10 ⁻²
0.701	30.23	7.27x10 ⁻⁴
0.901	30.23	4.86x10 ⁻⁴
0.5	0.75	4.85x10 ⁻⁵
0.7	0.75	2.70×10^{-5}
0.8	0.75	1.55x10 ⁻⁵
0.9	0.75	

length of the box, L, is 9.84σ , and the total number of steps is 10⁴, 2.397 picoseconds (ps). Table 2.1 lists the simulation results of the diffusion coefficients with different reduced number density for helium.

In the argon case, at $T^* = 0.75$ and $\rho^* = 0.805$, the number of particles is 864, $\Delta \overline{t}_{HD}$ is 0.032 (10^{-14} sec), the side length of box is 10.23 σ , and the number of steps is 5000 (50 picoseconds). The slope of $\langle R^2 \rangle$ versus time yields a diffusion coefficient 2.35×10^{-5} cm²/sec, which has 3% relative error compared with the data obtained by Rahman⁵⁰ and the experimental value^{52,53}, 2.43 $\times 10^{-5}$ cm²/sec.

2.2 THE SCHRÖDINGER EQUATION

The method we use to study the localization of an excess electron in fluids is based on the symmetrically split operator technique presented by Feit, Fleck, and Steiger⁴³ for solving the one-electron Schrödinger equation. The time-dependent Schrödinger equation is

$$i \frac{\partial \psi}{\partial t} = -\frac{\hbar}{2m} \nabla^2 \psi + \frac{\nabla_{\bullet p}(\underline{r})}{\hbar} \psi \qquad (2.13)$$

The split operator Fast Fourier Transform (FFT) method⁴³ provides a very efficient technique for propagating the solution. At each small time step Δt the propagator is split into kinetic and potential parts. According to the second-order accuracy of the symmetrically split operator solution to the propagation equation, we write the electronic wavefunction as

$$\psi(\mathbf{r},t+\Delta t) = \exp(\frac{i\Delta t \hbar}{4 m_{e}} \nabla^{2}) \exp(-i\Delta t \frac{\nabla_{ep}(\mathbf{r})}{\hbar}) \exp(\frac{i\Delta t \hbar}{4 m_{e}} \nabla^{2}) \psi(\mathbf{r},t) +O(\Delta t^{3}) \qquad (2.14)$$

 $\psi(\mathbf{r},t)$ is a given initial electronic wavefunction. An error proportional to (Δt^3) is due to the noncommutativity of the kinetic and potential energy operators. The symbol $O(\Delta t^3)$ means the solution is accurate to order $(\Delta t^3)^{54}$.

The FFT method yields the electronic wavefunction on a grid defined by integers N1, N2, and N3 which span on the simulation box with side lengths Lx, Ly, Lz. The grid spacing in the direction of x, y, z is $\Delta x=Lx/N1$, $\Delta y=Ly/N2$, and $\Delta z=Lz/N3$. The grid representation for the wavefunction implies a spatial periodicity. The split operator method involves performing the kinetic part of propagation in momentum space where the kinetic energy is diagonal and the potential part of propagation in coordinate space. The coordinate space $\psi(\mathbf{r},t) = \psi_{ijk}(t)$ and the momentum space $\psi_{fmn}(t)$ are related by

$$\psi_{ijk}(t) = \sum_{\ell=-N1/2+1}^{N1/2} \sum_{m=-N2/2+1}^{N2/2} \sum_{m=-N3/2+1}^{N3/2} \psi_{\ell m n}(t) \exp \left[2\pi i \left(\frac{\hat{c}_{x}}{L_{x}} + \frac{\pi y}{L_{y}} + \frac{\pi z}{L_{z}} \right) \right]$$
(2.15)

When the wavefunction propagates for a half time step $\Delta t/2$, the

156

solution of $\exp(\frac{i\Delta t\hbar}{4m_e}\nabla^2)\psi(r,t)$ can be obtained by the use of the band-limited Fourier series representation⁴³,

$$\psi_{\tilde{c}mn}(t+\Delta t/2) = \psi_{\tilde{c}mn}(t) \exp\left\{-\left(\frac{i\Delta t\hbar}{4m_{e}}\right) (2\pi)^{2} \left[\left(\frac{\tilde{c}}{Lx}\right)^{2} + \left(\frac{\pi}{Ly}\right)^{2} + \left(\frac{\pi}{Lz}\right)^{2}\right]\right\}$$
(2.16)

Eq. (2.13) can be rewritten as the dimensionless Schrödinger equation,

$$i \frac{1}{C_{F}} \frac{\partial \psi}{\partial \overline{t}} = -\frac{\hbar}{2m_{e}} \frac{1}{\sigma^{2}} \nabla_{\sigma}^{2} \psi + \frac{V_{ep}(r)}{\hbar} \psi, \qquad (2.17)$$

where

$$\overline{t} = t/C_{F}, \qquad (2.18)$$

$$x_{\sigma} = x/\sigma, \qquad (2.19)$$

and
$$C_F = \frac{2m_e \sigma^2}{\hbar}$$
. (2.20)

The scale factor is $C_F = 1.1286 \times 10^{-15}$ (sec) for the electron in the helium system.

The algorithm we use in our calculation is summarized in the following flow chart (see program Feit),

(1) + FFT Ψ_{ĉmn}(t) * Factor1 (2) $\Psi_{cmn}(t+\Delta t/2)$ (3) + IFFT $\psi_{ijk}(t+\Delta t/2)$ * Factor2 (4) DO LOOP, $\psi_{ijk}(t+\Delta t/2)$ Factor2 $T = ntime * \Delta t$ + FFT (5) Ψ_{lmn} (t+ $\Delta t/2$) * Factor1 (6) Ψ_{lmn}'(t+Δt) (7) • IFFT $\psi_{ijk}(t+\Delta t)$ (8) Normalization

Input initial wavefunction, $\psi_{ijk}(t)$ (Normalized)



In this flow chart, the following symbols and abbreviations are used :

FFT : Fast Fourier Transform.

IFFT : Inverse Fast Fourier Transform.

+ : Perform

* : Multiply

Factor1 = exp
$$\left\{-\left(\frac{i\Delta t \hbar}{4 m_{\bullet}}\right) \left(2\pi\right)^{2} \left[\left(\frac{\ell}{Lx}\right)^{2} + \left(\frac{\pi}{Ly}\right)^{2} + \left(\frac{\pi}{Lz}\right)^{2}\right]\right\}$$
 (2.21)

Factor2 = exp(-i\Delta t
$$\frac{V_{op}(\mathbf{r})}{\hbar}$$
) (2.22)

A full-step propagation, Δt , is from step (1) to step (8). The computation proceeds as a succession ntime full-step propagations. This flow chart is suitable for both real and imaginary time computation. In the 3-dimensional case, for the initial wavefunction we choose a Gaussian distribution function by adjusting the half-width
ζ according to the boundary where the wavefunction must go to zero. In our calculation, we place the central peak of the Gaussian distribution function on the position (xnpick, ynpick, znpick), which is the position of the removed molecule from the system with position nearest to the center point of the simulation box. The non-normalized initial wavefunction is

$$\Psi_{ijk}(t) = \exp\left\{-\left[\left(x-xnpick\right)^{2}+\left(y-ynpick\right)^{2}+\left(z-znpick\right)^{2}\right]/2\zeta^{2}\right\} (2.23)$$

where (x,y,z) is the position of grid point (i,j,k). The boundary condition $\psi(0,t) = \psi(L,t) \longrightarrow 0$ must be obeyed. Here L is the side length of the simulation box in units of σ and ζ is the standard deviation of Gaussian distribution in units of σ . We renormalize the wavefunction $\psi_{ijk}(t+\Delta t)$ for every full-step propagation. Most of the computing time is taken in doing the FFT and IFFT. One quench step is defined as a full-step propagation with i Δt . In the following we are going to summarize the applications of Feit's algorithm:

1). The Hamiltonian operator \mathcal{X} :

The Hamiltonian operator $\mathcal H$ of the electron is

$$\mathcal{X} = \frac{\mathcal{P}^2}{2\mathbf{m}} + \mathcal{V}(\mathbf{r}) \tag{2.24}$$

where the first term on the right hand side is the kinetic energy operator and the second term on the right hand side is the potential energy operator. For a given $\psi(\mathbf{r})$ the eigenvalues can be obtained from $\mathcal{R} \psi(\mathbf{r}) = E \psi(\mathbf{r})^{41,55}$

Since the wavefunction is represented on a set of discrete grid points, the expectation value $\langle V \rangle$ of the potential energy $\mathcal{V}(\underline{r})$ is evaluated by multiplying the electron density $\rho = \psi^{\dagger} \psi$ at grid point (i, j, k) in coordinate space by $\mathcal{V}(\underline{r})$ at grid point (i, j, k) and summing over (i, j, k). The expectation values $\langle K \rangle$ of the kinetic energy is evaluated by Fourier transforming to momentum space, and multiplying the electron density at grid point (ℓ, m, n) by $\mathcal{P}^2/2m_e$ and summing over (ℓ, m, n) . The momentum \mathcal{P} is equal to $(2\pi\ell/L_{\star}, 2\pi m/L_{\star}, 2\pi n/L_{\star})$.

2). Ground state: eigenfunction and eigenvalue

The procedure involves following the evolution of the wavefunction in imaginary time $\tau = i\Delta t^{11,12,21,55}$. Therefore, the solution of Schrödinger equation is given in terms of a sum of exponentially decaying terms

$$\psi(\underline{r},\tau) = \sum_{n=0}^{\infty} a_n \, \phi_n(\underline{r}) \, \exp(-E_n \tau/\hbar)$$
(2.25)

where a_n is the amplitude, $\phi_n(r)$ is the eigenfunction and E_n is the eigenvalue for the nth state. The principle is that as τ is sufficiently large (low temperature), Feit's algorithm quenches the electronic state down to minimum E_0 , the lowest eigenvalue (ground state). Meanwhile, the component of the nth state eigenfunction is reduced relative to the ground state by $\exp(-\Delta E \tau)$, $\Delta E = E_n - E_0$. If $\Delta E \tau >> 1$ is true, then the propagation time τ is enough. On the other

hand, we do procedure 1). until the energy converges within some tolerance value, and then E_0 and $\psi_0(r)$ are the ground state energy and the ground state wavefunction, respectively.

3). Projection operator method:

The projection operator method^{21,55} permits us to obtain the excited states of the electron. The operation of the projection operator, \mathcal{P} , on an arbitrary wavefunction $\psi_{tr}(\mathbf{r})$ is defined as

$$\mathcal{P}|\psi_{tr}\rangle = \exp(-\tau \mathcal{H})|\psi_{tr}\rangle$$
(2.26)

As \mathcal{P} can be represented by a spectral series, the above equation can be rewritten as

$$\mathcal{P}|\boldsymbol{\psi}_{\mathrm{tr}}\rangle = \sum_{n=0}^{\infty} \exp(-\tau E_n) |\boldsymbol{\psi}_n\rangle \langle \boldsymbol{\psi}_n | \boldsymbol{\psi}_{\mathrm{tr}}\rangle$$
(2.27)

From the above procedures 1) and 2), we can obtain the ground state. Then, we use this projection operator method to project out the ground state to obtain the next excited state. When a new wavefunction is produced after one quench step, we project out those known eigenstates with lower eigenvalues during quenching in order to obtain the excited state correctly. In our calculation, we reorthogonalized ψ after every quench step. In order to decrease the computation time, we can reorthogonalize after every two or more quench steps. The formal expression for reorthogonalization at nth eigenstate is

$$\Psi_{n}' = \Psi_{n}' - \sum_{l=0}^{n-1} \Psi_{l} \langle \Psi_{l} | \Psi_{n}' \rangle$$
(2.28)

163

Every step produces a new ψ_n , which is to be used as the initial wavefunction of the next quench step. If quenched enough, the final wavefunction will be the nth eigenstate. The new trial function is

$$\Psi_{tr}' = \Psi_{tr} - \sum_{l=0}^{n} \Psi_{l} \langle \Psi_{l} | \Psi_{n}' \rangle$$
 (2.29)

In our test, it is efficient to use a decreasing Δt during quenching. A trial test shows that we can use a large step Δt (0.2)²¹ for the initial few quench steps until the energy converges within tolerance (0.001). Then, we cut Δt in half and run the same procedure of quenching and energy-convergent testing to obtain the ground state. The procedure is iterated until Δt is less than 0.01. For the excited state we could not use such a large initial Δt ; for the first excited state we used $\Delta t = 0.01$ as the initial value. (See program Projector)

4). The spectral analysis:

For a real time evolution the wavefunction $\Psi_{ijk}(t+T)$ consists of a superposition of oscillating wavefunctions, which is useful for the spectral analysis of eigen-energies^{11,12,43,54}. During a real time evolution we can calculate the time correlation function $C(t+\Delta t) =$ $\langle \psi(t+\Delta t) | \psi(t) \rangle$ at every full-step time propagation, and after ntime iterations we Fourier transform C(t), $(I(E)=\int C(t)exp(-itE_n/\hbar)dt)$, to obtain the spectrum corresponding to the eigen-energies. The time step size Δt determines the maximum absolute spectral energy that can be obtained. The relation is $f_{max} = 1/2\Delta t$, where f_{max} is the maximum frequency⁵⁶. The number of the time increments, ntime, controls the resolution of the spectrum,

$$\Delta f = \frac{1}{\Omega t \, \text{ime} \, \Delta t} = \frac{1}{\overline{\Gamma}}.$$
(2.30)

A large ntime permits the resolution of fine spectral structure.

2.3 THE ADIABATIC SIMULATION METHOD:

The procedure¹² used to study the localization of an excess electron in classical fluids is discussed in this section. Let us consider a system consisting of an electron and several hundred classical molecules. The dynamics of the electron and molecules are characterized by widely different time scales, with the motion of the quantum electron much faster than the motion of the molecules. The motion of molecules can be treated classically. Therefore, the adiabatic or Born-Oppenheimer approximation is valid, and its use leads to the terminology adiabatic simulation method. For a given nuclear configuration we obtain the ground state of the electron by performing an imaginary time evolution with Feit's algorithm. The adiabatic simulation method is summarized as follows:

1). We freeze the electronic wavefunction and integrate the classical equations of motion for a time step $\Delta \overline{t} HD$.

2). A new potential is produced after the molecular motion. The

electronic wavefunction certainly will be no longer in the ground state with the new potential. Therefore, we freeze the molecular configuration and quench the electron to the new ground state by use of the imaginary time evolution method. We repeat the procedures: step 1) and step 2).

The interaction of the electron and molecules is given by a psuedopotential⁴⁴

$$V_{ep}(r) = \frac{A}{r^4} \left(\frac{B}{C + r^6} - 1 \right)$$
 (in a.u.) (2.31)

where for electron-helium case A = 0.655, B = 89099, and C = 12608 (in a.u.).

$$V_{ep}(r) = 3.157 \times 10^5 - \frac{A}{r^4} \left(-\frac{B}{C+r^6} - 1 \right)$$
 (in K) (2.32)

here
$$r = r_{\sigma}\sigma_{au}$$
, and $\sigma_{au} = \frac{\sigma (Å)}{0.529 (Å/a.u.)}$.

The units of $V_{ep}(r)$ and distance r between electron and molecules are in K and in a.u..

Every one or several molecular dynamics steps is followed by ntime quench steps in order to quench the electronic quantum state to the ground state or excited-state for a given frozen nuclear configuration. The number of quenching steps is determined by the energy convergence test²¹.

When we consider the molecular motion $^{6-7,11-12}$, we must include the contribution of the quantum force arising from the interaction between the electron and the molecules. The classical equations of motion are then written as

$$m \frac{d^{2} \mathcal{R}_{i}}{dt^{2}} = -\sum_{j \neq i}^{N} \frac{\partial V_{LJ}(\mathcal{R}_{ij})}{\partial \mathcal{R}_{i}} - \int d^{3} r |\psi(r,t)|^{2} \frac{\partial V_{ep}(r, \{\mathcal{R}_{ij}\})}{\partial \mathcal{R}_{i}}$$
(2.33)

The factor $\frac{m\sigma^2}{C_{MD}^2}$ is extracted from the above equation in order to

produce the dimensionless equation,

$$\frac{d^{2}R_{\sigma,i}}{d\overline{t}^{2}} = \sum_{j\neq i}^{N} \overline{\overline{F}}(R_{ij}) - \frac{C_{MD}}{m\sigma^{2}} \int d^{3}r |\psi(r,t)|^{2} \frac{\partial V_{op}(r, \{R_{ij}\})}{\partial R_{i}}$$
(2.34)

where,
$$\overline{F}(\underline{R}_{ij}) = -\frac{C_{MD}^2}{m\sigma^2} \frac{\partial V_{LJ}(\underline{R}_{ij})}{\partial R_i}$$
 (2.35)

The second term on the right hand side is the quantum force

$$-\frac{C_{MD}}{m\sigma^2}\int d^3r |\psi(r,t)|^2 \frac{\partial V_{\bullet p}(r, \{R_{ij}\})}{\partial R_{i}} = -\int d^3r_{\sigma} |\psi(r_{\sigma},t)|^2 \frac{\partial \overline{V}_{\bullet p}(r, \{R_{ij}\})}{\partial R_{\sigma,i}}$$
(2.36)

where
$$\overline{V}_{ep} = -\frac{C_{HD}^2}{m\sigma^2} V_{ep}(r_{\sigma}, \{R_{\sigma,ij}\}).$$
 (2.37)

There are two places we need to include this quantum force: 1) In the molecular equation of motion, $\overline{V}_{ep} = \frac{1}{48\epsilon}$ Vep, and 2) In the Schrödinger equation, $\overline{V}_{ep} = \frac{C_F}{\hbar} V_{ep}$.

The \overline{V}_{ep} and $\left(-\int d^{3}r_{\sigma} |\psi(r_{\sigma},t)|^{2} \frac{\partial \overline{V}_{ep}}{\partial R_{\sigma,i}}\right)$ terms are calculated by the minimum image convention method^{47,48}.

Since we quench the electron to the ground state with the lowest energy in a closed system, the decreasing energy will lower the temperature of the classical system and result in a deviation of temperature of the system from the original value. Therefore, the temperature fluctuations of 15% were allowed during the simulation. Otherwise, we renormalized velocities of molecules to restore the original temperature.

2.4 THE MOVING GRID TECHNIQUE: (SEE PROGRAM MGT)

This technique¹² was developed to monitor the behavior of the electron in a finite system extended to an infinite system via the application of periodic boundary conditions^{47,48}. The ground-state electronic wavefunction produced after a quench has very small values on the boundary of a grid box which is small compared to the simulation box. Therefore, a smaller grid box can be used relative to the simulation box. The advantage of this technique is that it allows us to use a smaller grid spacing and number of grid points which decreases

the computation time and increases the spatial resolution. The grid box is moved to follow the center of mass of the electronic wavefunction density distribution,

$$\mathbf{r}_{CM} = \sum_{i,j,k} \mathbf{r}_{ijk} \psi_{ijk}(t)^* \psi_{ijk}(t)$$
(2.38)

where r_{ijk} denotes the position of the grid point (i, j, k), and $\psi_{ijk}(t)$ is the electronic wavefunction on the grid point (i, j, k). For a given frozen nuclear configuration and a fixed grid box we quench the electronic state to the ground state and calculate the center of mass of the electron. Whenever we obtain the center of mass of the electron, we move the center point of the grid box close to the new center of mass of the electron and re-express the electronic wavefunction relative to this new origin of the grid box. When the center of mass of the electron doesn't move, the grid box won't move.

3. RESULTS AND DISCUSSIONS

In this Chapter, the various equilibrium and dynamical properties for both the electron and the helium, obtained by using the molecular dynamics adiabatic simulation method described in Section 2.2, will be presented and discussed.

Figure 3.1 shows that information concerning the spatial extent of the electron can be obtained from a correlation function such as the radial distribution function of the electronic probability density measured from the mean position of the electron, $r_{ce} = \int r_{c} |\phi(r)|^2 dr_{ce}$ ---- the center of mass of the electron. The results reported here are indicative of the various sizes of the localized electron versus the reduced number density ρ^* = 0.1, 0.5, 0.7, and 0.9 in a helium system at reduced temperature $T^* = 30.23$. In the present calculation, the electronic wavefunction was represented on 16³ grid points and the number of the helium atoms is 107. A typical imaginary time step used in this process was $\Delta t_r = 0.01063$. We have used 200 quench steps to obtain the ground state of electron for each different ρ^{\ddagger} . At $\rho^{\ddagger}=0.1$ the electron is not localized^{31b}, because the probability does not go to zero of large distance from the electron center of mass. Comparison of the results as the molecular density ρ^* is increased shows that the size of the localized electron decreases and that it is well localized in a given equilibrated helium configuration.



Figure 3.1 Plots of the radial distribution function of the electron's probability density vs. the distance from the electron center of mass at various densities in helium at $T^*=30.23$.



Figure 3.2 Contours of the excess electron density corresponding to the localized state wavefunction in the x-y plane.

More details of the probability density distribution, $|\Phi(\mathbf{r})|^2$, of the localized electron can be obtained from the contour plot. Figure 3.2 shows $\rho(\mathbf{x},\mathbf{y})$, a contour plot on the x-y plane, corresponding to the simulation of Figure 3.1, at the reduced density 0.9. Here $\rho(\mathbf{x},\mathbf{y})=\int |\Phi(\mathbf{r})|^2 d\mathbf{z}$. The values indicated on the contour plot are in arbitrary units. As can be seen, the ground state of the localized electron is quite symmetrical and has an s-like structure. (For data contour plotting, see subroutine CONTOUR).

Information about the local fluid environment around the electron was obtained from the helium radial distribution measured from the center of mass of the electron. In Figure 3.3, the number of the helium atoms is 107, the reduced number density is 0.7, and the temperature is 309 K. In this run, the first 1.1×10⁵ molecular dynamics steps were used to equilibrate the helium and the radial distribution function was calculated in the following 10⁴ steps. For the ground state quenches we have used 20 quench steps after each molecular dynamics step. The imaginary time step and the molecular dynamics time step are, respectively, 0.01063 and 9.4×10^{-4} . In this run, the total real evolution time is 2.3 ps. The results show that there is zero probability of finding the helium atoms in the region of the localized electron. As mentioned in Chapter 1, as the helium density is increased to liquid density, the electron becomes localized in a small region. A bubble-like structure occurs because the repulsive electron-helium interaction produces a cage effect which excludes the helium atoms from the region of the electron.



Figure 3.3 The radial distribution function of helium measured from the center of mass of the electron.

:



Figure 3.4 Plots of the electronic energy versus the number of quench steps.

In Figure 3.4 we show that the energy convergence of the ground state electron varies with the number of quench steps and the quench time step from 0.2 to 0.01. From this plot we know that, in this case, 150 quench steps are enough to obtain the lowest energy state.

We show the typical electronic configurations in Figure 3.5, which exhibits the localized ground state ϕ_{α} and first excited state ϕ_{α} obtained via the projection operator method, as mentioned in Section 2.2. Here, the number of helium atoms was 107, the reduced density was 0.9 and temperature was 309 K. In order to obtain the ground state, the initial $d\overline{t}_{F}$ was chosen to be 0.5 and the tolerance value of the energy convergence was 0.001. The total number of quench steps was 155 when the final $d\bar{t}_r$ was less than 0.01. The corresponding kinetic, potential, and total energy of the ground state electron are, respectively, 3.79, 1.78, and 5.57 (3.25 eV) in rescaled units (one rescaled unit is equal to 6,768 K). The parameters used to obtain the first excited state by projecting out the ground state were the initial $d\bar{t}_{\rm F}$ = 0.5, energy convergence tolerance 0.01, and final $d\bar{t}_{\rm F} \leq 0.001$. The total number of quench steps was 550. The corresponding kinetic, potential, and total energy of the first excited state are, respectively, 5.44, 2.87, and 8.31 (4.85 eV). Figure 3.5 shows that the ground and first excited state have, respectively, s-like and p-like structure. During the simulation process, ϕ_0 and ϕ_1 fluctuate leading to electronic configurations with considerable occasional distortion from s-like and p-like structure.

It is worth comparing the present results for the ratio of the

175



Contours of the electronic configurations for a typical a). ground state and b). first excited state. Figure 3.5

176



Figure 3.6 Plots of the fluctuation of the total electronic energy (E), kinetic energy (K), and potential energy (V) in the molecular dynamics adiabatic simulation.

total energies of the ground and first excited states with those obtained by Coker and Berne^{31b} for an electron in a helium configuration taken from the path-integral Monte Carlo simulation^{31a}. The ratio is 1.66 in their result and our ratio is 1.49 at ρ^{\pm} =0.9. In addition, our results for the energy are roughly 1.7 times larger than theirs. Our electron is systematically smaller and, as a result, our kinetic and potential energies are larger. These differences arise because Coker and Berne^{31b} quenched the electron without allowing the solvent configuration to relax. Since the Path-Integral Monte Carlo produces a thermally distributed electron, which is larger than the ground state electron we create, our solvent equilibrated electron will be smaller than their, leading to a higher kinetic energy. Also, our solvent molecules will be closer to the electron leading to a higher potential energy.

Figure 3.6 shows that the excess electron's ground state energy E, kinetic energy K, and potential energy V fluctuate as the helium system evolves in time. In this run, the number of particles and reduced density are, respectively, 255 and 0.9 at T = 309. The molecular dynamics time step is 2.63×10^{-3} and the quench time step is chosen from 0.2 down to 0.01 followed by the energy convergence. Quenching to the ground state followed after every 10 molecular dynamics steps. The real time span is 3000 steps (2ps). The computation time on the Titan was 32 hours. In this context we note that the time variation of the electronic potential energy exhibits a stronger fluctuation compared with that of the kinetic energy. In other words, the electron is very sensitive to the local fluid

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environment. The confined electron usually has higher kinetic energy than the potential energy. In accord with the model of a particle in a spherical box³, the simulation demonstrates a high kinetic energy for a well localized electron, which agrees with expectations. The averages of the electron kinetic and potential energy over the 3000 steps are, respectively, 3.49 and 3.45. Examination of the ground state energies shown in Figure 3.6, shows that the kinetic energy does not change significantly, but the potential energy does. It appears that the electron must go over a potential barrier during the electron transition from one localized state to another localized state. There is an intermediate state of high potential.

The diffusion constants of an excess electron in molten salt^{6,7}, polar water²⁰ and ammonia²⁴ have been obtained by simulation, and the results are in agreement with experiment⁵⁷⁻⁵⁹. The diffusion constants of the electron simulated in water²⁰ and in KCl⁶ are 3.3×10^{-5} and 2.0×10^{-3} cm² sec⁻¹, respectively. It is of great interest to simulate the diffusion constant of the excess electron in dense helium and we hope to understand the electron diffusion mechanism. We assume that the electron is well localized at all times. We monitored the electron dynamics by following the motion of the center of mass of the electron, as if it were a classical particle. Figure 3.7 shows the mean-square displacement of the center of mass of the electron as a function of time for an electron in helium. The number of helium atoms is 255 in the simulation box at $\rho^{\pm} = 0.9$ and T[±] = 30.23. The length of the grid box was chosen to be about 75% of the simulation box in order to obtain the same resolution as in the system of 107 particles. The grid points are fixed in number, at 16^3 . The result given is an average over 12 electron trajectories. The diffusion constant obtained is about 4.48×10^{-3} cm² sec⁻¹. Based on the results obtained by Rossky²⁰ and Selloni⁶, the diffusion of the electron in helium is faster than that in water, and it is the same order as in KCl. The mechanism is not clear. More numerical experiments are essential.



Figure 3.7 The time dependent mean-square displacement of the center-of-mass of an electron in helium.

4. CONCLUSIONS

We have described and programmed computational algorithms for a time-dependent quantum molecular dynamics simulation with application to both the molecular and electronic configurations in fluids. It is evident that the technique combines the quantum and classical aspects, and efficiently and quickly solves the problem. In the present context, we applied the method to the particular system, an excess electron in helium. We were able to obtain the ground state, the excited state, the corresponding energies of the electron, and the correlation functions of the electron and the local environment molecules. We have studied the diffusive behavior of an excess ground state electron in helium.

In order to progress further, there is the essential need for electron-molecular pseudopotentials, which are difficult to determine, and molecule-molecular interaction potentials, which are better known. An optimal molecular dynamics time step is necessary. With the electron dynamics process, in order to decrease the integration error, the final quench time step must be small enough and there must be a sufficient number of quench steps.

This technique will play an important role in future simulations because of its accuracy, flexibility, and efficiency, leading to

182

greater insight into dynamical molecular processes. The problems for future investigation include electron transfer dynamics in solution and in biological systems, and the electron transport rate. The transition from an excited state to the ground state, and the resulting optical absorption spectra can also be obtained by this approach. APPENDICES

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APPENDIX A

Reference Table A.1 lists the information on the simulation parameters to facilitate comparison.

ρ *	0.1	0.3	0.5	0.7	0.9	
N	107	107	107	107	107	
ć	10.23	7.09	5.98	5.35	4.92	(σ)
L	26.14	18.13	15.29	13.67	12.56	(Å), He
ρ _N	5.99 x 10 ²¹	1.8x109 ²²	3.0x10 ²²	4.2x10 ²²	5.39x10 ²²	(cm ⁻³)
ρ _m	0.04	0.12	0.20	0.28	0.36	(g cm ⁻³)
Φ	0.05	0.16	0.26	0.37	0.47	

Table A.1The list of the reference parameters:

The simulation box side length is $L = \ell \sigma$.

- ρ^* : The reduced number of density, N/ ℓ^3 .
- N: The number of particles.

 $\boldsymbol{\mathcal{C}}$: The box side length in units of the diameter of the particle, $\sigma.$

- $\rho_{\rm N}$: The number density of particles, N/L $^3.$
- $\boldsymbol{\rho}_{\mathrm{m}}$: The mass density, $\boldsymbol{\rho}_{\mathrm{N}}$ x m.
- m : The mass of particles, $m_{H_{\bullet}} = 4.0026 \times 1.6747 \times 10^{-24} \text{ gram}$.
- ϕ : The volume fraction, $\rho^* \pi/6$.

APPENDIX B

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B. LIST OF COMPUTER PROGRAMS

C****	***************************************	*
С	LIST OF NOTATIONS	*
С	ABC : ENERGY CONVERGENCE TOLERANCE, 0.001	*
С	ABCD : MINIMUN QUENCH TIME STEP, 0.01	*
С	CND : THE RESCALE FACTOR FOR MOLECULAR DYNAMICS	*
С	CMX, CMY, CMZ, CMXP, CMYP, CMZP : THE CENTER OF MASS OF	*
С	ELECTRON	*
C	CX(N), CY(N), CZ(N) : THE CUMULATED DISPLACEMENT OF	*
C	PARTICLES	*
ē	CXE.CYE.CZE : THE CUMULATED DISPLACEMENT OF ELECTRON	*
Ċ	DIS : MEAN SQUARE DISPLACEMENT OF PARTICLES	*
Ċ	DIFF : DIFFUSION CONSTANT OF PARTICLES	*
Ĉ	DISPMX : LARGEST DISPLACEMENT	*
C	DX : THE GRID SPACING IN X DIRECTION	*
Ċ	DY : THE GRID SPACING IN Y DIRECTION	*
Ċ	DZ : THE GRID SPACING IN Z DIRECTION	*
Ċ	DIMD. H : THE TIME STEP FOR MOLECULAR DYNAMICS	*
Ċ	DT. DTFT : THE TIME STEP FOR QUENCH	*
C	DIAM : THE DIAMETER OF PARTICLE IN ANGSTROM	*
Ĉ	EKIN : KINETIC ENERGY OF PARTICLES	*
Ċ	F : FORCE	*
C	FX(N), FY(N), FZ(N) : THE FORCES OF PARTICLES	*
С	G(IE) : RADIAL DIS. FUNC OF ELECTRON	*
С	CN(IH) : RADIAL DIS. FUNC. OF PARTICLES	*
С	IE : THE POINTS WHEN EVALUATES ELECTRON DENSITY	*
С	DISTRIBUTION	*
С	IH : THE POINTS WHEN EVALUATES PARTICLES PAIR	*
С	DISTRIBUTION FUNCTION	*
С	ITXS, ITYS, ITZS : CUMULATE THE DISPLACEMENT OF THE	*
С	CENTER OF GRID BOX	*
С	LIST(MAXNAB) : VERLET NEIGHBOR LIST	*
С	N : THE NUMBER OF THE PARTICLES	*
С	N1 : THE NUMBER OF GRID POINTS IN X DIRECTION	*
С	N2 : THE NUMBER OF GRID POINTS IN Y DIRECTION	*
С	N3 : THE NUMBER OF GRID POINTS IN Z DIRECTION	*
С	NDIM : THE TOTAL DIMENSIONS	*
С	NFMD, NTIME : THE NUMBER OF QUENCH STEPS	*
С	NT : THE TOTAL NUMBER OF THE GRID POINTS	*
С	NSTEP : NO. OF MD BETWEEN QUENCHES	*
С	POINT(N) : INDEX TO THE NEICHBOR LIST	*
С	POT(N1,N2,N3) : POTENTIAL ENERGY OF ELECTRON	*
С	QTSUM : TOTAL ELECTRONIC ENERGY	*
С	RAD(IE), RADS(IH) : RADIUS OF G-CM-E AND G-CM-HE	*
С	ROOFF : THE CUT OFF INTERACTION RANCE	*
С	RCUT : CUTOFF DISTANCE FOR FORCE	*
	185	

С RDEN : REDUCED DENSITY * С REF : FLUCTUATION OF TEMPERATURE, DTEMP=0.15 * С RLIST : THE NEAREST-NEIGHBOR LIST CUT OFF RANGE * С RSQ(N) : SQUARE DISPLACEMENT FOR PARTICLES ¥ С RSIDE : UNIT SIDE ¥ С RX(N), RY(N), RZ(N) : THE POSITIONS OF PARTICLES × С RXO(N), RYO(N), RZO(N) : THE POSITIONS OF PARTICLES ¥ С SIDE : THE LENGTH OF THE SIMULATION BOX ± С SIDEH : THE HALF LENGTH OF SIDE × С SIGMA : THE DIAMETER OF THE CLASSICAL PARTICLES IN * С REDUCED UNIT, 1 × С TE(N1,N2,N3) : KINETIC ENERGY OF ELECTRON * С TOT(N1,N2,N3) : TOTAL ENERGY OF ELECTRON * С TREF : DEFINED THE SYSTEM'S TEMPERATURE DEVIDED BY * С THE WELL DEPTH OF MOLECULAR POTENTIAL × С TEIMD : THE COEFFICIENT OF QUANTUM FORCE * С TEI : THE COEFFICIENT OF PSEUDOPOTENTIAL BETWEEN * С PARTICLES AND ELECTRON * С TIMEMX : THE MAX NUMBER OF MOLECULAR DYNAMIC STEPS * TIMEI : THE INITIAL NO. OF MD STEPS С * С UPDATE : IF TRUE THE LIST IS UPDATED ¥ С V : POTENTIAL ENERGY OF PARTICLES * С VX(N), VY(N), VZ(N) : THE VELOCITIES OF PARTICLES * С VEIX(N), VEIY(N), VEIZ(N) : THE QUANTUM FORCES INDUCED * С BY ELECTRON ON PARTICLES ± С W(N1,N2,N3) : THE WAVEFUNCTION OF ELECTRON ON THE GRID* С POINT (N1.N2.N3) С WO(N1,N2,N3) : THE INITIAL WAVEFUNCTION С * WTR(N1,N2,N3) : THE TRIAL WAVEFUNCTION С XP(N), YP(N), ZP(N) : THE POSITIONS OF PARTICLES ¥ С XNPICK, YNPICK, ZNPICK : THE POSITION OF THE TAKEN OUT * С PARTICLE, NPICK ×

С PROGRAM TITLE : MD С PURPOSE : GENERATE NUCLEAR CONFIGURATIONS BY * С MOLECULAR DYNAMICS * С METHOD : USE VERLET-VELOCITY ALCORITHM × С CONTAIN : CALL FORCE, CHECK, FEIT С DOUBLE PRECISION × С DATE : MAY, 1990 С PROCEDURE : (1) SET PARAMETERS (FIXED) BEFORE COMPILE * С (2) READ INPUT PARAMETERS (VARIABLE) * PROGRAM MD IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) С ---- SET PARAMETERS -----PARAMETER(N=255, RDEN=0.7) С --- MD VERLET FOR LENNARD-JONES POTENTIAL----DIMENSION RX(N), RY(N), RZ(N) * ,XP(N),YP(N),ZP(N)* ,RXO(N),RYO(N),RZO(N)* ,CX(N),CY(N),CZ(N),RSQ(N)* ,FX(N),FY(N),FZ(N)* ,VX(N),VY(N),VZ(N)* ,VEIX(N),VEIY(N),VEIZ(N) LOGICAL UPDATE INTEGER CLOCK, TIMEMX, TIMEI, POINT(N), LIST(N*N) COMMON /B/ SIDE, RSIDE, SIGMA, CLOCK, GTSUM COMMON /B1/ XNPICK, YNPICK, ZNPICK COMMON /BLOCK1/ RX, RY, RZ, FX, FY, FZ COMMON /BLOCK2/ POINT, LIST COMMON /BLOCK3/ RXO, RYO, RZO COMMON /C1/ DX, DY, DZ, CXE, CYE, CZE COMMON /C2/ ITXS, ITYS, ITZS, CMXP, CMYP, CMZP, PREF COMMON /C3/ ABC, ABCD, IE, IH, DIAM, NW, TIMEI С ---DEFINITION OF THE SIMULATION PARAMETERS---OPEN(1,FILE='CO7256TIT') OPEN(8, FILE='TINP') READ(8, *)ABC, ABCD, DTFT, TIMEMX, TIMEI, NFMD, NW, NSTEP С ---SET PARAMETERS-----CXE=0. CYE=0. CZE=0. ITXS=0

> ITYS=0 ITZS=0 CMXP=0. CMYP=0.

CMZP=0. DIAM=2.556 IE=5 IH=6 RSIDE=1. SIGMA=RSIDE SIDE=(FLOAT(N)/RDEN)**(1./3.)SIDEH=SIDE*0.5 TREF=309./10.22 ISEED =4759CMD=2.54 RCOFF=2.5*SIGMA RCUT=RCOFF RLIST=2.7*SIGMA UPDATE=.TRUE. READ(1,*)NS, RRDEN, MAXS, DTMD, TREF H=DTMD/2. PREF=(DIAM**2)/(6.*CMD*1000*H) HSQ=H*H HSQ2=HSQ*0.5RCOFFS=RCOFF*RCOFF TSCALE=16.*RSIDE*RSIDE/(1.*N-1.) VAVER=1.13*SQRT(TREF/24.)/RSIDE С ---WRITE OUT INFORMATION -----WRITE(6,*)'NUMBER OF PARTICLES IS ',N WRITE(6,*)'SIDE LENGTH OF THE BOX IS ',SIDE WRITE(6, *)'CUT OFF IS ',RCOFF WRITE(6,*)'REDUCED TEMPERATURE IS ', TREF WRITE(6,*)'BASIC TIME STEP IS ,H WRITE(6, *)'NO OF QUENCH STEPS ',NFMD WRITE(6,*)'QUENCH TIME STEP IS ',DTFT WRITE(6, *)'REDUCE DENSITY', RDEN WRITE(6,*)'PREFACTOR IS ', PREF С С ---INPUT EQUILIBRATED NUCLEAR CONFIGURATION ----С ---TAKE PARTICLE OUT, REPLACED BY ELECTRON ----С ---READ POSITION OF ELECTRON SHOULD BE ----READ(1, *)NPICK, XNPICK, YNPICK, ZNPICK NP=0 DO 74 I=1,N+1 IF(I.EQ.NPICK) THEN READ(1,*)NUMB, XC, YC, ZC READ(1, *)FFX, FFY, FFZ READ(1, *)VVX,VVY,VVZ GO TO 74 ENDIF NP=NP+1С ---POSITIONS, FORCES, VELOCITIES OF PARTICLES ----READ(1, *)NUMB, RX(NP), RY(NP), RZ(NP)READ(1, *)FX(NP), FY(NP), FZ(NP)READ(1, *)VX(NP), VY(NP), VZ(NP)

74 CONTINUE

С ---SET INITIAL DISPLACEMENT TO BE ZERO ----С CALL MXWELL(VX,VY,VZ,N,H,TREF,RSIDE,TSCALE) С DO 20 I=1,N С CX(I) = 0.0С CY(I)=0.0 С CZ(I)=0.0 С ---SET PREVIOUS POSITIONS OF PARTICLES TO XP(I) ---С XP(I)=RX(I)С YP(I)=RY(I)С ZP(I)=RZ(I)C20 CONTINUE С ---START OF THE ACTUAL MOLECULAR DYNAMICS ---DO 200 CLOCK=1, TIMEMX С ---ADVANCE POSITIONS ONE BASIC TIME STEP---DO 210 I=1,N RX(I)=RX(I)+VX(I)+FX(I)RY(I)=RY(I)+VY(I)+FY(I)RZ(I)=RZ(I)+VZ(I)+FZ(I)С ---CUMULATE DISPLACEMENT FOR EACH PARTICLE ---С CX(I)=CX(I)+(RX(I)-XP(I))С CY(I)=CY(I)+(RY(I)-YP(I))С CZ(I)=CZ(I)+(RZ(I)-ZP(I))210 CONTINUE С ---CALCULATE MEAN SQUARE DISPLACEMENT ------DIFFUSION CONSTANT ---С С IF((CLOCK/NW)*NW.EQ.CLOCK) THEN С SUM=0. С DO 118 I=1,N С RSQ(I)=CX(I)**2+CY(I)**2+CZ(I)**2С SUM=SUM+RSQ(I)C118 CONTINUE С DIS=SUM/FLOAT(N) С DIFF=PREF*DIS/FLOAT(CLOCK) С WRITE(515, *)CLOCK, DIS, DIFF С ENDIF С ---APPLY PERIODIC BOUNDARY CONDITION ---DO 215 I=1,N IF(RX(I).LT.O.) RX(I)=RX(I)+SIDE IF(RX(I).GT.SIDE) RX(I)=RX(I)-SIDE IF(RY(I).LT.0.) RY(I)=RY(I)+SIDEIF(RY(I).GT.SIDE) RY(I)=RY(I)-SIDE IF(RZ(I).LT.0.) RZ(I)=RZ(I)+SIDEIF(RZ(I).GT.SIDE) RZ(I)=RZ(I)-SIDE IF(RX(I).LT.0.) PRINT *, 'oops!!!! X(',I,')', RX(I), CLOCK IF(RX(I).GT.SIDE) PRINT *, 'oops!!!! X(',I,')', RX(I),CLOCK IF(RY(I).LT.0.) PRINT *, 'oops!!!! Y(',I,')', RY(I), CLOCK IF(RY(I).GT.SIDE) PRINT *, 'oops!!!! Y(',I,')',RY(I),CLOCK

IF(RZ(I).LT.0.) PRINT *, 'oops!!!! Z(',I,')', RZ(I),CLOCK IF(RZ(I).GT.SIDE) PRINT *, 'oops!!!! Z(',I,')', RZ(I),CLOCK ---RESET PREVIOUS POSITIONS ---С С XP(I)=RX(I)С YP(I)=RY(I)С ZP(I)=RZ(I)215 CONTINUE С ----COMPUTE THE PARTIAL VELOCITIES----DO 220 I=1,N VX(I)=VX(I)+FX(I)VY(I)=VY(I)+FY(I)VZ(I)=VZ(I)+FZ(I)220 CONTINUE ---SET INITIAL QUANTUM FORCE---С DO 400 I=1,N VEIX(I)=0.0 VEIY(I)=0.0 VEIZ(I)=0.0 400 CONTINUE С ---START TO QUENCH ---С ---SET NSTEP MD TO QUENCH ---IF(CLOCK.GE.TIMEI) THEN IF ((CLOCK/NSTEP) *NSTEP.EQ.CLOCK) THEN DT=DTFT NTIME=NFMD CALL FEIT(N,RX,RY,RZ,VEIX,VEIY,VEIZ,DT,NTIME) ENDIF ENDIF С ---COMPUTE CLASSICAL FORCE ---CALL CHECK (RCUT, RLIST, UPDATE) CALL FORCE (RCUT, RLIST, SIGMA, UPDATE, V, F, CLOCK) DO 275 I=1,N FX(I) = (FX(I) + VEIX(I)) + HSQ2FY(I) = (FY(I) + VEIY(I)) + HSQ2FZ(I) = (FZ(I) + VEIZ(I)) + HSQ2275 CONTINUE С ---COMPUTE THE VELOCITIES----DO 300 I=1,N VX(I)=VX(I)+FX(I)VY(I)=VY(I)+FY(I)VZ(I)=VZ(I)+FZ(I)300 CONTINUE С ---COMPUTE THE KINETIC ENERGY---EKIN=0.0 DO 305 I=1,N EKIN=EKIN+VX(I)*VX(I)+VY(I)*VY(I)+VZ(I)*VZ(I)305 CONTINUE EKIN=EKIN/HSQ

C ---COMPUTE THE AVERAGE VELOCITY---VEL=0.0 DO 306 I=1,N SQ=SQRT(VX(I)*VX(I)+VY(I)*VY(I)+VZ(I)*VZ(I)) SQT=SQ/H VEL=VEL+SQ 306 CONTINUE VEL=VEL/H

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- VEL=VEL/H TEMP=TSCALE*EKIN REF=ABS(TEMP-TREF)/TREF
- C ---NORMALIZE THE VELOCITIES TO OBTAIN THE SPECIFIED--

C ---REFERENCED TEMPERATURE---IF(REF.GT.0.15) THEN TS=TSCALE*EKIN SC=TREF/TS SC=SQRT(SC) DO 310 I=1,N VX(I)=VX(I)*SC VY(I)=VY(I)*SC VZ(I)=VZ(I)*SC310 CONTINUE EKIN=TREF/TSCALE ENDIF

- C ---COMPUTE VARIOUS QUANTITIES---EK=24.*EKIN/(SIGMA*SIGMA) EPOT=4.*V ETOT=EK+EPOT TEMP=TSCALE*EKIN
- C IF((CLOCK/10)*10.EQ.CLOCK) THEN
- C WRITE(6,6000)CLOCK,EK,EPOT,ETOT*10.22
- C STE=ETOT*10.22+QTSUM*6768.
- C WRITE(6,6001)STE, TEMP

IF((CLOCK/1000)*1000.EQ.CLOCK) THEN NFILE=89 OPEN(NFILE) DO 787 I=1,N WRITE(NFILE,*)RX(I),RY(I),RZ(I) CONTINUE

- 787 CONTINUE CLOSE(NFILE) ENDIF
- 200 CONTINUE
- 6000 FORMAT(116,3F15.6) 6001 FORMAT(2X,2F15.6)
 - STOP END

SUBROUTINE MXWELL⁶⁰ : GENERATE VELOCITIES OF PARTICLES * С С ACCORDING TO MAXWELL DISTRIBUTION * SUBROUTINE MXWELL(VX,VY,VZ,N,H,TREF,RSIDE,TSCALE) IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) DIMENSION VX(N), VY(N), VZ(N) ISEED=12349 N3=N*3 DO 10 I=1.N3.2 1 U1=RAN(ISEED) U2=RAN(ISEED) V1=2.0*U1-1.0 V2=2.0*U2-1.0 S=V1*V1+V2*V2 IF(S.GE.1.0) GO TO 1 R=-2.0*LOG(S)/SV1=V1*SQRT(R) V2=V2*SQRT(R)IF(I.LT.N) THEN. VX(I)=V1VX(I+1)=V2ENDIF IF(I.GE.N+1.AND.I.LT.2*N) THEN VY(I-N)=V1VY(I+1-N)=V2ENDIF IF(I.GE.2*N+1) THEN VZ(I-2*N)=V1 VZ(I+1-2*N)=V2ENDIF 10 CONTINUE EKIN=0.0 SP=0.0 DO 20 I=1,N SP=SP+VX(I) 20 CONTINUE SP=SP/FLOAT(N)DO 21 I=1,N VX(I)=VX(I)-SPEKIN=EKIN+VX(I) *VX(I) 21 CONTINUE SP=0.0 DO 22 I=1.N SP=SP+VY(I) 22 CONTINUE SP=SP/FLOAT(N) DO 23 I=1,N VY(I)=VY(I)-SPEKIN=EKIN+VY(I) *VY(I) 23 CONTINUE SP=0.0

```
DO 24 I=1,N
     SP=SP+VZ(I)
24
     CONTINUE
     SP=SP/FLOAT(N)
     DO 25 I=1,N
     VZ(I)=VZ(I)-SP
     EKIN=EKIN+VZ(I)*VZ(I)
25
     CONTINUE
     TS=TSCALE*EKIN
     SC=TREF/TS
     SC=SQRT(SC)
     SC=SC*H
     DO 30 I=1,N
     VX(I)=VX(I)*SC
     VY(I)=VY(I)*SC
     VZ(I)=VZ(I)*SC
30
     CONTINUE
     RETURN
     END
C FORCE ROUTINE USING A VERLET NEIGHBOR LIST"
C SUBROUTINE FORCE ( RCUT, RLIST, SIGMA, UPDATE, V, W)
C CALCULATE FORCES USING THE VERLET LIST, UPDATES THE LIST
C SUBROUTINE CHECK (RCUT, PLIST, UPDATE)
                                                              ±
C SETS UPDATE TO TRUE WHNE THE LIST NEEDS TO BE UPDATED
C SUBROUTINE SAVE
C SAVES CURRENT CONFIGURATION FOR FUTURE CHECKING.
С
C USAGE : AT THE START OF A RUN, FORCE IS CALLED WITH UPDATE SET
                                                              ×
C TRUE. THIS SETS UP THE INITIAL VERLET LIST AND SAVES THE
                                                              *
C POSITIONS THEREAFTER CHECK IS CALLED JUST BEFORE EACH CALL OF
                                                              *
C FORCE TO DECIDE WHETHER OR NOT A LIST UPDATE IS NECESSARY.
                                                              *
C THESE ROUTINES CAN BE USED IN A CONVENTIONAL MD PROGRAM AND
                                                              *
C CAN BE EASILY ADAPTED FOR USE IN AN MC PROGRAM. FORCES IS
                                                              *
C SPECIFIC TO A FLUID OF LENNARD JONES ATOMS.
                                                              ×
SUBROUTINE FORCE (RCUT, RLIST, SIGMA, UPDATE, V, F, CLOCK)
     IMPLICIT REAL*8(A-H,O-Z)
     IMPLICIT INTEGER*4(I-N)
     PARAMETER ( N=255, MAXNAB = N*N )
     DIMENSION RX(N), RY(N), RZ(N), FX(N), FY(N), FZ(N)
     INTEGER POINT(N), LIST(N*N), CLOCK
     LOGICAL UPDATE
     COMMON /BLOCK1/ RX, RY, RZ, FX, FY, FZ
     COMMON /BLOCK2/ POINT, LIST
     COMMON /B/ SIDE
     RLSTSQ = RLIST * RLIST
     SIGSQ = SIGMA * SIGMA
     RCUTSQ = RCUT * RCUT
С
     ---ZERO FORCES----
     DO 10 I = 1,N
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193

FX(I) = 0.0FY(I) = 0.0FZ(I) = 0.010 CONTINUE V = 0.0F = 0.0IF (UPDATE) THEN С --- SAVE CURRENT CONFIGURATION CONSTRUCT ---С --- NEIGHBOR LIST AND CALCULATE FORCES ---CALL SAVE NLIST = 0DO 100 I = 1, N - 1 POINT(I) = NLIST + 1RXI = RX(I)RYI = RY(I)RZI = RZ(I)= FX(I)FXI FYI = FY(I)FZI = FZ(I)DO 99 J = I + 1, N RXIJ = RXI - RX(J)RYIJ = RYI - RY(J)= RZI - RZ(J)RZIJ RXIJ = RXIJ -SIDE* ANINT (RXIJ/SIDE) RYIJ = RYIJ -SIDE* ANINT (RYIJ/SIDE) = RZIJ -SIDE* ANINT (RZIJ/SIDE) RZIJ RIJSQ = RXIJ * RXIJ + RYIJ * RYIJ + RZIJ * RZIJ IF (RIJSQ.LT.RLSTSQ) THEN MLIST = MLIST + 1LIST(NLIST) = JС --- REMOVE THIS CHECK IF NAXNAB IS APPROPRIATE ---IF (NLIST .EQ. MAXNAB) STOP 'LIST TOO SMALL' IF (RIJSQ .LT. RCUTSQ) THEN SR2 = SIGSQ / RIJSQ = SR2 * SR2 * SR2 SR6 = SR6 * (SR6 - 1.0) VIJ WIJ = SR6 * (SR6 - 0.5) V = V + VIJF = F + WIJFIJ = WIJ / (RIJSQ/(SICMA*SICMA)) FXIJ = RXIJ * FIJ FYIJ = RYIJ * FIJ FZIJ = RZIJ * FIJ FXI = FXI + FXIJ FYI = FYI + FYIJ FZI = FZI + FZIJ FX(J) = FX(J) - FXIJFY(J) = FY(J) - FYIJFZ(J) = FZ(J) - FZIJENDIF ENDIF 99 CONTINUE FX(I) = FXI

194
FY(I) = FYIFZ(I) = FZI100 CONTINUE POINT(N) = NLIST + 1ELSE С --- USE THE LIST to FIND THE NEIGHBOURS ---DO 200 I = 1, N-1JBEG = POINT(I)JEND = POINT(I+1) -1С --- CHECK THAT ATOM I HAS NEIGHBOURS ---IF (JBEG .LE. JEND) THEN RXI = RX(I)RYI = RY(I)RZI = RZ(I)FXI = FX(I)FYI = FY(I)FZI = FZ(I)DO 199 JNAB = JBEG, JEND J = LIST(JNAB) RXIJ = RXI - RX(J)RYIJ = RYI - RY(J)RZIJ = RZI - RZ(J)RXIJ = RXIJ -SIDE* ANINT (RXIJ/SIDE) RYIJ = RYIJ -SIDE* ANINT (RYIJ/SIDE) RZIJ = RZIJ -SIDE* ANINT (RZIJ/SIDE) RIJSQ = RXIJ * RXIJ + RYIJ * RYIJ + RZIJ * RZIJ IF (RIJSQ .LT. RCUISQ) THEN SR2 = SIGSQ / RIJSQ SR6 = SR2 * SR2 * SR2 VIJ = SR6 * (SR6 - 1.0) WIJ = SR6 * (SR6 -0.5) = V + VIJV F = F + WIJFIJ = WIJ /(RIJSQ/(SIGMA*SIGMA)) FXIJ = RXIJ * FIJ FYIJ = RYIJ * FIJ FZIJ = RZIJ * FIJ FXI = FXI + FXIJ FYI = FYI + FYIJ FZI = FZI + FZIJ FX(J) = FX(J) - FXIJFY(J) = FY(J) - FYIJFZ(J) = FZ(J) - FZIJENDIF 199 CONTINUE FX(I) = FXIFY(I) = FYIFZ(I) = FZIENDIF 200 CONTINUE ENDIF RETURN END

C SUBROUTINE CHECK : DECIDES WHETHER THE LIST NEEDS TO BE ż * С RECONSTRUCTED C USAGE : CHECK IS CALLED TO SET UPDATE BEFORE EVERY CALL TO FORCE* SUBROUTINE CHECK (RCUT, RLIST, UPDATE) implicit integer*4(i-n) implicit real*8(a-h,o-z) COMMON / BLOCK1 / RX, RY, RZ, FX, FY, FZ COMMON / BLOCK3 / RXO, RYO, RZO PARAMETER (N = 255)DIMENSION RX(N), RY(N), RZ(N), FX(N), FY(N), FZ(N)DIMENSION RXO(N), RYO(N), RZO(N) LOGICAL UPDATE С ---CALCULATE MAXIMUM DISPLACEMENT SINCE LAST UPDATE ---DISPMX = 0.0DO 30 I = 1.NDISPMX = MAX (ABS (RX(I) - RXO(I)), DISPMX)DISPMX = MAX (ABS (RY(I) - RYO(I)), DISPMX)DISPMX = MAX (ABS (RZ(I) - RZO(I)), DISPMX)30 CONTINUE С ---A CONSERVATIVE TEST OF THE LIST SKIN CROSSING ---DISPMX = 2.0 * SQRT (3.0 * DISPMX ** 2)UPDATE = (DISPMX .GT. (RLIST-RCUT)) RETURN END C SUBROUTINE SAVE : SAVES CURRENT CONFIGURATION FOR FUTURE С CHECKING × С USACE : SAVE IS CALLED WHENEVER THE NEW × С VERLET LIST IS CONSTRUCTED SUBROUTINE SAVE IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) COMMON / BLOCK1 / RX, RY, RZ, FX, FY, FZ COMMON / BLOCK3 / RXO, RYO, RZO PARAMETER (N = 255) DIMENSION RX(N), RY(N), RZ(N), FX(N), FY(N), FZ(N)DIMENSION RXO(N), RYO(N), RZO(N) DO 100 I = 1.NRXO(I) = RX(I)RYO(I) = RY(I)RZO(I) = RZ(I)100 CONTINUE RETURN END

С SUBROUTINE FOURN : FAST FOURIER TRANSFORM FOR N-DIMENSION * С REFERENCE : 'NUMERICAL RECIPE' ± SUBROUTINE FOURN(NN,NDIM,NT2,ISIGN) IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8 (A-H,O-Z) DIMENSION NN(NDIM), DATA(2*16*16*16) COMMON /A/ DATA NTOT=1 DO 11 IDIM=1,NDIM NTOT=NTOT*NN(IDIM) 11 CONTINUE NPREV=1 DO 18 IDIM=1,NDIM N=NN(IDIM) NREM=NTOT/(N*NPREV) IP1=2*NPREV IP2=IP1*N IP3=IP2*NREM I2REV=1 DO 14 I2=1, IP2, IP1 IF(I2.LT.I2REV) THEN DO 13 I1=I2, I2+IP1-2, 2 DO 12 I3=I1, IP3, IP2 I3REV=I2REV+I3-I2 TEMPR=DATA(I3) TEMPI=DATA(I3+1) DATA(I3)=DATA(I3REV) DATA(I3+1)=DATA(I3REV+1)DATA(I3REV)=TEMPR DATA(I3REV+1)=TEMPI 12 CONTINUE 13 CONTINUE ENDIF IBIT=IP2/2 1 IF(IBIT.GE.IP1.AND.I2REV.GT.IBIT) THEN I2REV=I2REV-IBIT IBIT=IBIT/2 GO TO 1 ENDIF I2REV=I2REV+IBIT 14 CONTINUE IFP1=IP1 2 IF(IFP1.LT.IP2) THEN IFP2=2*IFP1 THETA=ISIGN*6.28318530717959/FLOAT(IFP2/IP1) WPR=-2.*SIN(0.5*THETA)**2 WPI=SIN(THETA) WR=1. WI=0. DO 17 I3=1, IFP1, IP1 DO 16 I1=I3,I3+IP1-2,2

DO 15 I2=I1, IP3, IFP2 K1=I2 K2=K1+IFP1 TEMPR=(WR)*DATA(K2)-(WI)*DATA(K2+1)TEMPI = (WR) * DATA(K2+1) + (WI) * DATA(K2)DATA(K2) = DATA(K1) - TEMPRDATA(K2+1) = DATA(K1+1) - TEMPIDATA(K1)=DATA(K1)+TEMPR DATA(K1+1) = DATA(K1+1) + TEMPI15 CONTINUE 16 CONTINUE WTEMP=WR WR=WR*WPR-WI*WPI+WR WI=WI*WPR+WTEMP*WPI+WI 17 CONTINUE IFP1=IFP2 GO TO 2 ENDIF NPREV=N*NPREV 18 CONTINUE IF(ISIGN.EQ.-1) THEN DO 19 I=1,NT2 DATA(I)=DATA(I)/NTOT 19 CONTINUE ENDIF RETURN END С SUBROUTINE NORM : NORMALIZATION OF INTEGRATION ± С USAGE : INPUT W1 AND W2, CSUM=<W1W2> * SUBROUTINE NORM(W1, W2, CSUM) IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) PARAMETER (N1=16, N2=16, N3=16) COMPLEX*16 W1(N1,N2,N3) * ,W2(N1,N2,N3) ± ,CP(N1,N2),CH(N1),CSUMCOMMON /C1/ DX, DY, DZ DO 21 IX=1,N1 DO 21 IY=1,N2 CP(IX,IY) = (0.0,0.0)DO 21 IZ=1,N3-1 CP(IX, IY) = CP(IX, IY) + DZ * (CONJG(W1(IX, IY, IZ)) * W2(IX, IY, IZ) +* CONJG(W1(IX, IY, IZ+1)) * W2(IX, IY, IZ+1)) * 0.521 CONTINUE DO 31 IX=1.N1 CH(IX) = (0.0, 0.0)DO 31 IY=1,N2-1 CH(IX)=CH(IX)+DY*(CP(IX,IY)+CP(IX,IY+1))*0.5

31 CONTINUE CSUM=(0.0,0.0) DO 41 I=1,N1-1 CSUM=CSUM+(CH(I)+CH(I+1))*DX*0.5

41 CONTINUE RETURN END

С SUBROUTINE INTEGRAL : INTEGRATION IN 3-DIMENSION ¥ С USAGE : W2 CORRESPONDS TO POT, KIN AND TOTAL ENERGY * SUBROUTINE INTEGRAL(W2,CSUM) IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) PARAMETER (N1=16, N2=16, N3=16) COMPLEX*16 W2(N1,N2,N3),CP(N1,N2),CH(N1),CSUM COMMON /C1/ DX, DY, DZ DO 21 IX=1,N1 DO 21 IY=1,N2 CP(IX, IY) = (0.0, 0.0)DO 21 IZ=1,N3-1 CP(IX,IY)=CP(IX,IY)+DZ*(W2(IX,IY,IZ)+* W2(IX,IY,IZ+1))*0.5 21 CONTINUE DO 31 IX=1.N1 CH(IX) = (0.0, 0.0)DO 31 IY=1.N2-1 CH(IX)=CH(IX)+DY*(CP(IX,IY)+CP(IX,IY+1))*0.531 CONTINUE CSUM=(0.0,0.0)DO 41 I=1,N1-1 CSUM=CSUM+(CH(I)+CH(I+1))*DX*0.541 CONTINUE RETURN END

> SUBROUTINE CONTOUR(ISIGN) IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) PARAMETER(N1=16,N2=16,N3=16) COMPLEX*16 W(N1,N2,N3)

COMMON /A/ W COMMON /C1/ DX, DY, DZ С ---WRITE OUT DATA IN UNIT=NFILE---IF(ISIGN.EQ.1) NFILE=51 IF(ISIGN.EQ.2) NFILE=52 IF(ISIGN.EQ.3) NFILE=53 DO 42 I=1,N1+1 DO 42 J=1,N2+1 IX=I IY=J IF(IX.EQ.N1+1) IX=1 IF(IY.EQ.N2+1) IY=1SUM=0. DO 56 K=1,N3 IZ=K+1IF(IZ.EQ.N3+1) IZ=1IF(ISIGN.EQ.1) THEN SUM=SUM+(CONJG(W(K,IX,IY)) *W(K,IX,IY)+ * CONJG(W(IZ, IX, IY)) * W(IZ, IX, IY)) * DX * 0.5ELSE IF(ISIGN.EQ.2) THEN SUM=SUM+(CONJG(W(IX,K,IY))*W(IX,K,IY)+* CONJG(W(IX, IZ, IY)) * W(IX, IZ, IY)) * DX * 0.5ELSE IF(ISIGN.EQ.3) THEN SUM=SUM+(CONJG(W(IX,IY,K))*W(IX,IY,K)+ * CONJG(W(IX,IY,IZ))*W(IX,IY,IZ))*DX*0.5ENDIF 56 CONTINUE NNN=MOD(IX,2) MM=MOD(IY,2) IF(NNN.EQ.1.AND.MMM.EQ.1) THEN IF(SUM.LT.10E-6) SUM=0. wRITE(NFILE, *)REAL((I-1)*DX),REAL((J-1)*DY),REAL(SUM) ENDIF 42 CONTINUE RETURN END

С SUBROUTINE : FEIT, PROJECT, MGT С USAGE : SOLVE THE SCHRODINGER EQUATION * C * PROJECT OUT THE GROUND STATE С BY MOVING GRID TECHNIQUE × SUBROUTINE FEIT(N,RX,RY,RZ,VEIX,VEIY,VEIZ,DT,NTIME) IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) PARAMETER (NDIM=3, N1=16, N2=16, N3=16, * TEI=46.625, TEIMD=643.55) DIMENSION NN(NDIM), VEI(N1, N2, N3) * ,RX(N),RY(N),RZ(N)* ,VEIX(N),VEIY(N),VEIZ(N) * ,H(N1),P(N1,N2)* ,G(50),RAD(50+1),GN(50),RADS(50+1)COMPLEX*16 W(N1,N2,N3), W0(N1,N2,N3)* , THETA1 (N1, N2, N3)* ,FACT2(N1,N2,N3),FACT1(N1,N2,N3) * ,CP(N1,N2),CH(N1),CSUM,TSUM,PSUM * ,POT(N1,N2,N3),SW(N1,N2,N3)× ,CW(N1,N2,N3),TW(N1,N2,N3)± , TOT(N1, N2, N3), TE(N1, N2, N3), PP(N1,N2,N3), WN(N1,N2,N3) * INTEGER CLOCK, TIMEI COMMON /A/ W COMMON /B/ SIDE, RSIDE, SIGMA, CLOCK, QTSUM COMMON /B1/ XNPICK, YNPICK, ZNPICK COMMON /C1/ DX, DY, DZ, CXE, CYE, CZE COMMON /C2/ ITXS, ITYS, ITZS, CMXP, CMYP, CMZP, PREF COMMON /C3/ ABC, ABCD, IE, IH, DIAM, NW, TIMEI NN(1)=N1NN(2)=N2NN(3) = N3NT=N1*N2*N3 NT2=2*NT SIDEH=SIDE/2. GSIDE=(107./0.7)**(1./3.) GSIDEH=GSIDE/2. XL=GSIDE SIDE4=(SIDE-GSIDE)/2. SIDEF=SIDE4+GSIDE DX=XL/FLOAT(N1) DY=XL/FLOAT(N2) DZ=XL/FLOAT(N3)PI=4.*ATAN(1.)PI2=2.*PI CSUMP=0.

C ---SET INITIAL WAVE FUNCTION \$ POTENTIAL ---RR=4.83D0

AA=0.655D0 BB=89099.D0 CC=12608.D0 STANDV=SIGMA*0.5D0 С ----CLOCK COND MUST AGREE WITH PSL2.F---IF (CLOCK.EQ.TIMEI) THEN VIMG=0. DO 71 IX=1,N1 DO 71 IY=1,N2 DO 71 IZ=1,N3 С --- SHIFT POINTS TO SYMMETRIC INTERVAL FOR FFT---С --- INITAL GRID BOX IN CENTER OF SIMULATION BOX---SX=SIDE4+FLOAT(IX-1)*DX SY=SIDE4+FLOAT(IY-1)*DY SZ=SIDE4+FLOAT(IZ-1)*DZ VREAL=((EXP(-((SX-XNPICK)*(SX-XNPICK)+ * (SY-YNPICK)*(SY-YNPICK)+ * (SZ-ZNPICK)*(SZ-ZNPICK)) * /(2.*STANDV*STANDV)))WO(IX, IY, IZ) = CMPLX(VREAL, VIMG) 71 CONTINUE С --- NORMALIZE INITIAL WAVEFUNCTION ----CALL NORM(WO,WO,SUM) RSQRTSUM=1./SQRT(SUM) DO 232 IX=1,N1 DO 232 IY=1,N2 DO 232 IZ=1,N3 WO(IX, IY, IZ) = WO(IX, IY, IZ) * RSQRTSUM W(IX,IY,IZ)=WO(IX,IY,IZ)232 CONTINUE ENDIF С --- POTENTIAL MEASURED AT GRID POINT---С ----- SET UP SIDES OF GRID BOX---С ----FIRST TIME THRU ITXS=0 FROM MAIN, THEN OUTPUT OF FEIT---С ---FIRST TIME CMXP=0 FROM MAIN, THEN OUTPUT OF FEIT---С ----DECIDE WHICH BOXES TO USE-----NXP=ANINT(CMXP/SIDE) NYP=ANINT(CMYP/SIDE) NZP=ANINT(CMZP/SIDE) С -----LOOP 1 OVER GRID----DO 1 IX=1,N1 DO 1 IY=1,N2 DO 1 IZ=1,N3 SX=SIDE4+FLOAT(IX-1+ITXS)*DX SY=SIDE4+FLOAT(IY-1+ITYS)*DY SZ=SIDE4+FLOAT(IZ-1+ITZS)*DZ VEI(IX, IY, IZ) = 0.0С ----IF PARTICLE FROM ONE BOX IS IN GRID KEEP IT, OTHERWISE--

С ---CHECK IF IMAGE PARTICLE IS IN GRID -----С ---FOR PARTICLE IN GRID EVALUATE XX, PARTICLE -GRID DISTANCE-------LOOP 21 OVER PARTICLES -----С DO 21 I=1.N XP=RX(I)+SIDE*NXP XX=SX-XPIF(ABS(XX).GT.GSIDEH.AND.ABS(XX+SIDE).GT.GSIDEH) GO TO 21 IF(XX.LT.-SIDEH) XX=XX+SIDE IF(XX.GT. SIDEH) XX=XX-SIDE YP=RY(I)+SIDE*NYP YY=SY-YP IF(ABS(YY).GT.GSIDEH.AND.ABS(YY+SIDE).GT.GSIDEH) GO TO 21 IF(YY.LT.-SIDEH) YY=YY+SIDE IF(YY.GT. SIDEH) YY=YY-SIDE ZP=RZ(I)+SIDE*NZP ZZ=SZ-ZP IF (ABS (ZZ).GT.GSIDEH.AND.ABS (ZZ+SIDE).GT.GSIDEH) GO TO 21 IF(ZZ.LT.-SIDEH) ZZ=ZZ+SIDE IF(ZZ.GT. SIDEH) ZZ=ZZ-SIDE RIJSQ=(XX*XX)+(YY*YY)+(ZZ*ZZ)VEI(IX,IY,IZ)=VEI(IX,IY,IZ)+TEI*AA/((RR*RSIDE)**4)* ż. (BB/(CC+RIJSQ*RIJSQ*RIJSQ*(RSIDE*RR)**6)-1.) /(RIJSQ*RIJSQ) С ----- CLOSE LOOP OVER PARTICLES-----21 CONTINUE CONTINUE 1 С ----- BEGIN FEIT STEP ------DO 2 IT=1,NTIME С ----- CALCULATE ENERGY ------С -----POTENTIAL ENERGY------DO 133 IX=1.N1 DO 133 IY=1,N2 DO 133 IZ=1,N3 CW(IX, IY, IZ) = CONJG(W(IX, IY, IZ))POT(IX, IY, IZ) = CONJG(W(IX, IY, IZ)) * W(IX, IY, IZ) * VEI(IX, IY, IZ)133 CONTINUE -- IN USING FFT ONLY W IS TRANSFORMED PASSED IN COMMON A---С С ----- FFT ---FROM R SPACE TO K SPACE--CALL FOURN(NN, NDIM, NT2, 1) DO 3 IX=1,N1 DO 3 IY=1,N2 DO 3 IZ=1,N3 IIX=N1/2-ABS(IX-1-N1/2)IIY=N2/2-ABS(IY-1-N2/2)IIZ=N3/2-ABS(IZ-1-N3/2)THETA1(IX, IY, IZ)=DT*4.*PI*PI ± *FLOAT(IIX*IIX+IIY*IIY+IIZ*IIZ)/(2.*XL*XL) FACT1(IX, IY, IZ) = EXP(-THETA1(IX, IY, IZ))TW(IX, IY, IZ) = W(IX, IY, IZ) * THETA1(IX, IY, IZ) * 2./DT

```
3
      CONTINUE
С
      ---- IFFT ---FROM K SPACE TO R SPACE---
      CALL FOURN(NN, NDIM, NT2, -1)
      DO 4 IX=1,N1
      DO 4 IY=1.N2
      DO 4 IZ=1.N3
      FACT2(IX, IY, IZ) = EXP(-DT * VEI(IX, IY, IZ))
      SW(IX, IY, IZ) = W(IX, IY, IZ) * FACT2(IX, IY, IZ)
      W(IX, IY, IZ) = TW(IX, IY, IZ)
4
      CONTINUE
С
      --- CALCULATE KINETIC ENERGY ---
      CALL FOURN(NN,NDIM,NT2,-1)
      DO 54 IX=1,N1
      DO 54 IY=1,N2
      DO 54 IZ=1,N3
      TW(IX,IY,IZ) = W(IX,IY,IZ)
      TE(IX, IY, IZ) = CW(IX, IY, IZ) * TW(IX, IY, IZ)
      W(IX,IY,IZ)=SW(IX,IY,IZ)
54
      CONTINUE
С
      ---- FFT ---- FROM R SPACE TO K SPACE ----
      CALL FOURN (NN, NDIM, NT2, 1)
      DO 5 IX=1,N1
      DO 5 IY=1,N2
      DO 5 IZ=1,N3
      IIX=N1/2-ABS(IX-1-N1/2)
      IIY=N2/2-ABS(IY-1-N2/2)
      IIZ=N3/2-ABS(IZ-1-N3/2)
      THETA1(IX,IY,IZ)=DT*4.*PI*PI
     ±
                           *FLOAT(IIX*IIX+IIY*IIY+IIZ*IIZ)/(2.*XL*XL)
      FACT1(IX, IY, IZ) = EXP(-THETA1(IX, IY, IZ))
      W(IX, IY, IZ) = W(IX, IY, IZ) * FACT1(IX, IY, IZ)
5
      CONTINUE
С
      ---- IFFT ---FROM K SPACE TO R SPACE ---
      CALL FOURN(NN, NDIM, NT2, -1)
С
      ----- NORMALIZE WAVEFUNCTION W(T)-----
      CALL NORM(W,W,CSUM)
      RSQRTSUM=1./SQRT(CSUM)
      DO 12 IX=1,N1
      DO 12 IY=1,N2
      DO 12 IZ=1,N3
      W(IX,IY,IZ)=W(IX,IY,IZ)*RSQRTSUM
12
      CONTINUE
      ----- CALCULATE ENERGY ------
С
С
      --- ENERGY CONVERGENCE TEST ----
      CALL INTEGRAL (POT, PSUM)
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CALL INTEGRAL (TE, TSUM)
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CSUM=REAL(PSUM)+REAL(TSUM) QTSUM=CSUM IF(ABS(REAL(CSUM)-CSUMP).LT.ABC) DT=DT/2. CSUMP=REAL(CSUM) IF(DT.LT.ABCD) GO TO 999 2 CONTINUE С --- END OF FEIT-----999 CONTINUE С ----DECIDE IF GRID IS TO BE MOVED-----С -----EVALUATE MAX PROB------С -----EVALUATE CM OF ELECTRON-----SUMP=0. DO 772 IX=1,N1 DO 772 IY=1,N2 DO 772 IZ=1.N3 PPP=CONJG(W(IX,IY,IZ))*W(IX,IY,IZ) SUMP=SUMP+PPP 772 CONTINUE CMX=0. CMY=0. CMZ=0. DO 712 IX=1,N1 DO 712 IY=1,N2 DO 712 IZ=1,N3 SX=SIDE4+FLOAT(IX-1+ITXS)*DX SY=SIDE4+FLOAT(IY-1+ITYS)*DY SZ=SIDE4+FLOAT(IZ-1+ITZS)*DZ PPP=CONJG(W(IX, IY, IZ)) *W(IX, IY, IZ)/SUMP CMX=CMX+PPP*SX CMY=CMY+PPP*SY CMZ=CMZ+PPP*SZ 712 CONTINUE IF (CLOCK.EQ.TIMEI) THEN CMXP=CMX CMYP=CMY

С --- FOLLOWING IS THE MOVING GRID TECHNIQUE---SUMP=0. DISO=(3.*(DX/2.)**2) PP1=CONJG(W(1,1,1))*W(1,1,1)DO 1450 IX=1,N1 DO 1450 IY=1.N2 DO 1450 IZ=1,N3 SX=SIDE4+FLOAT(IX-1+ITXS)*DX SY=SIDE4+FLOAT(IY-1+ITYS)*DY SZ=SIDE4+FLOAT(IZ-1+ITZS)*DZ DIS=((SX-CMX) **2+(SY-CMY) **2+(SZ-CMZ) **2)PPP=CONJG(W(IX,IY,IZ))*W(IX,IY,IZ) SUMP=SUMP+PPP IF(DIS.LT.DISO) THEN IF(PPP.LT.PP1) THEN

С

CMZP=CMZ ENDIF

с

PP1=PPP IXX=IX IYY=IY IZZ=IZ

DISO=DIS

ENDIF

1450 CONTINUE

- C --NOW HAVE SET IXX,.. AS GRID POINT CLOSEST TO CM---C -----EXPRESS THIS POINT RELATIVE TO BOX CENTER-----ITX=IXX-(N1/2+1) ITY=IYY-(N2/2+1) ITZ=IZZ-(N3/2+1)
- C ---- NEW GRID BOX CENTER -----ITXS=ITXS+ITX ITYS=ITYS+ITY ITZS=ITZS+ITZ

.

- DO 910 IX=1,N1 DO 910 IY=1,N2
- DO 910 IZ=1,N2
- C ----GRID RELATIVE TO GRID BOX CENTER-----II=IX+ITX JJ=IY+ITY KK=IZ+ITZ IF(II.LE.0) II=II+N1 IF(II.GT.N1) II=II-N1
 - IF(JJ.LE.O) JJ=JJ+N2 IF(JJ.GT.N2) JJ=JJ-N2 IF(KK.LE.O) KK=KK+N3 IF(KK.GT.N3) KK=KK-N3
- C -----RENAME WAVEFUNCTION -----WN(IX,IY,IZ)=W(II,JJ,KK)
- 910 CONTINUE
- C --- RENAME WN BACK TO W---
- C -RELABEL WAVEFUNCTION TO USE IN EVALUATING---
- C --- PARTICLE-ELEC FORCE---DO 212 IX=1,N1 DO 212 IY=1,N2
 - DO 212 IZ=1,N3
 - W(IX,IY,IZ)=WN(IX,IY,IZ)
- 212 CONTINUE
- C --- END THE MOVING GRID TECHNIQUE---
- C --- CUMULATE ELECTRON DISPLACEMENT---

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C --- CALCULATE DIFFUSION COEFFICIENT OF ELECTRON---
CXE=CXE+(CMX-CMXP)
CYE=CYE+(CMY-CMYP)
CZE=CZE+(CMZ-CMZP)
RSQ=CXE**2+CYE**2+CZE**2
IF((CLOCK/NW)*NW.EQ.CLOCK) THEN
```

С С С С	WRITE OUT CM OF ELECTRON IN UNIT=66 WRITE OUT NO. OF QUENCH IN UNIT=6 WRITE OUT POT, KIN, TOT ENERGY IN UNIT=44 WRITE OUT <r**2> AND DIFF. CONSTANT IN UNIT=330</r**2>
	WRITE(66,*)CLOCK-TIMEI,CMX,CMY,CMZ WRITE(6,*)'NO OF QUENCH',IT-1 WRITE(44,*)CLOCK,REAL(PSUM),REAL(TSUM),REAL(CSUM) DIFF=PREF*RSQ/FLOAT(CLOCK) WRITE(330,*)CLOCK,RSQ,DIFF ENDIF
С	RELABEL CM TO 'PREVIOUS' CM CMXP=CMX CMYP=CMY CMZP=CMZ
С	IF((CLOCK/NW)*NW.EQ.CLOCK) THEN PAIR DISTRIBUTION FUNCTION RAD(1)=0.0 DR=GSIDEH/FLOAT(IE-1) CONST=4.0*3.141590/3.0 DO 13 I=1,IE G(I)=0. RAD(I+1)=RAD(I)+DR
13 C	CONTINUE G(R) - CM - E SUMPP=0. DO 84 I=1,N1 DO 84 J=1,N2 DO 84 K=1,N3 SX=SIDE4+FLOAT(I-1+ITXS)*DX-CMXP SY=SIDE4+FLOAT(J-1+ITYS)*DY-CMYP SZ=SIDE4+FLOAT(K-1+ITZS)*DZ-CMZP DIS=SQRT(SX**2+SY**2+SZ**2) PPP=CONJG(W(I,J,K))*W(I,J,K) DO 51 IR=1,IE IF(DIS.GT.RAD(IR).AND.DIS.LE.RAD(IR+1)) THEN G(IR)=G(IR)+PPP*(1.0/((RAD(IR+1)**3-RAD(IR)**3)*CONST))) SUMPP=SUMPP+PPP GO TO 84 ELSE ENDLE
51 84	ENDIF CONTINUE CONTINUE RHOW=SIMP/(GSIDE##3)
С	WRITE(10, *)CLOCK
С	DO 7 K=1,IE
C	r=(rad(k)+rad(k+1))*DIAM/2.
C C7	write(10,*) r,G(K)/KHOW
C C	CONTINUE
č	CALL CONTOUR(1)
J	ENDIF

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С ---- CALCULATE PARTICLE-ELECTRON FORCE -----С ---LOOP 169 OVER PARTICLES, 170 OVER GRID-----С ----FOR FIXED PARTICLE SUM OVER GRID-----С -----FIND PARTICLE LOCATIONS IN GRID BOX----С ---IF PARTICLE NOT IN GRID BOX, SET VEIX, ..=0----IF ((CLOCK/NW) *NW.EQ.CLOCK) THEN RAA=GSIDEH RADS(1)=0.0DRS=RAA/FLOAT(IH-1) CONST=4.0*3.141590/3.0 DO 33 I=1, IH RADS(I+1)=RADS(I)+DRS GN(I)=0.33 CONTINUE ENDIF С --SET THE RANGE OF GRID BOX---DIS1=SIDEF+ITXS*DX DIS2=SIDE4+ITXS*DX DIS3=SIDEF+ITYS*DY DIS4=SIDE4+ITYS*DY DIS5=SIDEF+ITZS*DZ DIS6=SIDE4+ITZS*DZ NXP=NINT(CMXP/SIDE) NXM=NINT(CMXP/SIDE)-1 NYP=NINT(CMYP/SIDE) NYM=NINT(CMYP/SIDE)-1 NZP=NINT(CMZP/SIDE) NZM=NINT(CMZP/SIDE)-1 DO 169 J=1.N С XM=RX(I)+SIDE*NXM С XP=RX(I)+SIDE*NXP С IF(XM.LT.DIS1.AND.XM.GT.DIS2) THEN С XX = XMС ELSE IF(XP.LT.DIS1.AND.XP.GT.DIS2) THEN С XX=XP С ELSE С GO TO 666 С ENDIF С IF(XX.LT.-SIDEH) XX=XX+SIDE С IF(XX.GT. SIDEH) XX=XX-SIDE С YP=RY(I)+SIDE*NYP С YM=RY(I)+SIDE*NYM С IF (YM.LT.DIS3.AND.YM.GT.DIS4) THEN С YY=YM С ELSE IF (YP.LT.DIS3.AND.YP.GT.DIS4) THEN С YY=YP С ELSE С GO TO 666 С ENDIF С IF(YY.LT.-SIDEH) YY=YY+SIDE

209

- C IF(YY.GT. SIDEH) YY=YY-SIDE
- C ZP=RZ(I)+SIDE*NZP
- C ZM=RZ(I)+SIDE*NZM
- C IF(ZM.LT.DIS5.AND.ZM.GT.DIS6) THEN
- C ZZ=ZM
- C ELSE IF(ZP.LT.DIS5.AND.ZP.GT.DIS6) THEN
- C ZZ=ZP
- C ELSE
- C GO TO 666
- C ENDIF
- C IF(ZZ.LT.-SIDEH) ZZ=ZZ+SIDE
- C IF(ZZ.GT. SIDEH) ZZ=ZZ-SIDE
- C -----CALCULATE RADIAL DISTRIBUTION OF PARTICLES---IF((CLOCK/NW)*NW.EQ.CLOCK) THEN
- C ----G(R) CM PARTICLES----DO 112 IR=1,IH XX=RX(J)+SIDE*NXP-CMXP IF(XX.LT.-SIDEH) XX=XX+SIDE IF(XX.GT. SIDEH) XX=XX-SIDE YY=RY(J)+SIDE*NYP-CMYP IF(YY.LT.-SIDEH) YY=YY+SIDE IF(YY.GT. SIDEH) YY=YY-SIDE ZZ=RZ(J)+SIDE*NZP-CMZP IF(ZZ.LT.-SIDEH) ZZ=ZZ+SIDE IF(ZZ.GT. SIDEH) ZZ=ZZ-SIDE
- C -----CALCULATE RADIAL DISTRIBUTION OF PARTICLES---DIS=sqrt((XX)**2+(YY)**2+(ZZ)**2) IF(DIS.GT.RADS(IR).AND.DIS.LE.RADS(IR+1)) THEN GN(IR)=GN(IR)+1./((RADS(IR+1)**3-RADS(IR)**3)*CONST) ENDIF
- 112 CONTINUE ENDIF
- C ----EVALUATE FORCE COMPONENTS-----

C ----SUM OVER GRID POINTS, TO DO INTEGRAL-----DO 170 I=1,3 DO 1172 IX=1,N1 DO 1172 IY=1,N2 P(IX,IY)=0.0 DO 1172 IZ=1,N3-1

> SX=SIDE4+FLOAT(IX-1+ITXS)*DX SY=SIDE4+FLOAT(IY-1+ITYS)*DY SZ=SIDE4+FLOAT(IZ-1+ITZS)*DZ SZ1=SIDE4+FLOAT(IZ+ITZS)*DZ

- C -----PARTICLE-GRID DISTANCES------
- C --- EVALUATE FORCES BY MINIMUN IMAGE METHOD--XP=RX(J)+SIDE*NXP XXX=SX-XP IF(XXX.LT.-SIDEH) XXX=XXX+SIDE

IF(XXX.GT. SIDEH) XXX=XXX-SIDE YP=RY(J)+SIDE*NYP YYY=SY-YP IF(YYY.LT.-SIDEH) YYY=YYY+SIDE IF(YYY.GT. SIDEH) YYY=YYY-SIDE ZP=RZ(J)+SIDE*NZP ZZZ=SZ-ZP IF(ZZZ.LT.-SIDEH) ZZZ=ZZZ+SIDE IF(ZZZ.GT. SIDEH) ZZZ=ZZZ-SIDE ZZ1=SZ1-ZP IF(ZZ1.LT.-SIDEH) ZZ1=ZZ1+SIDE IF(ZZ1.GT. SIDEH) ZZ1=ZZ1-SIDE RIJSQ= (XXX*XXX+ YYY*YYY+ ZZZ*ZZZ)*RR*RR RIJ6=RIJSQ*RIJSQ*RIJSQ WIJ=TEIMD*AA*((4.*(1./RIJ6))*(BB*(1./(CC+RIJ6))-1.) * +6.*BB*(1./((CC+RIJ6)*(CC+RIJ6)))) RIJSQ1= (XXX*XXX+ YYY*YYY+ ZZ1*ZZ1)*RR*RR RIJ61=RIJSQ1*RIJSQ1*RIJSQ1 WIJ1=TEIMD*AA*((4./RIJ61)*(BB/(CC+RIJ61)-1.))* +6.*BB/((CC+RIJ61)*(CC+RIJ61))) ----EVALUATE THE DIFFERENT FORCE COMPONENTS----С IF(I.EQ.1) GO TO 61 IF(I.EQ.2) GO TO 31 IF(I.EQ.3) GO TO 41 P(IX, IY) = P(IX, IY) + DZ * (XXX * RR * WI J * CONJG(W(IX, IY, IZ)) * W(IX, IY, IZ))61 * +XXX*RR*WIJ1*CONJG(W(IX,IY,IZ+1))*W(IX,IY,IZ+1))*0.5 GO TO 1172 P(IX, IY) = P(IX, IY) + DZ * (YYY * RR * WIJ * CONJG(W(IX, IY, IZ)) * W(IX, IY, IZ))31 * +YYY*RR*WIJ1*CONJG(W(IX,IY,IZ+1))*W(IX,IY,IZ+1))*0.5 GO TO 1172 P(IX, IY) = P(IX, IY) + DZ * (ZZZ * RR * WIJ * OONJG(W(IX, IY, IZ)) * W(IX, IY, IZ))41 * +ZZ1*RR*WIJ1*CONJG(W(IX,IY,IZ+1))*W(IX,IY,IZ+1))*0.5 GO TO 1172 1172 CONTINUE DO 1173 IX=1.N1 H(IX) = 0.0DO 1173 IY=1,N2-1 H(IX)=H(IX)+DY*(P(IX,IY)+P(IX,IY+1))*0.51173 CONTINUE SUM=0.0 DO 1174 K=1,N1-1 SUM=SUM+(H(K)+H(K+1))*DX*0.51174 CONTINUE IF(I.EQ.1) VEIX(J)=-SUM IF(I.EQ.2) VEIY(J)=-SUM IF(I.EQ.3) VEIZ(J)=-SUM 170 CONTINUE

169 CONTINUE

IF((CLOCK/NW)*NW.EQ.CLOCK) THEN RHO=FLOAT(N)/(SIDE**3) WRITE(11,*)CLOCK

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DO 17 K=1,IH R=(RADS(K)+RADS(K+1))*DIAM/(2.) WRITE(11,*) R, G(K)/RHOW, GN(K)/RHO CONTINUE

ENDIF RETURN END

17

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PROGRAM TITLE : PROJ3D С С PURPOSE : OBTAIN THE EIGENSTATES × С METHOD : USE THE PROJECTION OPERATOR METHOD * С .CONTAIN : CALL FOURN, CONTOUR * С DOUBLE PRECISION С DATE : MAY, 1990 С INPUT : W(N1,N2.N3), VEI(N1,N2,N3), TINP SUBROUTINE PROJ3D(W, VEI) IMPLICIT INTEGER*4(I-N) IMPLICIT REAL*8(A-H,O-Z) PARAMETER (NDIM=3, N1=16, N2=16, N3=16) DIMENSION NN(NDIM), VEI(N1, N2, N3), THETA1(N1, N2, N3) COMPLEX = 16 W(N1, N2, N3), WO(N1, N2, N3), WNO(N1, N2, N3)* ,WN1(N1,N2,N3),WTR(N1,N2,N3) * ,FACT2(N1,N2,N3),FACT1(N1,N2,N3)* ,CSUM,CSUM1 * POT(N1, N2, N3), SW(N1, N2, N3)* ,CW(N1,N2,N3),TW(N1,N2,N3) × , TOT(N1, N2, N3), TE(N1, N2, N3)COMMON /A/ W COMMON /B/ SIDE, SIDEH, SIGMA, NCLOCK COMMON /C1/ DX, DY, DZ OPEN(1, FILE = 'TINP') READ(1,*)DT, NTIME, NCLOCK, NSTATE NN(1)=N1NN(2)=N2NN(3)=N3NT=N1*N2*N3 NT2=2*NT XL=SIDE DX=SIDE/FLOAT(N1) DY=SIDE/FLOAT(N2)DZ=SIDE/FLOAT(N3) PI=4.*DATAN(1.DO)PI2=2.*PI DTH=DT/2.0----- NORMALIZE INITIAL WAVEFUNCTION W(0)----С С ----- CREATE FACT1 AND FACT2 -----CALL NORM(W,W,CSUM) DO 232 I=1,N1 DO 232 J=1,N2 DO 232 K=1,N3 W(I,J,K) = W(I,J,K) / SQRT(CSUM)WO(I,J,K) = W(I,J,K)

232 CONTINUE ----- BEGIN QUENCHING STEP -----С DO 2 IT=1,NTIME С ----- CALCULATE ENERGY ------DO 133 I=1,N1 DO 133 J=1,N2 DO 133 K=1,N3 CW(I,J,K) = CONJG(W(I,J,K))POT(I,J,K)=CONJG(W(I,J,K))*W(I,J,K)*VEI(I,J,K)133 CONTINUE С ----- FFT --FROM R SPACE TO K SPACE------CALL FOURN (NN, NDIM, NT2, 1) DO 3 I=1,N1 DO 3 J=1,N2 DO 3 K=1,N3 IX=N1/2-ABS(I-1-N1/2)IY = N2/2 - ABS(J - 1 - N2/2)IZ=N3/2-ABS(K-1-N3/2)THETA1(I, J, K)=DT*4.*PI*FLOAT(IX*IX+IY*IY+IZ*IZ) * /(2.*XL*XL)FACT1(I,J,K) = EXP(-THETA1(I,J,K))TW(I,J,K) = W(I,J,K) + THETA1(I,J,K)/DTHW(I,J,K) = W(I,J,K) + FACT1(I,J,K)3 CONTINUE С ----- IFFT --FROM K SPCE TO R SPACE-----CALL FOURN(NN,NDIM,NT2,-1) DO 4 I=1,N1 DO 4 J=1,N2 DO 4 K=1,N3THETA2=DT*VEI(I,J,K) FACT2(I, J, K) = EXP(-THETA2)SW(I,J,K)=W(I,J,K)*FACT2(I,J,K)W(I,J,K) = TW(I,J,K)4 CONTINUE С ----- CALCULATE KINETIC ENERGY ------IF((IT/NCLOCK) *NCLOCK.EQ.NCLOCK) THEN С ----- IFFT --FROM K SPCE TO R SPACE------CALL FOURN (NN, NDIM, NT2, -1) ENDIF DO 54 I=1,N1 DO 54 J=1,N2 DO 54 K=1,N3 TW(I,J,K) = W(I,J,K)TE(I,J,K)=CW(I,J,K)*TW(I,J,K)W(I,J,K)=SW(I,J,K)54 CONTINUE

С	FFTFROM R SPACE TO K SPACE CALL FOURN(NN,NDIM,NT2,1) DO 5 I=1,N1 DO 5 J=1,N2 DO 5 K=1,N3 IX=N1/2-ABS(I-1-N1/2) IY=N2/2-ABS(J-1-N2/2) IZ=N3/2-ABS(K-1-N3/2) THETA1(I,J,K)=DT*4.*PI*PI*FLOAT(IX*IX+IY*IY+IZ*IZ)
5	FACT1(I,J,K)=EXP(-THETA1(I,J,K)) W(I,J,K)=W(I,J,K)*FACT1(I,J,K) CONTINUE
С	IFFTFROM K SPACE TO R SPACE CALL FOURN(NN,NDIM,NT2,-1)
C 1 2	NORMALIZE WAVEFUNCTION W(T) CALL NORM(W,W,CSUM) DO 12 I=1,N1 DO 12 J=1,N2 DO 12 K=1,N3 W(I,J,K)=W(I,J,K)/SQRT(CSUM) TOT(I,J,K)=POT(I,J,K)+TE(I,J,K) CONTINUE
ССССС	ENERGY CONVERGENCE TESTING CALCULATE ENERGY WRITE OUT POTENTIAL E TO UNIT 40 WRITE OUT KINETIC E TO UNIT 42 WRITE OUT TOTAL E TO UNIT 44 IF((IT/NCLOCK).EQ.NCLOCK) THEN CALL INTEGRAL(POT,CSUM) WRITE(40,*)IT,REAL(CSUM) CALL INTEGRAL(TE,CSUM) WRITE(42,*)IT,REAL(CSUM) CALL INTEGRAL(TOT,CSUM) WRITE(44.*)IT,REAL(CSUM)
С	ENERGY CONVERGENCE TEST IF (ABS (REAL (CSUM) -CSUMP).LT.0.001) DT=DT/2. CSUMP=REAL (CSUM) ENDIF
С	REORTHOGONALIZATION WITH THE KNOWN LOWER STATES IF(NSTATE.NE.0) THEN IF((IT/NCLOCK)*NCLOCK.EQ.NCLOCK) THEN IF(NSTATE.EQ.1) THEN CALL NORM(W,WNO,CSUM) DO 311 I=1,N1 DO 311 J=1,N2 DO 311 K=1,N3 W(I,J,K)=W(I,J,K)-WNO(I,J,K)*CSUM

311	CONTINUE ELSE IF(NSTATE.EQ.2) THEN CALL NORM(W,WN0,CSUM) CALL NORM(W,WN1,CSUM1) DO 312 I=1,N1 DO 312 J=1,N2 DO 312 K=1,N3
312	W(I,J,K)=W(I,J,K)-WNO(I,J,K)*CSUM-WN1(I,J,K)*CSUM1 CONTINUE ENDIF ENDIF ENDIF
2 999 C	IF(DT.LT.0.01) GO TO 999 CONTINUE CONTINUE END QUENCHING STEPS=NTIME
C C C C	IF ENERGY TESTING IS CONVERGENT, THEN W(T) MUST BE WITH THE LOWEST EIGENENERGY AND EIGENSTATE WE USE THIS W(T) TO PRODUCE A NEW TRIAL WAVEFUNCTION TRIAL FUNCTION
С	CALCULATE OVERLAP= <w(t)w(0)> CALL NORM(W,W0,CSUM)</w(t)w(0)>
	DO 441 I=1,N1 DO 441 J=1,N2 DO 441 K=1.N3
С	SAVE THE LOWEST EIGENSTATE IN UNIT 10 WRITE(10,*)W(I,J,K) WTP(I,J,K)=W0(I,J,K)=W(I,J,K)*CSLM
С	SAVE TRIAL WAVEFUNCTION IN UNIT 90
441	WRITE(100,*/WIR(1,3,K) CONTINUE WRITE(6,*)'OVERLAP',CSUM
С	PLOT THE PROBABILITY DENSITY CALL CONTOUR(1) CALL CONTOUR(2) CALL CONTOUR(3) STOP

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END

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C*************************************		
С	PROGRAM TITLE : FT *	
С	THE PROCEDURES: *	
С	DATA READ IN CORRELATION FUNCTION C(T) *	
С	DATA WINDOWINGC(T)*WINDOW(T) *	
С	FOURIER TRNSFORM C(F) *	
C****	*****************	
C	PRODUKAM FI	
C	IMPLICIT INTEGER#1(I-N)	
	IMPLICIT DOUBLE PRECISION(a-b-o-z)	
С		
C	INPUT PARAMETERS	
	PARAMETER (NDIM=1, NTIME=8192, DT=0.015D0)	
с		
	COMPLEX*16 C(NTIME)	
	DIMENSION NN(NDIM)	
	COMMON/A/C	
	OPEN(7,FILE='CF')	
	OPEN(8,FILE='FT')	
С		
	NN(1) = NTIME	
	$P1=4.D0 \neq DATAN(1.D0)$ $D12=2.D0 \neq DT$	
	P12=2.D0*P1	
	DO 88 I=1.NTIME/2	
	$\frac{1}{2} \frac{1}{2} \frac{1}$	
88	CONTINUE	
	SWINDOW=0.D0	
	DO 81 IT=0,NTIME-1	
	IF(IT.LT.NTIME/2) THEN	
	T=DT*DFLOAT(IT)	
	C(NTIME-IT)=CONJG(C(IT+2))	
	ELSE	
	T = -(DT*NTIME/2) + DT*DFLOAT(IT-NTIME/2)	
	ENDIF	
C	$PEAD(7 \pm)C(TT+1)$	
C	(1, +) = (1, +) = (1, +)	
	WINDOW=(1.DO-DCOS(PI*2.DO*T/(NTIME*DT)))	
	SWINDOW=SWINDOW+WINDOW	
	C(IT+1)=WINDOW*C(IT+1)	
81	CONTINUE	
	CALL FOURN (NN, NDIM, NTIME, 1)	
	DU 63 I=1,NTIME	
	$WW = UUNJU(U(1)) \neq U(1)$ $TE / UNJ (U(1)) \neq U(1)$	
	IF (WW.GI.IUE-IU) INEN IF/I IT NTIME /2) THEN	
	$\frac{1}{1} \frac{1}{1} \frac{1}$	
	FISE	
	FREQ=-2.D0*PI*DFLOAT(NTIME-I+1)/(NTIME*DT)	

ENDIF WRITE(8,*)FREQ,WW/SWINDOW ENDIF 83 CONTINUE STOP END

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LIST OF REFERENCES

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LIST OF REFERENCES

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