



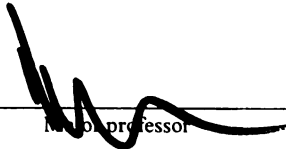


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CURVATURE ENERGY OF NUCLEI,
ELECTRONIC EXCITATIONS OF CARBON CLUSTERS,
AND THERMAL PROPERTIES OF SODIUM CLUSTERS
presented by

Nengjiu Ju

has been accepted towards fulfillment
of the requirements for
Ph.D. degree in Physics



Instructor

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CURVATURE ENERGY OF NUCLEI,
ELECTRONIC EXCITATIONS OF CARBON
CLUSTERS, AND THERMAL PROPERTIES
OF SODIUM CLUSTERS

By

Nengjiu Ju

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ABSTRACT

CURVATURE ENERGY OF NUCLEI, ELECTRONIC EXCITATIONS OF CARBON CLUSTERS, AND THERMAL PROPERTIES OF SODIUM CLUSTERS

BY

Nengjiu Ju

This thesis consists of three separate parts. In the first part we calculated the nuclear correlation energy E_{corr} in the RPA approximation with particular attention paid to the A -dependence. We found that E_{corr} has a very different A -dependent behavior from the mean-field total ground state energy E_{mean} . In this way, we want to shed some new light on the longstanding contradiction between the curvature coefficient value a_c resulting from mean-field calculation which is always close to 10 MeV and that from the direct adjustment of mass-formula to nuclei ground state masses which is zero.

Part two is dedicated to the study of the multipole electronic collective excitations in carbon clusters using linear response theory. The single-particle wave and energy levels are determined by a tight-binding Hamiltonian, whose parameters have been determined by a fit to the LDA results. Because C_{60} , the so-called buckyball, has a spherical symmetry, its treatment is much simpler than that of an arbitrary cluster, it is naturally our first choice to apply our model. With some work, we were also able to completely solve the RPA problem within the tight-binding framework for an arbitrary geometry of the cluster. We applied this new formalism to other carbon

clusters. The equivalents of both π and σ plasmons in graphite are predicted for these clusters. Since only dipole excitation is optically allowed, the other multipole excitations are best studied by electron energy-loss spectroscopy (EELS). To this end, we calculated the differential cross sections of inelastic electron scattering off these carbon clusters. We compared our dipole electronic excitations with available photoionization experimental data and our differential cross sections with available EELS data. Good agreement is obtained between our calculations and available experimental results where they are available.

The third part addresses the thermal properties of sodium clusters using the isothermal molecular dynamics developed recently by Aurel Bulgac and Dimitri Kusnezov. A wide range of properties of small sodium clusters are investigated and presented. We found that sodium clusters undergo two “phase transitions”, one around 200 K from a crystal to a glassy or molten state, and a second one around 800 K, from a molten to a fluid state. At low temperatures these clusters are essentially incompressible, but relatively easy to deform. At high temperatures they become extremely soft and evaporation of atoms sets in.

To my wife, Wenge Zhang, for her love, understanding, tolerance and to our
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Chapter 1

Introduction

1.1 Nuclear Correlation Energy

One of the well-established approaches to obtain nuclear binding energies is based on the analogy of a nucleus to a drop of incompressible fluid. The first evidence in support of such a simple “liquid drop” model for the nucleus comes from the fact that per nucleon binding energy is about the same for all nuclei. If we are willing to ignore the small local departures, it is possible to develop a simple formula that expresses the binding energy of a nucleus in terms of its number of nucleons (in other words, its volume since the volume is proportional to its number of nucleons) along with surface correction, curvature correction and higher-order corrections.

The liquid drop model (LDM) has been very successful in determining many nuclear properties. An expansion of the nuclear energy of a finite nucleus into volume, surface, curvature and higher-order contributions has proved enormously useful in calculating fission barriers, ground-state masses and deformation, and other nuclear properties [1, 2, 3]. However, a serious anomaly exists between the value of the curvature energy coefficient a_c obtained theoretically and that from adjustments to experimental data [4]. Direct adjustment of mass-formula to the ground state masses

of nuclei throughout the periodic table yields values of the curvature energy coefficients a_c (a_c in the term $a_c A^{1/3}$ in the mass-formula) close to zero. On the other hand, many previous theoretical calculations have given a typical value 10 MeV for a_c .

By summing up all the ring diagrams, we calculated the nuclear correlation energy E_{corr} in the RPA approximation with particular attention paid to the A -dependence. We found that E_{corr} has a very different A -dependent behavior from that of the mean-field total ground state energy E_{mean} . In this way, we want to shed some new light on the anomaly aforementioned.

1.2 Atomic Clusters

Clusters are aggregates composed of a countable number of atoms, which can be as small as two or as large as hundreds of thousand. The real breakthrough comes through the discovery of quantal shell structure in small droplets of sodium metal, with characteristic “magic numbers”, by Knight and coworkers [5], see fig. 1.1. Since then, cluster physics has been an active field of theoretical and experimental investigation. Many properties of a large variety of clusters have been examined [6] – mass abundance spectra, fragmentation spectra and binding energy, supershell structure [7], ionization potential [8, 9], photoelectron spectra and electron affinity, static [11, 12, 13] and dynamical [14, 15, 16] polarizability, plasmon resonance spectra [17] and thermal properties [18, 19], to name just a few. With the advent of new technology, it has become possible to have well-controlled cluster sources, thus to make clusters of well-defined sizes and to measure their properties precisely. Because clusters lie somewhere between a solid and an atom, they provide for a test of our understanding of bonding and of the transition from atomic to molecular and

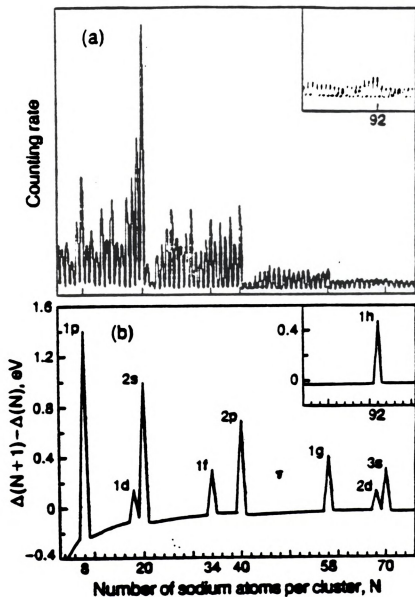


Figure 1.1: Mass abundance spectrum of Na_N clusters. (a) Mass abundance spectrum of Na_N clusters, $N=4-75$. (b) The electronic energy difference, $\Delta(N+1) - \Delta(N)$ vs N . The labels of the peaks correspond to the closed-shell orbitals. [From Knight et al, Phys. Rev. Lett. 52, 2141 (1984)].

ultimately bulk properties. A compelling stimulus has been the desire to understand how an extended crystalline solid develops from growing cluster aggregates. Clusters possess many unique properties and they can be used to make new materials. Stimulated perhaps by its potential use, from its very beginning, cluster physics has been a very active field, bringing methods and concepts from atomic and condensed matter physics, quantum chemistry, thermodynamics, surface science, optics, nuclear physics and others into unprecedented combinations.

The most thoroughly studied clusters are the sodium clusters. Since sodium clusters can be generated in conventional sources under supersonic adiabatic expansion conditions, they can be studied for a longer time than it is possible for most other clusters that require the use of the Smalley laser vaporization source [43]. The first evidence of shell structures in clusters comes from the study of sodium clusters [5]. Recently, abundance spectrum has been measured up to 22,000 atoms and has revealed interesting new shell structures [45]. The persistence of the strong shell effects up to very large numbers of atoms in a cluster is a quite remarkable phenomenon [46, 45].

The most interesting clusters studied so far are certainly the carbon clusters, especially the so-called fullerenes including the celebrated buckyball C_{60} .

To explain the large abundance of clusters with 60 carbon atoms, the existence of a stable, spherical C_{60} molecule, the so-called buckyball, has been proposed [44]. In the suggested structure, twelve regular pentagons and twenty hexagons are connected to form an icosahedral structure, see fig. 1.2.

The most exciting development of the study of C_{60} has been the discovery of the fourth form of pure carbon solid, the so-called fullerite, which was discovered about only three years ago if we consider the amorphous carbon also as a pure solid form

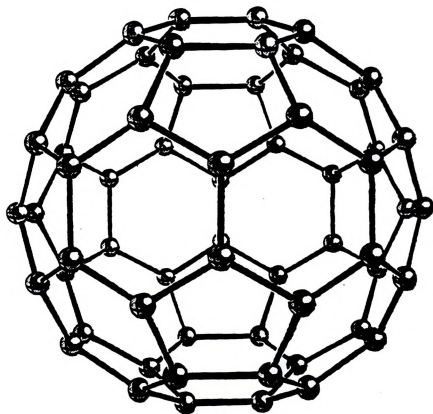


Figure 1.2: Structure of the C₆₀ "buckyball" cluster.

(the other two forms are sp^3 -bonded diamond and sp^2 -bonded graphite). In the fall of 1990, W. Krätschmer et al [47] made a major breakthrough in the synthesis and separation of C_{60} . By chemical extraction methods, they obtained large quantities of C_{60} . This breakthrough has led to the intense experimental and theoretical studies of the structural [48, 49, 50, 51] and electronic properties [52] of this novel solid form of carbon.

The most striking property of fullerite is perhaps its superconductivity when it is doped. Although the highest critical temperature of doped fullerite is still well below that of the the high- T_c superconductors, these intercalated fullerites have polarized the interest of many investigators because they have superior material properties and hence bear a higher potential for applications.

Many theories have been developed to explain a large variety properties of different clusters, for example, the magic numbers of alkali metals. The simplest of these is the spherical jellium model [6] of alkali metal clusters. Because of the delocalized character of the valence s -electrons of alkali atoms, they are shared by all ions in a cluster and this feature leads to shell effects similar to those observed in atomic nuclei. To a very good approximation, the ions can be thought of as simply providing an almost uniform positive background, and a jellium approximation is quite reasonable [69]. The valence s -electrons move in a common mean field and the ensuing strong shell effects account very well for both the enhanced stability of the magic clusters, shapes corresponding to different numbers of atoms and the character of the optical response (Mie resonance), which has analogous features to the well known giant dipole resonance in nuclei. Spheroidal or ellipsoidal extensions of the jellium model are derived in order to study deviations from sphericity and are used to provide general shapes of cluster as oblate or prolate ellipsoids [22]. The spheroidal jellium model

also shows that within the jellium model, special stability at shell closing is associated with vanishing distortion from sphericity.

Among the more sophisticated methods are the density functional theory (DFT) based on the local density approximation (LDA), configuration interaction (CI) calculation, and calculation based on the Car–Parrinello method, to just name a few. In these studies, it has been found that generally each cluster has several isomers at $T = 0$ K with a very similar total energy, therefore thermal effects may have important implications about the properties of the clusters [73].

Although there are many theoretical studies on a variety of different clusters, we will concentrate on two studies of two classes of clusters in this thesis. The first one is the study of the electronic excitations in fullerenes, which is presented in chapter 3. Fullerenes are a group of carbon clusters with hollow cage structures, with only pentagons and hexagons on their surfaces. The second one is the study of the thermal properties of small sodium clusters using the newly developed isothermal molecular dynamics [18, 19, 40, 39], which is the subject of chapter 4. Although many theoretical studies have been done on clusters, most of them are concerned with ground state properties, such as ground state geometrical and electronic structures. Without justification, these calculations have been compared with experimental data. On the other hand, clusters are produced at high temperatures [41]. Therefore the study thermal properties of clusters is very important. The choice of sodium clusters is pragmatic. Sodium clusters have been most thoroughly investigated [5].

1.2.1 Multipolar Responses of Fullerenes

Fullerenes are carbon clusters with hollow cage structure, with only pentagons and hexagons on their surfaces. The best known member of fullerenes is the aforemen-

tioned buckyball C_{60} . Since fullerenes are essentially hollow graphite shells, they should support multipolar plasmon oscillations, closely related to the plasmons in graphite. G. Barton and C. Eberlein [57] estimated the frequencies of these multipolar plasmons by adapting the reasonably successful hydrodynamic approach familiar from bulk and surface plasmons [58, 59], with just one parameter calibrated on graphite. They predicted π plasmons in the range between 6 and 8 eV, and σ plasmons near and above 25 eV. In a more serious and physical treatment of the dipole plasmon of C_{60} , Bertsch et al [60] used the linear response theory (RPA) to study the collective plasmon excitations in C_{60} clusters, they found that the valence electrons are quite delocalized and show collective excitations. They predicted a giant dipole resonance at an unusually high energy of 20 eV, see fig. 1.3. Their prediction is somewhat lower than the prediction 25 eV from the hydrodynamic model. The existence of a giant dipole resonance in C_{60} was subsequently confirmed by an independent photoionization experiment on a C_{60} gas target [61], see fig. 1.4. In computing the matrix elements of the residual Coulomb interaction arising from the $l = 0$ transitions in Ref. [60] for the dipole response, it was assumed that the spatial extent of the s - and p -states is vanishingly small, this approximation results in a slight overestimate of the Coulomb matrix elements. Another approximation in ref. [60] was to neglect the $l = 2$ component in the particle-hole state $|ph\rangle$ resulting from a p -hole state to a p -particle state transition. These approximations make their approach unsuitable to study other multipolar responses and also the multipolar responses of other non-spherical fullerenes. It is part of our interest in chapter 3 to extend their calculation without these approximations and to see to what extent their approximations are valid. It is also our interest to extend the calculation to other multipoles.

In chapter 3, besides studying the multipolar responses of the C_{60} , we also study

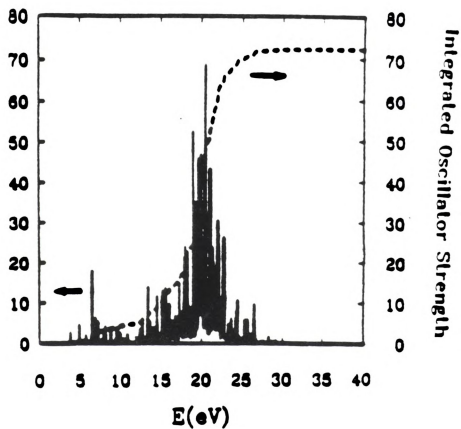


Figure 1.3: Dipole response of C_{60} clusters to an external electromagnetic field [From G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. **67**, 2690 (1991)].

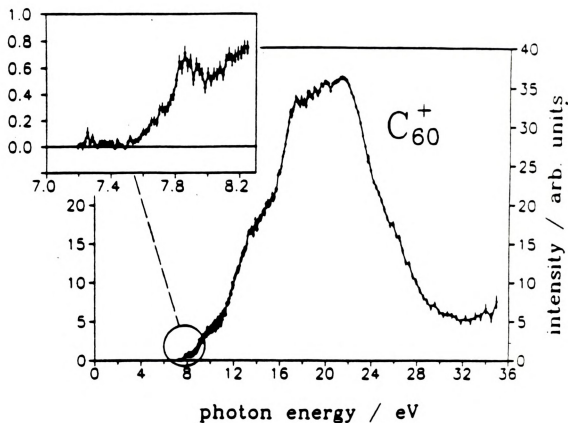


Figure 1.4: Observed C_{60}^+ photoion yield as a function of photon energy. [From I. V. Hertel et al, Phys. Rev. Lett. 68, 784 (1992)].

the multipolar responses of other fullerenes. We have two aims. First of all, we are interested in seeing how the plasmons vary with the sizes of the clusters. In the classical picture of Mie, the energy of the plasmon is independent of the size of the cluster and is totally determined by the free electron charge density of the cluster. Secondly, we want to know how the plasmons behave with nonsphericity. Since other fullerenes do not have spherical symmetry as C_{60} does, each plasmon of C_{60} should split in other fullerenes. The extension from the RPA calculations of C_{60} to those of other fullerenes is not trivial. Usually the nonsphericity of the system under study presents a formidable technical problem in RPA, fortunately we are able to solve the RPA equation for any geometry of the system considered in the tight-binding framework for the single particle description of the electrons

Since only dipole excitation is optically allowed, the other multipolar excitations are best studied by electron energy-loss spectroscopy (EELS). For this reason, we calculate the differential cross sections of inelastic electron scattering off the fullerenes. We compare our dipole electronic excitations with available photoionization experimental data and our differential cross sections with available EELS data. Good agreement are found between our calculations and available experimental results where they are available.

1.2.2 Thermal Properties of Sodium Clusters

There are several reasons why it is interesting to study finite temperature properties of atomic clusters, in particular of simple metal clusters. The most obvious one is the fact that experimental results obtained so far are for relatively hot clusters [6, 74]. Even though the experimentalists do not have at the moment a way of determining the temperature of the clusters they produce, and only relatively rough estimates are

available, it is very likely that these clusters are melted. An estimated temperature of $T \approx 500\text{--}600$ K seems to be realistic under experimental conditions [41]. On the other hand, most of the theoretical studies are performed at zero temperature. Without further justification, these results have been compared with experimental data. Therefore properties and the behaviour of finite systems at nonzero temperatures are of unquestionable theoretical interest.

We will try to elucidate to some extent the role of a finite temperature in sodium cluster in chapter 4. Although it is unquestionable that the most ‘fundamental’ way to describe atomic clusters at zero as well as at finite temperatures is *ab initio* calculations, the computer time required to extract relevant physical information is appalling. It is for this reason that we will adopt a less ambitious approach. We will treat the electrons implicitly by using an effective many-body-alloy (MBA) Hamiltonian. The parameters of this Hamiltonian were determined from *ab initio* calculations with no free parameters [75].

1.3 Thesis Organization

In chapter 2, we use RPA to calculate the nuclear correlation energy to address the longstanding contradiction between the curvature coefficient value a_c resulting from mean-field calculation and that from the direct adjustment of mass-formula to nuclei ground state masses.

We discuss the multipolar responses and differential cross sections of inelastic electron scattering of C_{60} and other fullerenes in chapter 3. Comparison is made between our calculations and available experimental data and good agreement is obtained.

We elucidate the thermal properties of sodium clusters in chapter 4. The electrons

are treated implicitly by a MBA Hamiltonian. The possible link between the red shift of the Mie plasmon in sodium clusters and their thermal expansion is discussed.

A summary of the results obtained and how to extend the works discussed in this thesis are presented in chapter 5.

Finally the appendices are an integral part of this thesis, they provide the formulas used. We discuss the formulas of the multipolar responses and EESL of C_{60} in appendix A and their extension to nonspherical fullerenes in appendix B. This extension is nontrivial and the formulas are much more complicated than those in appendix A.

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Chapter 2

Correlation Energy and Curvature Energy of Nuclei

2.1 Introduction

Direct adjustment of mass-formula to the ground state masses of nuclei throughout the periodic table yields values of the curvature-energy coefficients a_c (a_c in the term $a_c A^{1/3}$ in the mass-formula) close to zero. However many previous theoretical calculations give a typical value 10 MeV for a_c . Calculations within mean-field methods have yielded the value 9.34 MeV for the Seyler-Blanchard effective two-nucleon interaction [1], values ranging from 9.52 to 12.99 MeV for six representative Skyrme interactions [2]. And also in a HF calculation of a sequence of large mirror nuclei with the Coulomb force turned off, the value 11.86 MeV has been obtained [3]. Stocker et al [4] have made a systematic study of the problem. From their analysis they concluded that the mean-field approximations are unable to reproduce the entire set of nuclear mass-formula coefficients when the saturation density and surface diffuseness are constrained to their experimental values. However, there is one very important effect, not yet considered, which might be responsible for this discrepancy; namely the quantum corrections arising from the zero point oscillations of the nuclear surface.

It seems very natural to link the curvature corrections to the binding energy with the surface oscillation, which modifies the local curvature when it is excited.

By summing up all the ring diagrams, we calculate the correlation energy E_{corr} for spherical nuclei in the RPA approximation with particular attention paid to the A -dependence. We assume that the total ground state energy is the sum of E_{mean} and E_{corr} , here E_{mean} is the ground state energy in the mean-field approximation, E_{corr} is the correlation energy in the ring RPA approximation. Since the fit of E_{HF} or other mean-field values of the total ground state energies gives the right values for all the coefficients except a_c which is far away from its experimental value zero, we hope that the fit of E_{corr} to the same formula gives an a_c about the same magnitude as that of the fit of E_{mean} but with an opposite sign and all other coefficients to be small compared with their corresponding values in the fit of E_{mean} . In order to have fewer coefficients to be fitted, we have used a set of imaginary nuclei with $N = Z$ and with Coulomb interaction turned off. Then we only have the volume term, surface term, and curvature term to fit. The extracted curvature energy coefficient a_c indeed has the right order of magnitude and sign.

2.2 RPA Formalism of Correlation Energy

The formula to sum up all the ring diagrams is derived in many textbooks, e.g [5]. Because of the finite sizes of the nuclei, we will use the coordinate representation of the RPA theory. In this representation, the formula for the correlation energy is given by

$$\begin{aligned} E_{corr} &= \frac{1}{2}i \int_0^1 \frac{d\lambda}{\lambda} d^3x d^3x' \frac{d\omega}{2\pi} \sum_{n=3}^{\infty} (\lambda V G^0)^n \\ &= \frac{1}{2}i \int_0^1 \frac{d\lambda}{\lambda} d^3x d^3x' \frac{d\omega}{2\pi} (\lambda V G^0)^3 \frac{1}{1 - \lambda V G^0} \end{aligned}$$

$$= \frac{1}{2}i \int_0^1 \frac{d\lambda}{\lambda} d^3x d^3x' \frac{d\omega}{2\pi} (\lambda V G^0)^2 \lambda V G_\lambda^{RPA}, \quad (2.1)$$

with the RPA Green's function given by

$$G_\lambda^{RPA} = G^0 \frac{1}{1 - \lambda V G^0}. \quad (2.2)$$

Note that the second order ring diagram is not included in the summation, since it is already taken into account in the effective interaction in the usual mean-field calculations. Also as it is usually done, we make an angular momenta decomposition of G^0 and V , this procedure permits RPA to be calculated from independent radial equations for each multipole, and also permits the E_{corr} to be calculated for each multipole [7]. The following defines the multipolar interaction V_L and Green's function G_L^0 ,

$$\begin{aligned} V(\mathbf{r}, \mathbf{r}') &= \sum_{LM} V_L(r, r') Y_{LM}^*(\hat{r}) Y_{LM}(\hat{r}'), \\ G^0(\mathbf{r}, \mathbf{r}') &= \sum_{LM} G_L^0(r, r') Y_{LM}^*(\hat{r}) Y_{LM}(\hat{r}') / (rr')^2. \end{aligned}$$

Then the correlation energy is calculated as the sum of that of each multipole,

$$E_{corr} = \sum_{L=0}^{L_{max}} (2L+1) E_{corr}^L. \quad (2.3)$$

Here L_{max} is the maximum multipole which is included in the summation, E_{corr}^L is the correlation energy corresponding to each multipole L and is given by

$$E_{corr}^L = \frac{1}{2}i \int_0^1 \frac{d\lambda}{\lambda} dr dr' \frac{d\omega}{2\pi} (\lambda V_L G_L^0)^2 \lambda V_L G_L^{RPA}, \quad (2.4)$$

where

$$G_L^{RPA} = G_L^0 \frac{1}{1 - \lambda V_L G_L^0}. \quad (2.5)$$

G_L^{RPA} is usually found by matrix inversion if we treat both $G_L(r, r')$ and $V_L(r, r')$ as matrices in coordinate space. In the following, we will assume that the multipolar interaction V_L is of separable form [6]

$$V_L(r, r') = \alpha \frac{dv(r)}{dr} \frac{dv(r')}{dr'} = \alpha f(r)f(r'), \quad (2.6)$$

where v is the central part of the Wood-Saxon potential. The coefficient α is constrained by requiring G_L^{RPA} to have a pole at $\omega = 0$ for $L=1$, the spurious state. In the case of separable interaction, G_L^{RPA} can be found analytically and therefore the integration over λ can be done analytically, this amounts to an enormous saving of computational time.

Note that G^{RPA} satisfies a Dyson-like equation

$$G^{RPA} = G^0 + G^0 V G^{RPA}. \quad (2.7)$$

For each multipole, we have

$$G_L^{RPA}(r, r') = G_L^0(r, r') + \alpha \int G_L^0(r, r_1) f(r_1) dr_1 \int dr_2 f(r_2) G_L^{RPA}(r_2, r'). \quad (2.8)$$

If we now multiply $f(r)$ on both sides and integrate over r , we would get

$$\int dr f(r) G_L^{RPA}(r, r') = \frac{\int dr f(r) G_L^0(r, r')}{1 - \alpha \int f(r_1) G_L^0(r_1, r_2) f(r_2) dr_1 dr_2}. \quad (2.9)$$

Therefore G_L^{RPA} is given by

$$G_L^{RPA}(r, r') = G_L^0(r, r') + \frac{\alpha \int G_L^0(r, r_1) f(r_1) dr_1 \int dr_2 f(r_2) G_L^0(r_2, r')}{1 - \alpha \int f(r_1) G_L^0(r_1, r_2) f(r_2) dr_1 dr_2}. \quad (2.10)$$

If isospin is included, G_L^{RPA} , G_L^0 and V_L become 2×2 matrices. A similar argument leads to

$$G_L^{RPA} = G_L^0 + G_L', \quad (2.11)$$

$$G_L^0(r, r') = \Pi^0(r, r') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (2.12)$$

$$G_L'(r, r') = \frac{1}{1 - 2\alpha a} \alpha \int \Pi^0(r, r_1) f(r_1) dr_1 \int dr_2 f(r_2) \Pi^0(r_2, r') \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad (2.13)$$

$$a = \int f(r) \Pi^0(r, r') f(r') dr dr'. \quad (2.14)$$

Here $\Pi^0(r, r')$ is the free ph Green's functions for protons and neutrons (in our case, since $N = Z$ and the Coulomb interaction is turned off, it is the same for both protons and neutrons), so it can be factored out in front of the matrices. From the condition that G_L^{RPA} has a pole at $\omega = 0$ for $L = 1$, we have

$$\alpha = 1/2a \text{ at } \omega = 0 \text{ } L = 1. \quad (2.15)$$

Finally the correlation energy is given by

$$\begin{aligned} E_{corr}^L &= Tr \left(\frac{1}{2} i \int_0^1 \frac{d\lambda}{\lambda} dr dr' \frac{\omega}{2\pi} (\lambda V_L G_L^0)^2 \lambda V_L G_L^{RPA} \right) \\ &= 4i \int_0^1 \frac{(\lambda \alpha a)^3}{1 - 2\lambda \alpha a} \frac{\omega}{2\pi}. \end{aligned} \quad (2.16)$$

Here Tr is the trace of the matrix. After the integration over λ is done, the final result is quite simple,

$$E_{corr}^L = -i \int \frac{d\omega}{2\pi} [2(\alpha a)^2 + 2(\alpha a) + clog(1 - 2(\alpha a))], \quad (2.17)$$

$clog$ is the complex natural logarithm. Of course the energy is real, and we should take the real part of equation 2.17.

2.3 Numerical Details and Results

In our calculation, the single particle spectra and wave functions are obtained by solving the Schrodinger equation using the Wood-Saxon potential. In order to be

able to treat the open-shell nuclei, we have included pairing and occupation numbers for the open-shell levels in our calculation, the corresponding formulas for the Green's function are given by Migdal [8]. We have chosen the empirical value of the gap parameter $\Delta = 12A^{-1/2}$ for all the open-shell levels, and $\Delta = 0$ for the fully occupied levels. The occupation numbers for the open-shell are calculated from the BCS equation,

$$v_k^2 = \frac{1}{2} \left(1 - \frac{\epsilon_\lambda - \epsilon_f}{\sqrt{(\epsilon_\lambda - \epsilon_f)^2 + \Delta_\lambda^2}} \right). \quad (2.18)$$

The Fermi energy ϵ_f is of course determined by

$$2 \sum_{k>0} v_k^2 = N, \quad (2.19)$$

N is the number of particles in the open shell and $N = 0$ for magic nuclei. The separable potential has the same weight for all multipoles. But there must be a cutoff at the high momenta. A natural cutoff for L_{max} would be around $k_f R$, this turns out to be around $2A^{1/3}$. Since $2A^{1/3}$ is seldom an integer, we take the nearest integer larger than $2A^{1/3}$. We further assume a Fermi-type weight function $(1 + e^{(L-L_0)/L_1})^{-1}$ with $L_0 = 1.2A^{1/3}$ for each multipole. For the integration over ω , we have integrated from $\omega = 0$ to $\omega = 200$ MeV with step size 0.5 MeV. The calculated energies and the least-square fitted coefficients along with their variance σ^2 of magic number nuclei with different choice of L_1 are shown in tables 2.1 and 2.2, and those of open-shell nuclei are shown in tables 2.3 and 2.4.

2.4 Summary and Conclusion

The macroscopic part of standard nuclear mass formulas comes from an expansion of nuclear energy on powers of $A^{1/3}$. Such an approach is based on the geometry

of the nucleus, which consists of a bulk part separated from a thin skin, and is not associated with approximations like HF, ETF, which however have been used to reproduce empirical mass–formula coefficients. Direct adjustment of mass–formula coefficients to ground state masses of nuclei yields values of the curvature coefficient a_c close to zero, whereas values of a_c resulting from mean–field calculations are always close to 10 MeV. We have pointed out in this short chapter that E_{corr} has a very different A –dependent behavior from that of the mean–field total ground state energy E_{mean} and that there is still room to account for the apparent discrepancy if higher corrections to the mean–field calculation is taken into account.

Table 2.1: Correlation energies divided by $A^{1/3}$ for magic number nuclei with $L_1 = 1, 2, 3$

$N = Z$	$E/A^{1/3} (L_1=1)$	$E/A^{1/3} (L_1=2)$	$E/A^{1/3} (L_1=3)$
8	-3.1120	-2.9525	-2.8785
20	-3.9128	-3.7988	-3.7343
28	-3.6554	-3.6105	-3.5724
50	-3.9785	-3.9963	-3.9989
82	-4.7833	-4.7949	-4.7881
126	-6.0657	-6.0786	-6.0864

Table 2.2: The least-square fitted coefficients of $E_{corr}/A^{1/3}$ to the formula $E_{corr}/A^{1/3} = a_c + a_s A^{1/3} + a_v A^{2/3}$, a_c is the curvature coefficient.

L_1	a_c	a_s	a_v	σ^2
1	-4.2535	0.8008	-0.1690	0.590E-1
2	-3.6783	0.5965	-0.1514	0.513E-1
3	-3.4686	0.5345	-0.1471	0.475E-1

Table 2.3: Correlation energies divided by $A^{1/3}$ for open-shell nuclei with $L_1 = 1, 2, 3$

N = Z	$E/A^{1/3} (L_1=1)$	$E/A^{1/3} (L_1=2)$	$E/A^{1/3} (L_1=3)$
18	-5.1386	-4.9301	-4.8263
22	-5.1053	-4.9685	-4.8997
30	-5.7112	-5.4141	-5.3198
48	-5.1914	-5.1599	-5.1360
52	-5.4939	-5.4422	-5.4045
80	-5.8130	-5.7859	-5.7556
84	-5.8491	-5.8521	-5.8565
122	-6.7240	-6.6967	-6.6769
124	-6.5299	-6.5247	-6.5203

Table 2.4: The least-square fitted coefficients of $E_{corr}/A^{1/3}$ to the formula $E_{corr}/A^{1/3} = a_c + a_s A^{1/3} + a_v A^{2/3}$, a_c is the curvature coefficient.

L_1	a_c	a_s	a_v	σ^2
1	-7.7925	1.4116	-0.1945	0.413E-1
2	-6.7973	1.0972	-0.1695	0.215E-1
3	-6.3635	0.9599	-0.1584	0.182E-1

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Chapter 3

Collective Electronic Excitations in Fullerenes

The large number of active electrons in a carbon cluster and the strong Coulomb interaction among them lead to a rich spectrum of collective states. States with total angular momentum up to $L = 8\hbar$ have a strong collective character. The equivalents of both π and σ plasmons in graphite are predicted for a whole range of carbon clusters $C_{20, 60, 70, 100}$. The theoretical results compare very well with experimental photoexcitation results in $C_{60, 70}$ and EELS data on gas targets $C_{60, 70}$.

3.1 Introduction

The discovery of C_{60} cluster and the successful synthesis of macroscopic quantities of C_{60} crystal have spurred a flurry of activity in the study of properties of both C_{60} cluster and other fullerene carbon clusters [1]. Since these fullerenes are essentially hollow graphite shells, they should support multipolar plasmon oscillations, closely related to the plasmons in graphite. Indeed, the existence of the giant dipole plasmon mode in C_{60} was first predicted [2, 3] and then an independent photoionization experiment on a C_{60} gas target [4] confirmed its presence.

The presence of the strong collective dipole plasmon in C_{60} suggests the existence of other multipolar excitations and the multipolar collective excitations in other fullerenes as well. In this chapter we shall present an analysis of the collective excitations in C_{20} , C_{60} , C_{70} and C_{100} and compare our predictions with available experimental results on isolated fullerenes (gas targets). The dipole excitations are put into evidence by photoionization experiments [4] and the other multipole excitations are evidenced by EELS experiments [5, 6, 7].

We should mention that there is a multitude of experimental results, concerning plasmon excitation in pure solid C_{60} targets and doped solid C_{60} as well [8, 9, 10]. The main difference between the plasmons in isolated fullerenes and fullerites [8, 9, 10] and graphite and diamond [11, 12, 13] is mostly an upward shift of the σ plasmon in fullerites, by approximately 8 eV or more, because of the strong long range Coulomb interaction between electrons belonging to different neighboring molecules. At the same time, the properties of the π plasmon seem to be affected little by the presence of other molecules.

3.2 Theoretical Description

We use the linear response theory (Random Phase Approximation – RPA), which is the most appropriate theory for large systems with mobile electrons where screening is significant, to describe the excitation of plasmon-like collective states in these fullerenes. We determine the single-particle wave functions and energy levels using a tight-binding (TB) Hamiltonian, which has been used to study the relative stability of different carbon cluster structures [14] and the multipole response functions of fullerenes [2, 5, 7].

3.2.1 Description of the Tight-binding Hamiltonian

The tight-binding Hamiltonian, which considers only the s and p valence electrons of carbon, is given by [14]

$$H = \sum_{\alpha,i} \epsilon_{\alpha} a_{\alpha,i}^{\dagger} a_{\alpha,i} + \sum_{\alpha,\beta,i,j} t_{\alpha\beta}(r_{ij}) a_{\alpha,i}^{\dagger} a_{\beta,j} . \quad (3.1)$$

Here, i labels the atomic sites and $\alpha = s, p_x, p_y, p_z$ labels the atomic orbitals. ϵ_{α} is the orbital energy, and $t_{\alpha\beta}$ are the hopping matrix elements between different sites. The parameters have been obtained from a global fit to Local Density Approximation (LDA) [15, 16] calculations of the electronic structure of C_2 , a graphite monolayer, and bulk diamond, for different nearest-neighbor distances [14], similar to what had been done previously to describe silicon clusters [17]. The diagonal elements of this Hamiltonian are the energy levels $\epsilon_s = -7.3$ eV and $\epsilon_p = 0.0$ eV. The off-diagonal matrix elements $t_{\alpha\beta}(r)$ are assumed to have a distance dependence $\sim r^{-2}$. Their values at $r = 1.546$ Å, which is the equilibrium nearest-neighbor distance in diamond, are $V_{ss\sigma} = -3.63$ eV, $V_{sp\sigma} = 4.20$ eV, $V_{pp\sigma} = 5.38$ eV, and $V_{pp\pi} = -2.24$ eV in the Slater-Koster parameterization [18]. In this Hamiltonian, we consider those atoms as nearest neighbors which are closer than the cutoff distance $r_c = 1.67$ Å. This is the average of the nearest- and second nearest-neighbor distances in bulk diamond, and hence near the minimum of the radial distribution function.

The equilibrium nearest-neighbor distance between carbon atoms in C_{60} is 1.453 Å on pentagons (“single bonds”) and 1.369 Å between pentagons (“double bonds”) [2], corresponding to a buckyball of radius $R \approx 3.5$ Å. The spectrum of C_{60} obtained using this tight-binding Hamiltonian is shown in fig. 3.1. This spectrum is in good agreement with previous *ab initio* calculations. The total width of the occupied band is 19.1 eV, to be compared with the LDA values of 18.8 eV of ref. [19]. The level ordering near the Fermi level agrees with results based on the LDA and other methods

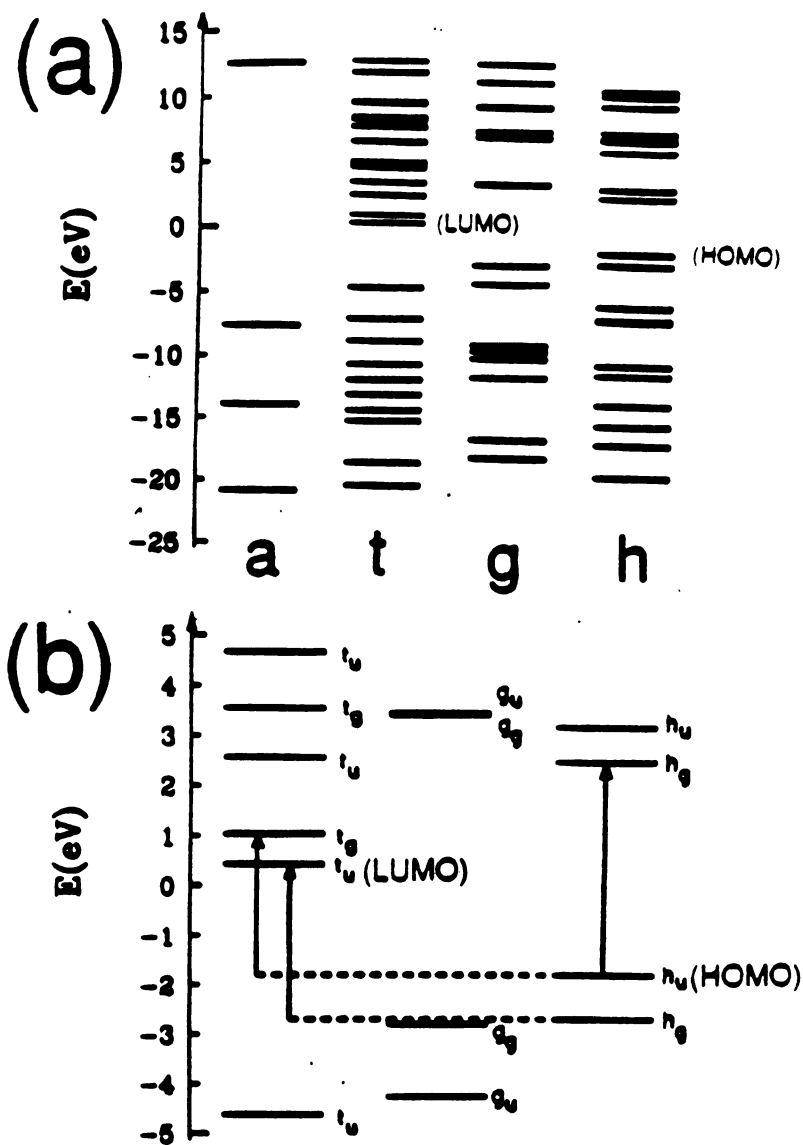


Figure 3.1: (a) Tight-binding Single-particle energy level spectrum of a C_{60} cluster. The levels have been sorted by symmetry. (b) Expanded region of the energy level spectrum near the Fermi level. Allowed dipole transitions between states with gerade (g) and ungerade (u) parity are shown by arrows [From G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. **67**, 2690 (1991)].

[19, 20, 21, 8, 23]. The gap 2.2 eV between the highest occupied (HOMO) and lowest unoccupied (LOMO) level compares well with the LDA values of 1.8 eV from [19] and the experimental value [8] of 1.9 eV.

The HOMO to LOMO transition is forbidden by parity, and the lowest optically allowed transitions are $H_u \rightarrow T_{1g}$, $H_g \rightarrow T_{1u}$, and $H_u \rightarrow H_g$, with the tight-binding excitations energies of 2.8 eV, 3.1 eV, and 4.3 eV. These results compare well with the LDA values 2.9 eV, 3.1 eV, and 4.1 eV [19].

3.2.2 Linear Response Theory of the Tight-binding Hamiltonian

The free particle-hole propagator in the energy representation is defined by

$$G_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{p,h} \frac{\langle \mathbf{r} | ph \rangle 2(\varepsilon_p - \varepsilon_h) \langle ph | \mathbf{r}' \rangle}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2}, \quad (3.2)$$

where p and h denote particle and hole states, $\varepsilon_{p,h}$ their corresponding energies, ω the excitation energy and η is an imaginary part.

The TB single-particle wave functions have the following structure

$$\psi_n(\mathbf{r}) = \sum_i \left[f_n(\mathbf{R}_i) \frac{1}{\sqrt{4\pi}} \phi_0(r_i) + \mathbf{g}_n(\mathbf{R}_i) \cdot \hat{\mathbf{r}}_i \sqrt{\frac{3}{4\pi}} \phi_1(r_i) \right], \quad (3.3)$$

where n denotes either a hole state or a particle state, $\mathbf{r}$ is the electron coordinate, $\mathbf{R}_i$ are the carbon ion positions, $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_i$, the summation is over the carbon sites, $\phi_{0,1}(r)$ are the LDA carbon $2s$ - and $2p$ - electron wave functions. $f_n(\mathbf{R}_i)$ and $\mathbf{g}_n(\mathbf{R}_i)$ are the amplitudes to find an electron at site i either in the $2s$ -state or in one of the three $2p$ -states. The particle-hole state then reads

$$\begin{aligned} \langle \mathbf{r} | ph \rangle = & \sqrt{\frac{1}{4\pi}} \sum_i \left[f_p(\mathbf{R}_i) f_h(\mathbf{R}_i) \phi_0^2(r_i) + \mathbf{g}_p(\mathbf{R}_i) \cdot \mathbf{g}_h(\mathbf{R}_i) \phi_1^2(r_i) \right] Y_{00}(\hat{\mathbf{r}}_i) + \\ & \sqrt{\frac{1}{4\pi}} \sum_{im} (-1)^m \left[f_p(\mathbf{R}_i) g_{h,-m}(\mathbf{R}_i) + f_h(\mathbf{R}_i) g_{p,-m}(\mathbf{R}_i) \right] \phi_0(r_i) \phi_1(r_i) Y_{1m}(\hat{\mathbf{r}}_i) + \end{aligned}$$

$$\sqrt{\frac{3}{10\pi}} \sum_{im} (-1)^m [\mathbf{g}_p(\mathbf{R}_i) \times \mathbf{g}_h(\mathbf{R}_i)]_{2,-m} \phi_1^2(r_i) Y_{2m}(\hat{\mathbf{r}}_i). \quad (3.4)$$

In the above formulas we have used interchangeably Cartesian and spherical notations.

The Random Phase Approximation (RPA) Green's function is determined as the solution of the integral equation $G = G_0 - G_0 V G$, where $V = e^2/|\mathbf{r} - \mathbf{r}'|$ is the Coulomb interaction among electrons. The matrix elements of the Coulomb interaction are computed through its Fourier representation

$$V = \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_l + \mathbf{R}_k - \mathbf{R}_l|} = \frac{e^2}{2\pi^2} \int d^3q \frac{1}{q^2} \exp[i\mathbf{q} \cdot (\mathbf{r}_k - \mathbf{r}_l + \mathbf{R}_k - \mathbf{R}_l)], \quad (3.5)$$

where $\mathbf{r}_{k,l}$ are the electron coordinates with respect to sites k, l and $\mathbf{R}_{k,l}$ are the coordinates of the corresponding carbon ions. The response function (transition strength) of the system to a weak external one-particle multipolar field $F(\mathbf{r})$ is given by $S = \text{Im} \langle F | G | F \rangle / \pi$.

In computing the matrix elements of the residual Coulomb interaction arising from the $l = 0$ transitions in Ref. [2] for the dipole response, it was assumed that the spatial extent of the s - and p -states is vanishingly small, this approximation results in a slight overestimate of the Coulomb matrix elements. Another approximation in ref. [2] was to neglect the $l = 2$ component in the particle-hole state $|ph\rangle$ (see eq. (3.4)) resulting from a p -hole state to a p -particle state transition. These approximations make their approach unsuitable to study other multipolar responses and also the multipolar responses of other nonspherical fullerenes. The present calculations are performed without these approximations.

Since only dipole excitation is optically allowed, one can put into evidence higher multipole plasmons in an inelastic electron scattering experiment. In the Born approximation the differential cross section of electron scattering is [24]

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{e^2 m}{\hbar^2} \right)^2 \frac{4p'}{pq^4} \sum_n | \langle n | \exp(-i\mathbf{q} \cdot \mathbf{r}) | 0 \rangle |^2 \delta(E_n - E_0 - \omega)$$

$$= \left(\frac{e^2 m}{\hbar^2} \right)^2 \frac{4p'}{pq^4} S(\omega, \mathbf{q}), \quad (3.6)$$

where p and p' are the initial and final linear momenta of the electron, $\mathbf{q} = \mathbf{p} - \mathbf{p}'$ is the transferred linear momentum, m the mass of the electron, ω the energy of the excited state and $S(\omega, \mathbf{q})$ the spectral function of the cluster, which depends solely on the properties of the cluster.

In the following two subsections, we will outline the application of the RPA theory of a tight-binding Hamiltonian to a spherical cluster (C_{60}) and nonspherical clusters ($C_{20}, 70, 100$). The detailed treatment of C_{60} is given in Appendix A, and that of other nonspherical clusters in Appendix B.

3.2.3 Outlines of the Calculations of C_{60}

The treatment of C_{60} is relatively simple. Because C_{60} has nearly perfect spherical symmetry, good angular momentum quantum numbers can be introduced [2, 5, 7], and the the RPA equation is solved for each multipole (see Appendix A). The total angular momentum of a ph -state (see eq. (3.4)) has two components $\mathbf{L}$ and $\mathbf{l}$, i.e. $\mathbf{J} = \mathbf{L} + \mathbf{l}$, where $\mathbf{L}$ comes from the $f_n(\mathbf{R}_i)$ and $\mathbf{g}_n(\mathbf{R}_i)$ amplitudes alone and $\mathbf{l}$ from the transitions on each site: $l = 0$ from $s \rightarrow s$ and $p \rightarrow p$; $l = 1$ from $s \rightarrow p$ and $p \rightarrow s$; $l = 2$ from $p \rightarrow p$. The three terms of the ph -wave function correspond to $l = 0$, $l = 1$ and $l = 2$ transitions on each site. Since we will be concerned with natural parity states only and the spin variables merely double the number of available states, the following selection rule applies $(-1)^{J+L+l} = 1$. As a result for $J \geq 2$ only the following (L, l) configurations are allowed: $(J, 0)^2, (J - 1, 1), (J + 1, 1), (J - 2, 2), (J, 2)$ and $(J + 2, 2)$. For $J = 0$: $(0, 0)^2, (1, 1)$ and $(2, 2)$ and for $J = 1$: $(1, 0)^2, (0, 1), (2, 1), (1, 2)$ and $(3, 2)$ are allowed. The two $(J, 0)$ configurations arise from two $l = 0$ types of transitions, see eq. (3.4).

Using the expansion of a plane wave into spherical harmonics, we can rewrite the Coulomb interaction eq. (3.5) as

$$\begin{aligned}
 V &= \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2|} = \frac{e^2}{2\pi^2} \int \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2)] dk d\hat{\mathbf{k}} \\
 &= \frac{(4\pi)^3 e^2}{2\pi^2} \int \sum_{LM} i^L j_L(kR_1) Y_{LM}(\hat{\mathbf{R}}_1) Y_{LM}^*(\hat{\mathbf{k}}) \sum_{L'M'} i^{-L'} j_{L'}(kR_2) Y_{L'M'}^*(\hat{\mathbf{R}}_2) \\
 &\quad Y_{L'M'}(\hat{\mathbf{k}}) \sum_{lm} i^l j_l(kr_1) Y_{lm}(\hat{\mathbf{r}}_1) Y_{lm}^*(\hat{\mathbf{k}}) \sum_{l'm'} i^{-l'} j_{l'}(kr_2) Y_{l'm'}^*(\hat{\mathbf{r}}_2) Y_{l'm'}(\hat{\mathbf{k}}) dk d\hat{\mathbf{k}}. \quad (3.7)
 \end{aligned}$$

After the integration over $\mathbf{k}$, $\mathbf{r}_{k,l}$ is done by using the *ph*-wave function eq. (3.4), one can represent the residual Coulomb interaction as a matrix in the representation (L, l) described above. In a similar fashion to Ref. [2], the integral equation $G = G_0 - G_0 V G$ is then reduced to a matrix equation in the (L, l) representation of dimension 4×4 for $J = 0$, 6×6 for $J = 1$, and 7×7 for $J \geq 2$. The resulting matrix equation is solved by matrix inversion. The multipolar responses are obtained by applying the multipolar fields $F(\mathbf{r}) = r^l Y_{lm}(\hat{\mathbf{r}})$ ($F(\mathbf{r}) = r^2 Y_{00}(\hat{\mathbf{r}})$ for $l = 0$).

In the case of spectral function, the external field is the plane wave $\exp(i\mathbf{q} \cdot \mathbf{r})$, here $\mathbf{q} = \mathbf{p} - \mathbf{p}'$ is momenta transfer. It is computed by expanding the plane wave into spherical harmonics and all excited states with angular momentum up to $L = 20$ are included (see Appendix A for details). We have checked that the responses and the spectral function of C_{60} computed either by assuming spherical symmetry (as described here and the details in Appendix A) or by taking into account the actual 3-dimensional ionic configuration of the C_{60} molecule (as described below and the details in the Appendix B), lead to essentially the same results.

3.2.4 Outlines of the Calculations of $C_{20, 70, 100}$

Since these clusters do not have spherical symmetry, good angular momentum quantum numbers can not be introduced for them, and because of that the actual numerical

implementation of the RPA is computationally more demanding (e.g. the calculation of the whole dynamical structure function for C_{60} requires 1–2 hours, while performed in the 3–dimensional manner described here and Appendix B, it requires about 300 hours on a CONVEX–240). To this end, we have formulated the RPA method for arbitrary 3–dimensional structures in the TB approximation and used it to compute (or recompute in the case of C_{60}) the electromagnetic response of isolated fullerenes (the details are given in Appendix B). The matrix elements of the Coulomb interaction are computed through its Fourier representation, but this time instead of treating $\mathbf{R}_1$ and $\mathbf{R}_2$ as two different vectors (as we do in the case of C_{60}), we treat $\mathbf{R}_1 - \mathbf{R}_2$ as one vector, and perform the expansion of the plane wave into spherical harmonics accordingly,

$$\begin{aligned}
 V &= \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2|} = \frac{e^2}{2\pi^2} \int \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2)] dk d\hat{\mathbf{k}} \\
 &= \frac{(4\pi)^3 e^2}{2\pi^2} \int \sum_{lm} i^l j_l(kr_1) Y_{lm}(\hat{\mathbf{r}}_1) Y_{lm}^*(\hat{\mathbf{k}}) \sum_{l'm'} i^{-l'} j_{l'}(kr_2) Y_{l'm'}^*(\hat{\mathbf{r}}_2) Y_{l'm'}(\hat{\mathbf{k}}) \\
 &\quad \sum_{LM} i^L j_L(kR_{12}) Y_{LM}(\hat{\mathbf{R}}_{12}) Y_{LM}^*(\hat{\mathbf{k}}) dk d\hat{\mathbf{k}} \quad (3.8)
 \end{aligned}$$

Instead of solving the RPA equation for each multipole, we solve the whole RPA Green's function $G(\mathbf{r}, \mathbf{r}')$ as a function of $\mathbf{r}$ and $\mathbf{r}'$. Essentially, the integral equation is transformed to a matrix equation in the (lmi) basis after the integration over $\mathbf{k}$, $\mathbf{r}_{k,l}$ is done, here $l = 0, 1, 2$ denotes the particle–hole transitions on each site i and m denotes the corresponding third components of l . There are two terms for $l = 0$ (see eq. (3.4)), three terms for $l = 1$ and five terms for $l = 2$. Therefore there are 10 lm terms for each site i and $10N$ terms in the particle-hole states in the (lmi) basis, where N is the number of atoms in the cluster. A particular multipolar response ¹ is

¹strictly speaking there is no one-to-one correspondence between the multipolarity of the external field and the corresponding one for the excited plasmons, the results presented were averaged over all possible spatial orientations.

obtained by applying a multipolar external field. The spectral function is computed by applying the external field $\exp(i\mathbf{q} \cdot \mathbf{r})$ and averaged over the direction of $\mathbf{q}$, see Appendix B for details.

3.3 Theoretical Results and Comparison with Experimental Data

In figs. 3.2–3.5, we present the computed free (no residual Coulomb interaction among electrons) and the RPA responses of $C_{20, 60, 70, 100}$ clusters to a multipole external field $F(\mathbf{r}) = r^l Y_l(\hat{\mathbf{r}})$, for $l = 0 - 8$ ($F(\mathbf{r}) = r^2$ for $l = 0$). C_{20} has only 12 pentagons, while C_{70} and C_{100} can be obtained basically from a C_{60} molecule, by cutting it into two equal semispheres and joining them by one and four additional carbon rings respectively. We compare our predictions of the photoexcitation probabilities of C_{60} and C_{70} with the measured photoionization spectra [4] in figs. 3.6 and 3.7. One should note the good agreement between our predictions and the experimental data, even the width seems to be well obtained.

It is obvious from these figures that a strong screening is obtained at low energies for all of the multipole responses of all these carbon clusters. Except for the monopole responses in C_{60} and C_{70} , all other multipole responses have a very similar structure, a low-energy mode around 6–10 eV and a high-energy mode around 18–22 eV. These two modes are the obvious analogues of the π and σ plasmons in graphite [11, 12, 13] and the corresponding plasmons seen in solid C_{60} [8, 9, 10]. In both graphite and solid C_{60} the σ plasmon is at a higher energy than it is in an isolated fullerene.

The states with higher angular momenta show no collective behavior or in other words the corresponding multipole responses are single-particle in character. The

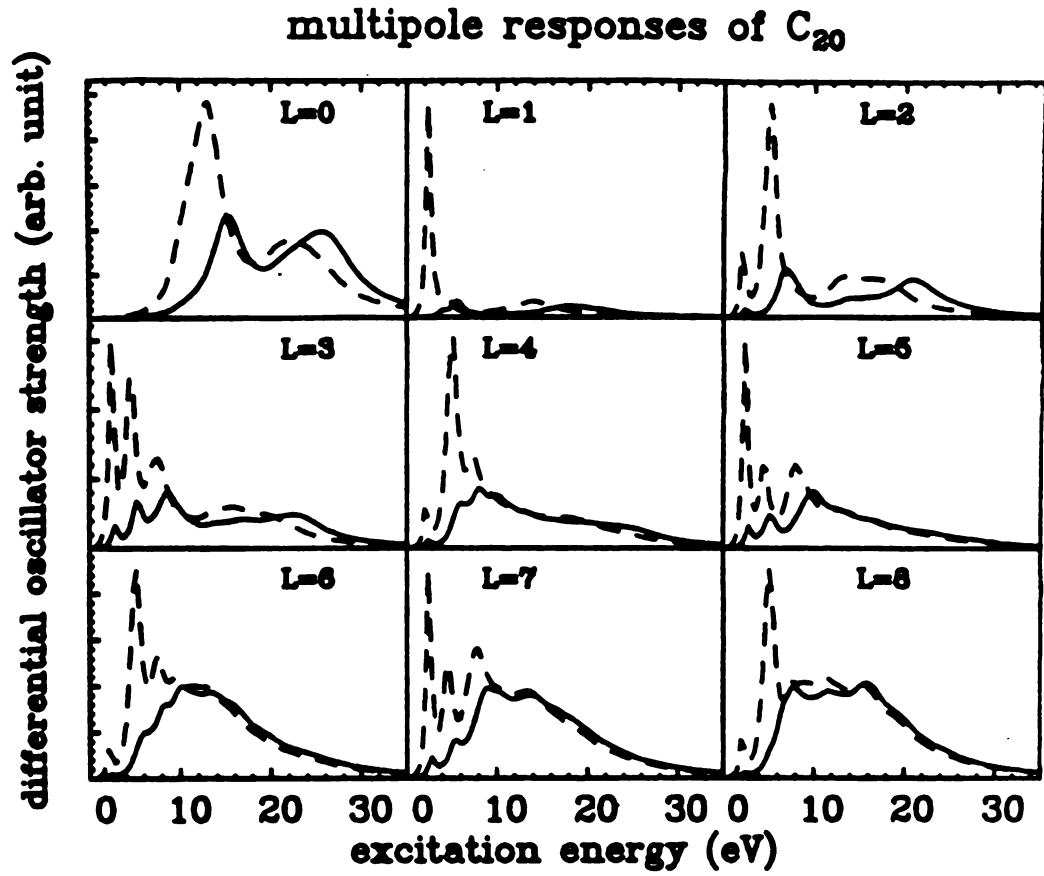


Figure 3.2: Multipolar free (dashed lines) and RPA (solid lines) responses of C_{20}

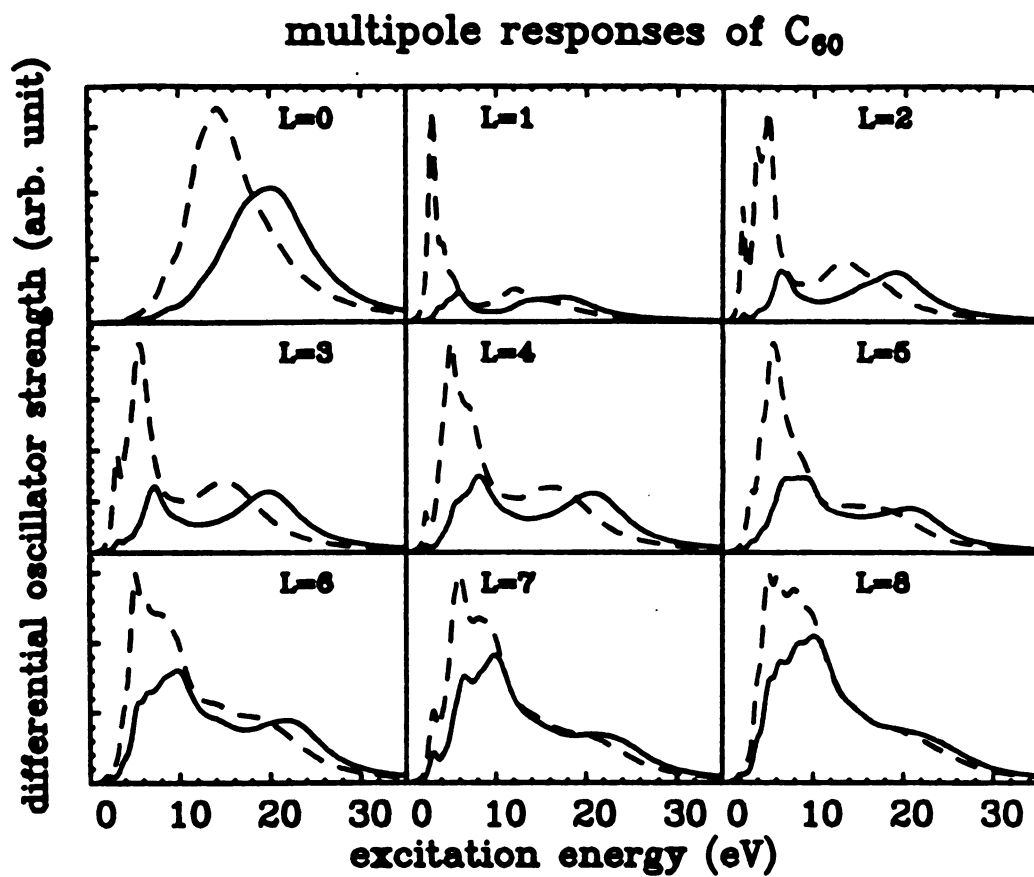


Figure 3.3: Multipolar free (dashed lines) and RPA (solid lines) responses of C_{60}

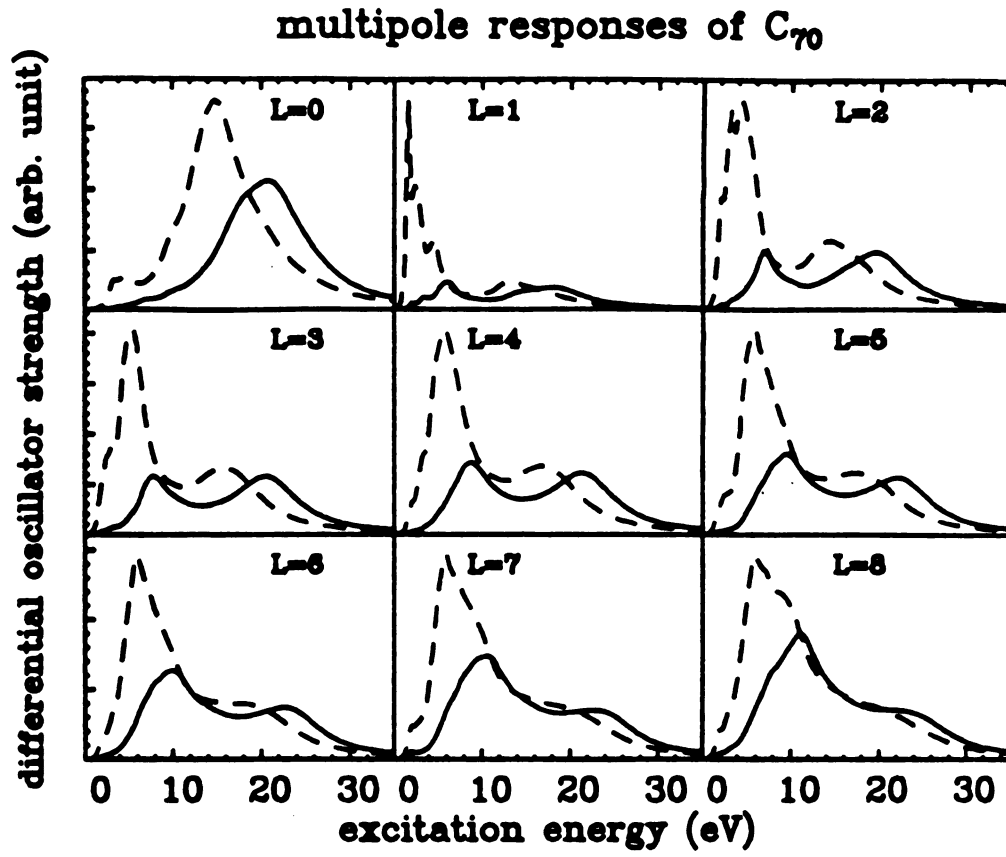


Figure 3.4: Multipolar free (dashed lines) and RPA (solid lines) responses of C_{70}

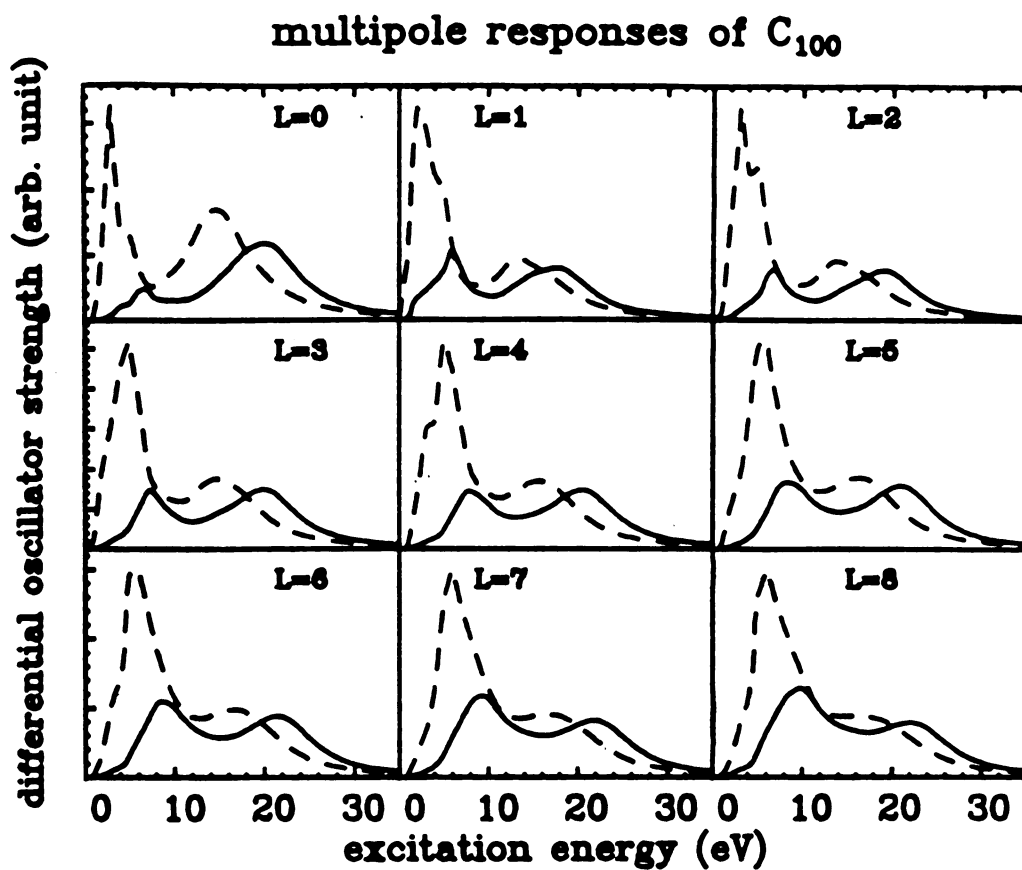


Figure 3.5: Multipolar free (dashed lines) and RPA (solid lines) responses of C_{100}

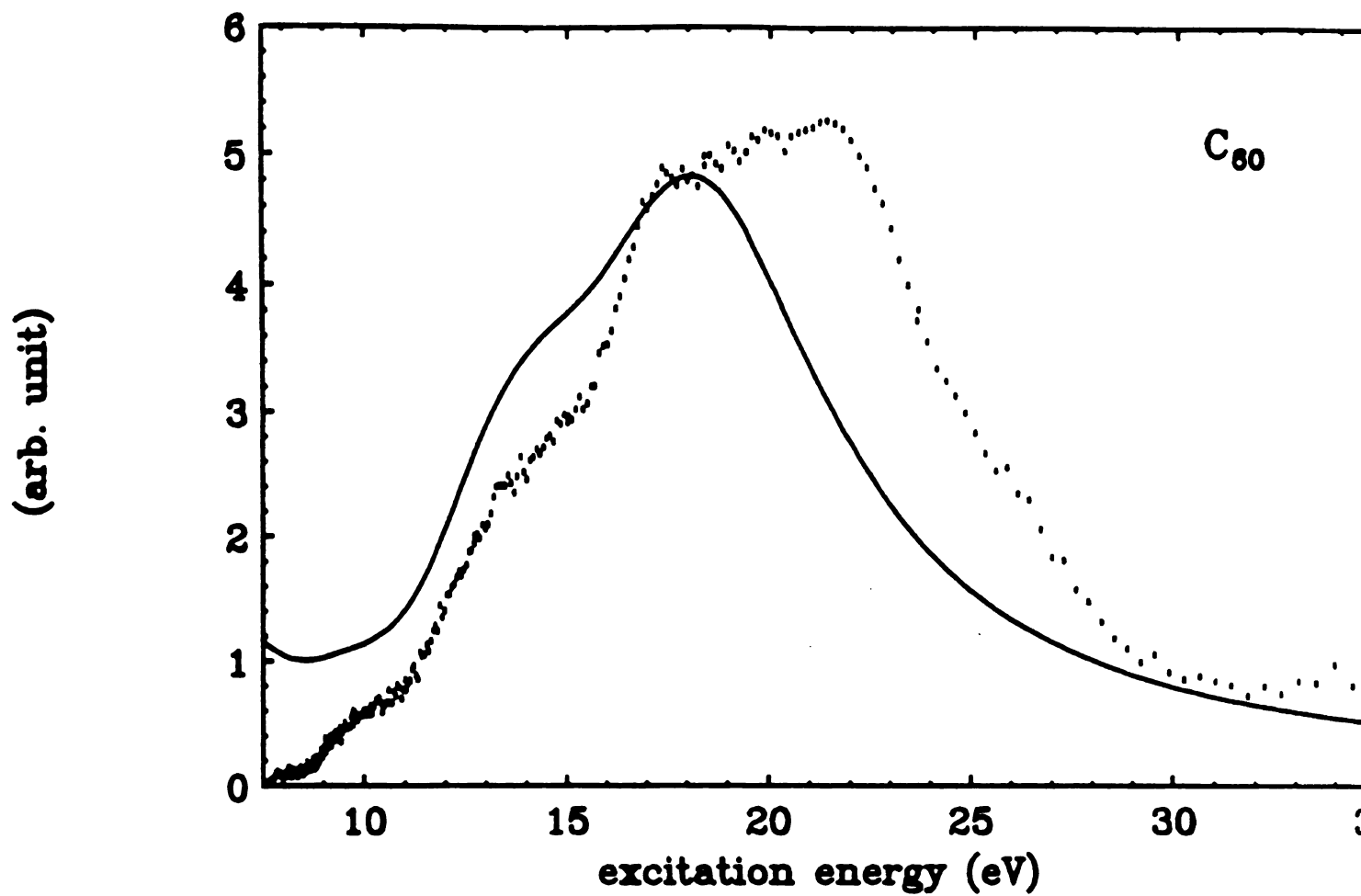


Figure 3.6: Dipole RPA photoexcitation probability (solid line) and measured photoionization cross section (arbitrary units) [4] of C_{60}

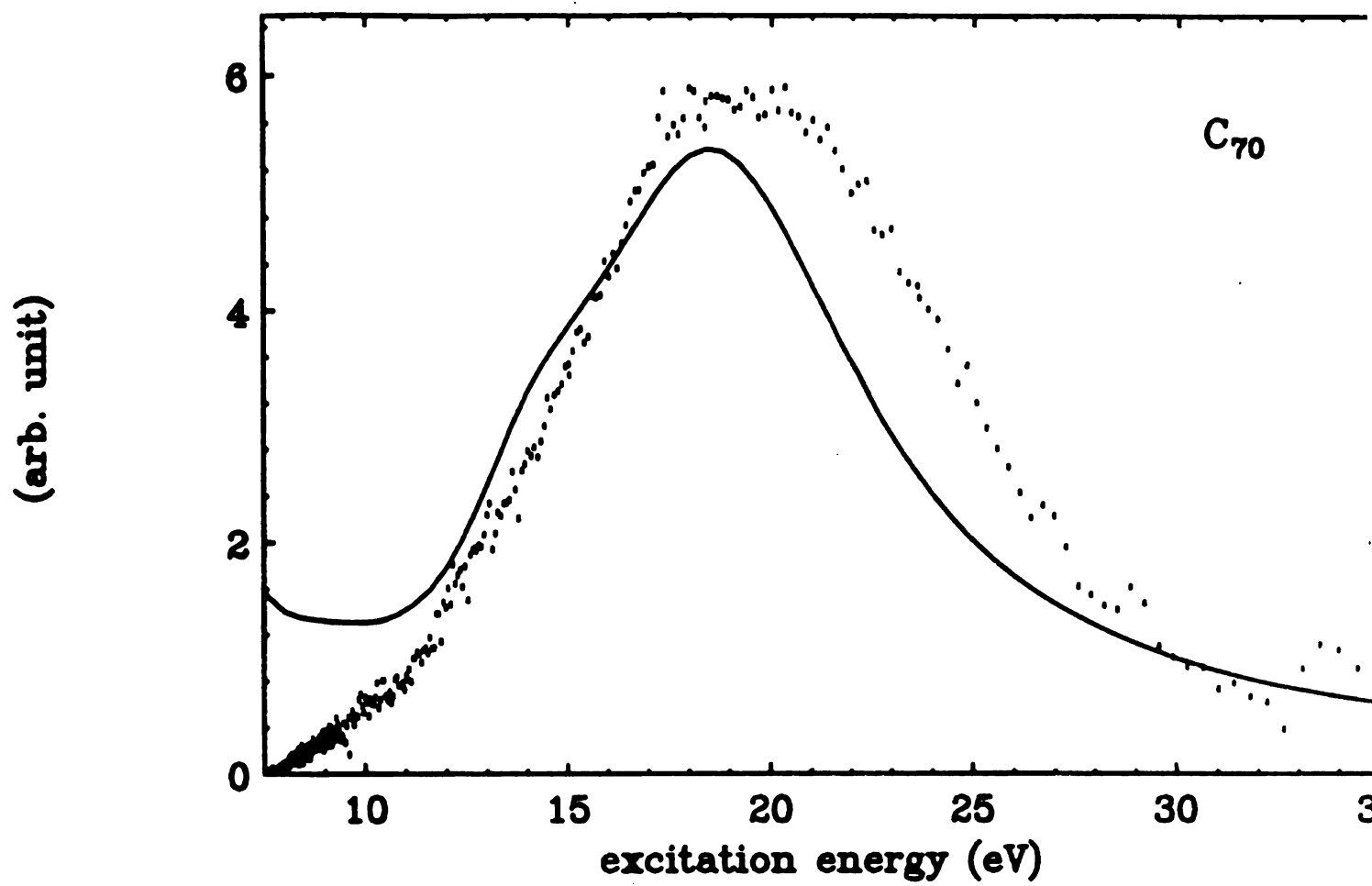


Figure 3.7: Dipole RPA photoexcitation probability (solid line) and measured photoionization cross section (arbitrary units) [4] of C_{70}

physical reason is relatively simple. For these multipoles the wave length of the excitation is comparable with the C–C bond length and no electron collectivity exists at such length scales. Take, for example, C_{60} , the maximum expected multipole of a plasmon $L_{max} = q_{max}R = R\pi/d \approx 8$, where R is the radius of the buckyball, d the C–C bond length and $q_{max} = \pi/d$ is the momentum of the excitation with a half-wave length equal to the C–C bond, compares extremely well with the RPA results in fig. 3.3.

As remarked earlier, one should note that strictly speaking only in C_{60} there is an essentially one-to-one correspondence between the multipolarity of the external field and the corresponding one for the excited plasmons. For other fullerenes, which lack spherical symmetry, the presented results were averaged over all possible spatial orientations of the cluster with respect to the laboratory reference frame (or in other words the orientation of the external field).

Since C_{100} is a rather deformed object and one might expect that one can detect the deformation by observing the splitting of the dipole plasmon. However, as our results show, when one applies the external field either along or perpendicular to the symmetry axis of this cluster, the dipole response changes insignificantly, see figs. 3.8, 3.9, in contradistinction to what one sees for example in deformed nuclei or metallic clusters [25, 26]. To some extent this is surprising. This feature of the plasmon modes in fullerenes simply reflects the specific character of the structure of the single-particle wave functions, which are strongly localized around the ionic shell. The curvature of the shell is less important than the π or σ character of the single particle wave functions, and therefore of the corresponding plasmon modes.

Recently [27], the energies and oscillator strengths for a number of allowed dipole transitions have been measured for C_{60} in solution. A comparison between the calcu-

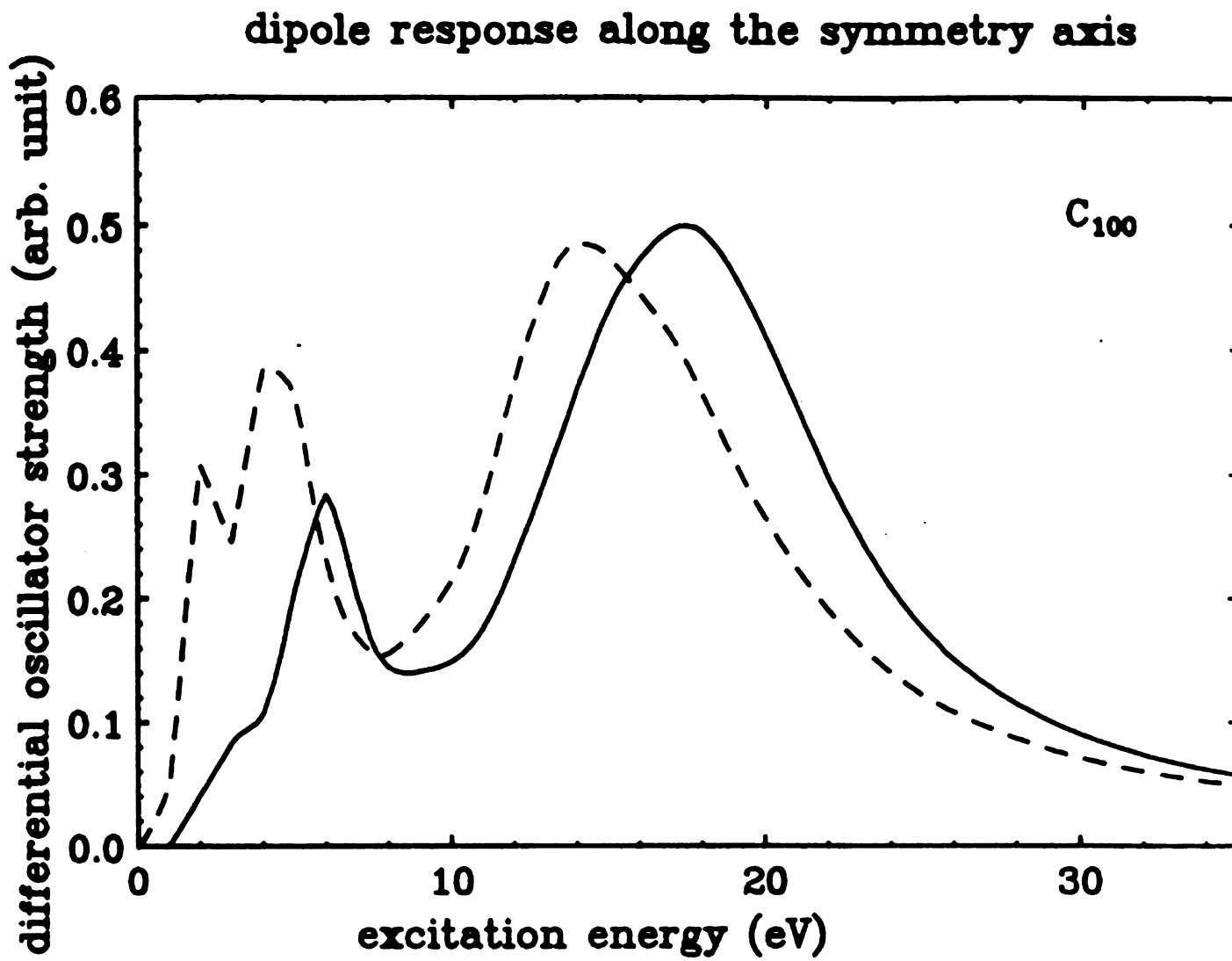


Figure 3.8: RPA (solid line) and free (dashed line) dipole response of C_{100} when the external field is along the symmetry axis.

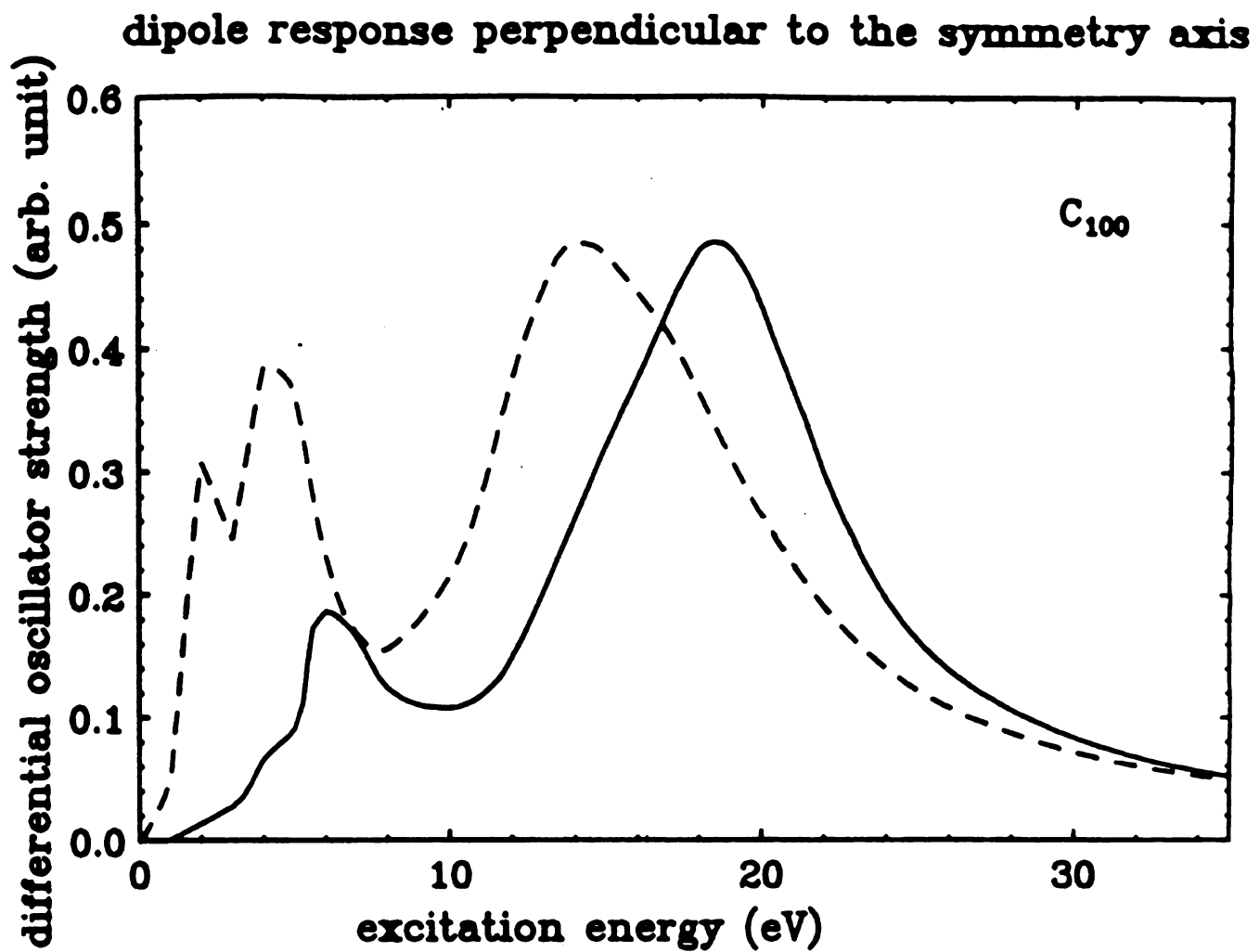


Figure 3.9: RPA (solid line) and free (dashed line) dipole response of C₁₀₀ when the external field is perpendicular to the symmetry axis.

Table 3.1: The free and RPA dipole response of C_{60} (energies and oscillator strengths), computed using two different tight-binding (TB) parameterizations [14, 29] compared to the calculations of Ref. [28] and experimental results [27]. A * next to a transition means that several close in energy levels have been represented as one. A + sign means that the oscillator strengths of the two or three consecutive levels have been added. The measured oscillator strength for the 3.04 eV transition is 0.015 ± 0.005 . The last row is the sum of the oscillator strengths quoted in the table.

Free TB [14]		RPA TB [14]		Free TB [29]		RPA TB [29]		Ref. [28]		Ref. [27]	
eV	f	eV	f	eV	f	eV	f	eV	f	eV	f
2.88	4.04	2.94	0.027	2.6	3.5	2.68	0.015	3.4	0.08	3.04	0.015
3.12	6.09	3.74	0.66	2.82	5.41	3.37	0.43	4.06	0.41	3.30	
4.28	3.95	4.78	1.37	3.84	4.01	4.39	1.24	4.38	2.37	3.78	0.37
5.20+		5.22+				4.83	0.029	4.70+		4.06+	
5.26+		5.28+	0.64	4.93	2.70	5.17	0.44	5.07+	0.30	4.35+	0.10
5.37+	2.88	5.69	1.15	5.38*	1.36	5.32	0.13	5.24	7.88	4.84	2.27
5.86		5.94	0.21	6.03	0.35	5.47	0.12	5.54	0.22	5.46	0.22
5.97+	0.86	6.13	2.48	6.31	0.24	5.80*	2.86	5.78	10.74	5.88	3.09
6.73		6.26	0.50			6.14	1.64	6.28		6.36	
		6.76	0.40			6.40	1.99				
		6.90	0.15								
	17.82		7.49		17.57		8.90		22.00		6.07

lated free and RPA predictions, using two different parameterizations for the tight-binding Hamiltonian, the calculations of Ref. [28] and experimental results of Ref. [27] are presented in the Table 3.1. Even though a detailed correspondence between computed and measured transitions cannot be established yet, the significant dynamical screening emerging from the RPA description compares very well with the observed transition strengths, including the large suppression of the first allowed dipole transition. It is unclear to us however, to what extent the computed properties of an isolated C_{60} cluster are related to absorption spectra of C_{60} in solution. A measurement of the gas form will be highly desirable. The static polarizability of a buckyball, $\alpha_{Free} = 195$ and 207 and $\alpha_{RPA} = 56$ and 57 using parameterizations [14, 29] respectively, shows the same order of rather strong screening.

The dynamical structure factors for C_{60} and C_{70} are represented in figs. 3.10 and 3.11. One can see that they are very similar, there are two “mountains”, one at an excitation energy around 6–10 eV and a second one around 18–22 eV, corresponding to the π and σ plasmons respectively and their corresponding energies increase monotonically with the increase of the transferred linear momentum. The profile of the spectral function in the q direction is rather structureless, due to the fact that states with different angular momenta are very close in energy. The dispersion laws for the π and σ plasmons, inferred from the profile of $S(\omega, \mathbf{q})$ ($\omega_\pi \approx 6 + q^2$ and $\omega_\sigma \approx 18 + 2q$, when energy and momentum is in eV and $\text{\AA}^{-1}$ respectively), are rather distinct from classical estimates for a charged spherical shell [31]. The maxima of the spectral function are at transferred momenta $\approx 1.5\text{--}2 \text{ \AA}^{-1}$, indicative at the fact that states with $L \approx qR \approx 5\text{--}7$ are mainly excited in this process. The σ plasmon always has a higher intensity. At relatively high transferred linear momenta we do not expect these computed dynamical structure factors to be very reliable though, because of

the limited TB Hilbert space we have used, but on the other hand we do not expect a significant collectivization of the transition strength either when the transferred momentum becomes comparable with π/d , where d is the C-C bond length.

In figs. 3.12 and 3.13, we compare the RPA predictions for the excitation of the plasmon modes in C_{60} and C_{70} with recent EELS experimental results on a gas target at an incident electron energy of 1 keV and at 1.5 deg for C_{60} and 1 keV and at 2.0 deg for C_{70} [5, 6, 7] .

The linear transferred momentum in the C_{60} experiment is $\approx 0.41 \text{ \AA}^{-1}$, this corresponds to an almost equal contribution from the dipole and quadrupole excitations, and the linear transferred momentum in the C_{70} experiment is $\approx 0.55 \text{ \AA}^{-1}$, and it corresponds mainly to the quadrupole excitation. But in both experiments, the excited multipoles are far from the main maxima of the spectral functions.

A few words about the experimental setup are in order. The detector used in both experiments has a circular finite area, it forms a cone with the scattering center of the sample, the surfaces of the cones are 1° off their axis. The axis of the cone in the C_{60} experiment is 1.5° off the beam of the incident electrons, and that in the C_{70} experiment is 2.0° off the beam of the incident electrons. The actual geometry of the detector has been accounted for in our calculations for the differential cross sections.

In figs. 3.12 and 3.13 the computed differential cross sections of the plasmon excitation are compared with the EELS data on C_{60} and C_{70} . Since only relative cross sections were available and the experimental data have been thus renormalized. One can see that both the shape and the position of the plasmon modes agree very well with the experimental data. Moreover, even some rather fine details of the experimental results seem to be reproduced by the theoretical model. In photoexcitation experiments one can excite only dipole states, while with electrons one can in principle

the dynamical structure factor of C_{60}

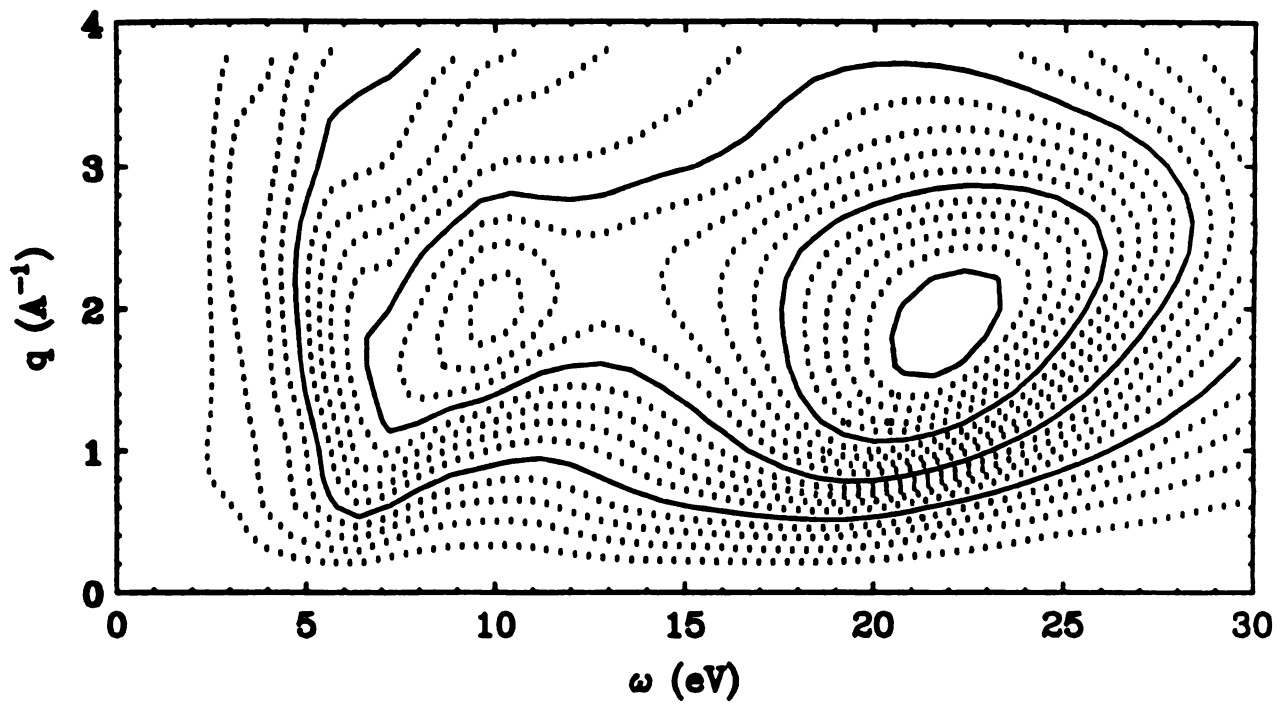


Figure 3.10: The dynamical structure factor (spectral function) of C_{60}

the dynamical structure factor of C_{70}

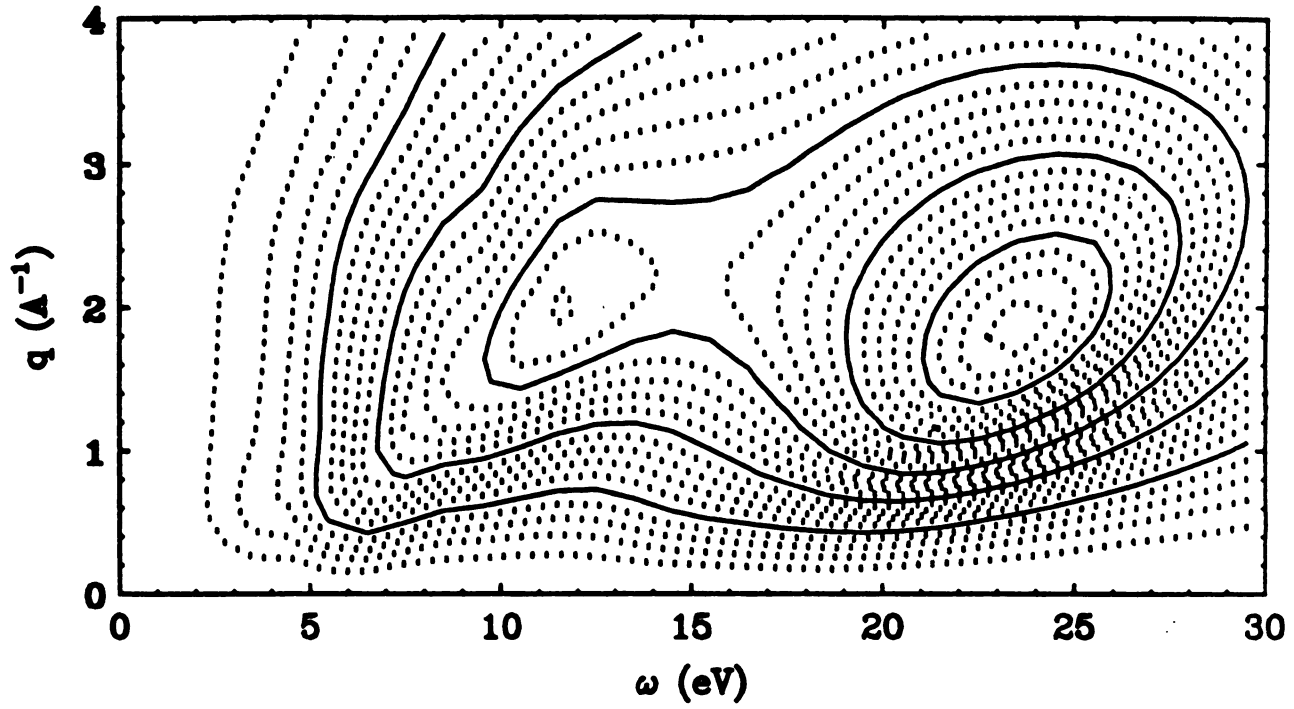


Figure 3.11: The dynamical structure factor (spectral function) of C_{70}

excite any multipolarity, depending on the amount of linear momentum transferred to the target. In the semiclassical approximation, the angular momentum of the excited state is given by $L \approx qR$, where L is the multipolarity of excited state, R is the radius of the target and $\mathbf{q} = \mathbf{p}_{fin} - \mathbf{p}_{in}$ is the transferred linear momentum. The EELS C_{60} data in fig. 3.12 thus correspond to approximately an equal contribution of dipole and quadrupole states and the EELS C_{70} data in fig. 3.13 correspond to approximately quadrupole state, therefore these are the first experimental evidence of quadrupole states in isolated C_{60} and C_{70} molecules.

3.4 Discussions

In an RPA treatment one cannot describe the fragmentation of the oscillator strength due to the coupling to more complicated states. The Landau damping (i.e. fragmentation of the strength due to the 1 particle – 1 hole background) is accounted for in RPA, but this mechanism is not sufficient to explain the significant width especially of the σ plasmon, see the results presented in Ref. [2]. Since these clusters are essentially 2-dimensional objects, the damping due to more complicated particle – hole configurations was imitated with an imaginary part $\eta \approx \omega/8$ eV in eq. (3.2) (chosen as to describe the experimentally observed width of the dipole plasmon in C_{60}), characteristic of the coupling of the RPA modes to surface electronic oscillations only [32].

However, one cannot fail to observe that the predicted peaks are about 2–3 eV lower than the measured ones. We suspect that the reason for this discrepancy lies in the very special structure of the plasmon spectra of these clusters, namely that depending on the amount of linear momentum transferred to the cluster by the external field, $2\omega_\pi$ and $3\omega_\pi$ are very close in energy to ω_σ , see the dynamical spectral

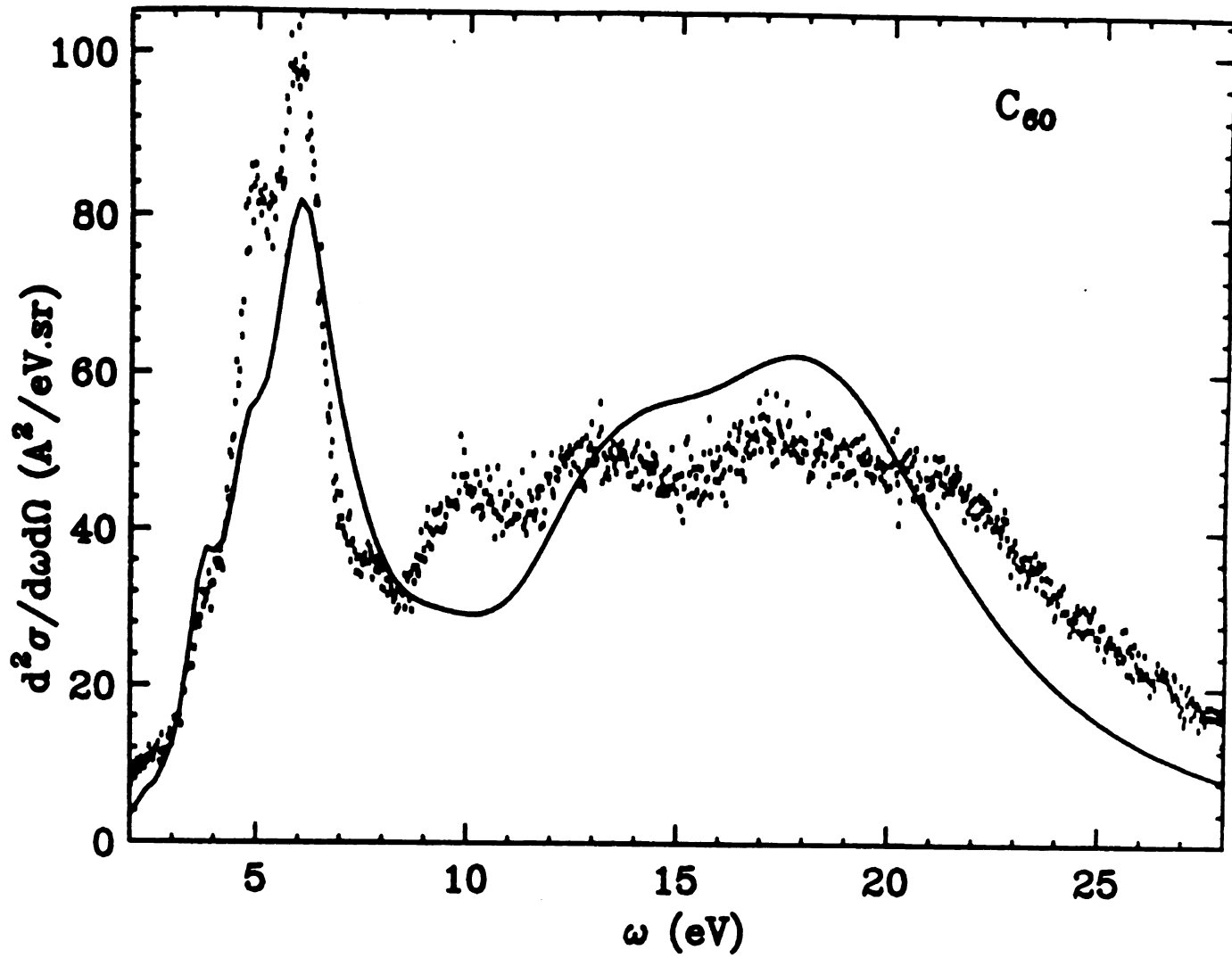


Figure 3.12: Computed (solid line, absolute values) and measured (points) inelastic electron excitation cross section of plasmon in C₆₀ with incident 1 keV electrons at $1.5 \pm 1^\circ$. In the computed results, the actual geometry of the detector has been accounted for.

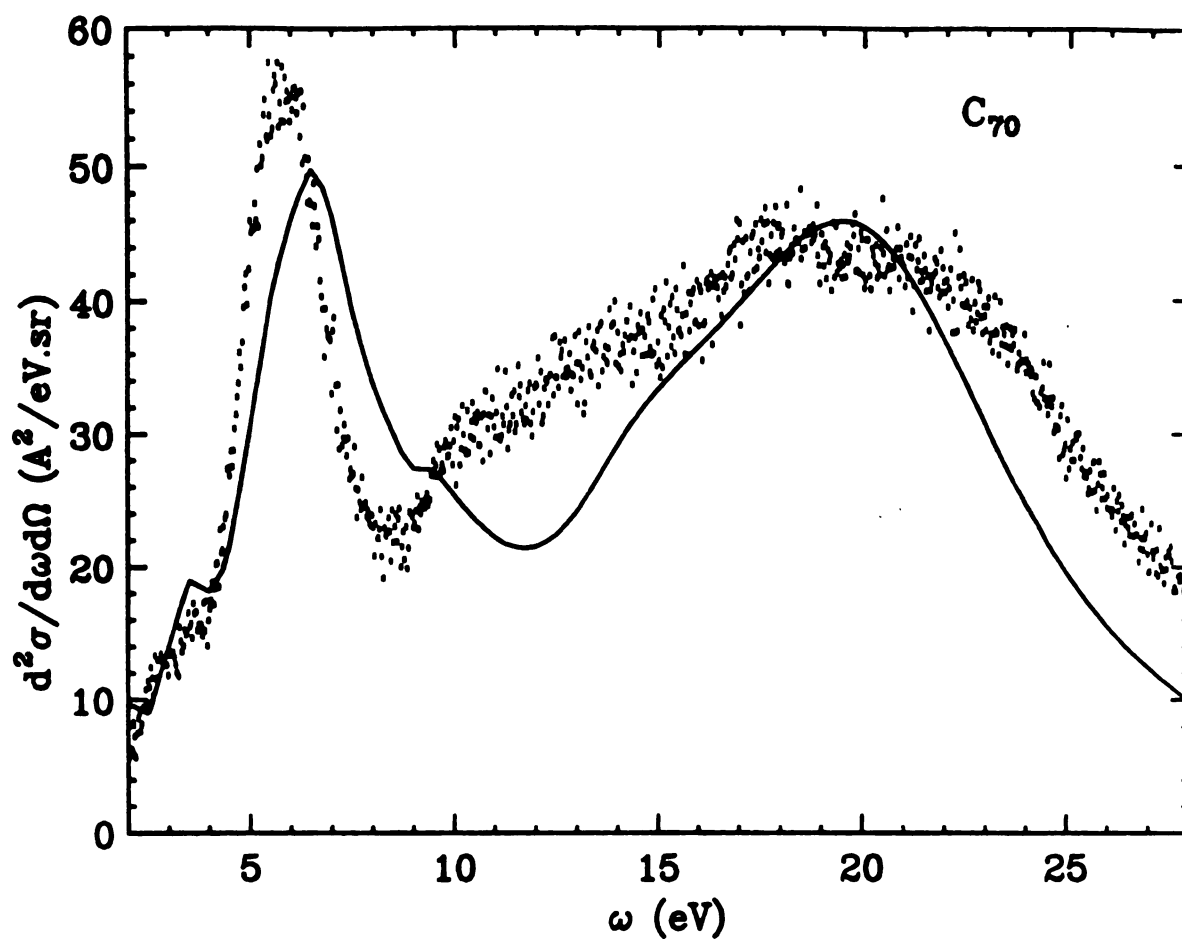


Figure 3.13: Computed (solid line, absolute values) and measured (points) inelastic electron excitation cross section of plasmon in C_{70} with incident 1 keV electrons at $2.0 \pm 1^\circ$. In the computed results, the actual geometry of the detector has been accounted for.

functions in figs. 3.10 and 3.11. In this respect it seems that these clusters are very peculiar and the structure of the plasmon spectra indicates that there may be a strong, essentially resonant coupling between these modes (namely $2\omega_\pi$ or $3\omega_\pi$ with ω_σ), unlike other many-fermion systems studied until now. A plasmon is similar to a photon in QED. In QED it is known that the Furry's theorem forbids the $\gamma \rightarrow 2\gamma$ process (γ is a photon), but at the same time the $\gamma \rightarrow 3\gamma$ process is allowed. For similar reasons (in particular because there is an approximate symmetry between the particle and hole spectrum) we expect that $\sigma \rightarrow 2\pi$ process should be to some extent less important than the $\sigma \rightarrow 3\pi$ process, see fig. 3.14. The finite geometry of the carbon clusters, phase space considerations and the fact that a plasmon is not exactly a free photon may lead to the fact that these two processes are actually equally important. The coupling between the 1p-1h and 2p-2h and 3p-3h electronic excitations may also lead to a rather strong non-linear optical response of the carbon clusters and to an upward shift in energy of the high-lying mode, besides the large fragmentation of the strength of the σ -plasmon. A proper theoretical treatment of these effects goes well beyond the framework of the RPA and it is a rather involved computational procedure (never before attempted in the literature to our knowledge).

A couple of aspects of our theoretical treatment deserve a few comments. In the present approach we have approximated the continuum states with a set of discrete states and thus we are not able to describe electron escape widths. On the other hand one can suspect that a proper treatment of the continuum might change significantly our results. We do not expect this to be the case. In Ref. [2] the continuum has been accounted for in the jellium approximation and the electron escape widths turned out to be much smaller than the fragmentation width of the plasmon. We have also neglected exchange-correlation contributions to the residual Coulomb interaction, which

are much smaller than the direct Coulomb part, which has been taken exactly into account in the present approach. Yabana and Bertsch [33] have analysed explicitly the role of certain Coulomb exchange diagrams in inelastic electron excitation of C_{60} and found that they are relatively unimportant, even at small energies of the incident electrons, where one might expect the exchange Feynman diagrams to be relatively important.

The most debatable approximation is the use of a limited TB space for the electrons. As a consequence the total oscillator strength accounted for is only a fraction of the total (one has about 70 instead of 240 for C_{60} and approximately the same ratio is obtained for the other fullerenes). This is a rather serious drawback of the present approach. However, we have reasons to expect that the missing strength is at much higher energies, than the ones considered here. First of all, the present formalism seems to describe quantitatively pretty well the oscillator strength in the low energy region, where absolute measurements are available [2, 5, 27]. At the same time the relative intensity of the π and σ plasmons (as seen in EELS experiments on gas targets, see Refs. [5, 6, 7]. and the present results, where only relative intensities are available so far) seems to be reproduced also very well. In a recent study of the plasmon states in C_{60} in the framework of the jellium model, including however the icosahedral distortion of the single particle spectrum, where most of the oscillator strength is accounted for in the formalism, Yabana and Bertsch [34] have shown that in the RPA up to an excitation energy of approximately 30 eV only about 30 % of the total energy weighted sum rule, i.e. approximately 80 units of oscillator strength out of 240, are present. The rest are located at much higher excitation energies. There are some experimental indications as well that this might be the case, from the double (and even triple) photoionization experiments on $C_{60/70}$ gas targets [35]. A theoretic-

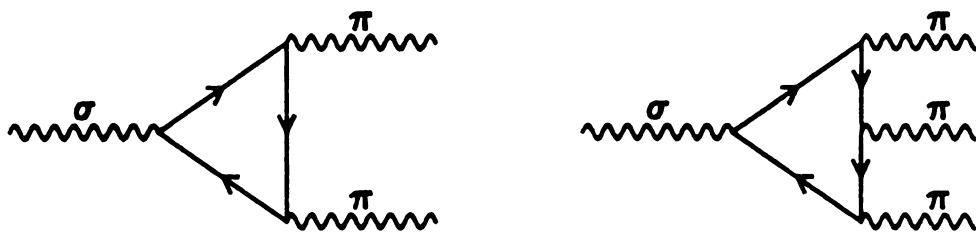


Figure 3.14: Feynman many-body diagrams responsible for the fragmentation width of the plasmon modes in carbon clusters. Solid lines represent the electron propagators and wavy lines the plasmon modes, while the residual interaction is represented through a point vertex.

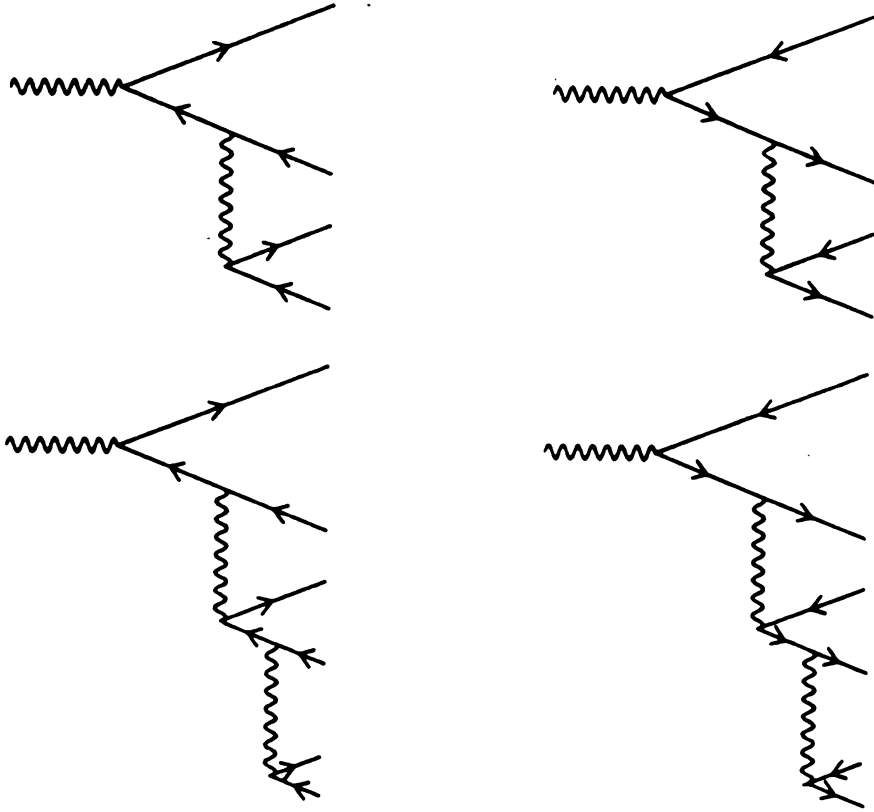


Figure 3.15: Feynman diagrams of the decay of a plasmon through the emission of 2 or 3 electrons

cal analysis of the double and triple photoionization processes is warranted. One can expect that a highly excited plasmon can easily decay through the emission of 2 or even 3 electrons, in a 2- or 3-step process, see fig. 3.15. When a high energy plasmon (more than 30 eV) decays through the emission of an electron (particle state), the residue is left in a relatively deep hole state or again in a relatively highly excited particle state, which subsequently might easily couple to a lower energy plasmon, which subsequently decays through the emission of a second electron. This type of process seems much more probable than a double photon or electron excitation. It is a straightforward procedure to disentangle experimentally these two excitation mechanisms. In the course of the EELS experiment on C_{60} [6] multipole ionized states up to C_{60}^{+4} have been observed, with ionization states 1 to 4 in the ratio of 1 : 0.6 : 0.1 : 0.01. The proper treatment of such processes is beyond the framework of the present paper and we plan to address these questions later. It will be highly desirable to have experimental spectra for the emitted electrons, not only the ion yields as it is presently the case, in order to be able to disentangle different possible channels.

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Chapter 4

Finite Temperature Properties of Small Sodium Clusters

In this chapter, we will present geometric and energetic properties of sodium clusters with 8, 14, 20, 30 and 40 atoms at finite temperatures using an effective many-body interaction among sodium atoms in the framework of an improved isothermal molecular dynamics approach. We shall show that these clusters undergo two phase transitions and that the two transition temperatures go up with the cluster size. The two phase transitions are the equivalents of bulk melting and of boiling in a finite system. At low temperatures, these sodium clusters are essentially incompressible, but relatively easy to deform. At high temperatures they become extremely soft. However, strong finite particle effects are observed. In particular, these clusters show a more pronounced thermal expansion than the bulk.

4.1 Introductory Remarks

There are several reasons why it is interesting to study finite temperature properties of atomic clusters, in particular of simple metal clusters. The most obvious one is the fact that experimental results obtained so far are for relatively hot clusters [1, 2, 3]. Even though the experimentalists do not have at the moment a way of determining

the temperature of the clusters they produce, and only relatively rough estimates are available, it is very likely that these clusters are melted. On the other hand, most of the theoretical studies are performed at zero temperature. The properties and the behaviour of finite systems at nonzero temperatures are of unquestionable theoretical interest. While in the bulk there are well defined phase transitions (melting and boiling) and statistical physics concepts (such as temperature, microcanonical, canonical ensembles, etc.) are well defined, the validity of such terminology for finite systems still raises some eyebrows, in spite of the fact that the usefulness and correctness of such an approach have been justified for quite a while [4, 5, 6, 7]. Although the study of finite systems opens an avenue towards understanding the way a piece of bulk material emerges this field has its own set of problems. The relative role of the surface versus volume effects is significantly enhanced compared to the bulk. An important aspect is the presence of at least two types of degrees of freedom – electronic and ionic – with vastly different characteristic time and correspondingly energy scales. This fact seems to lend support to the validity of the traditional adiabatic approach. Since the ion cores are so much heavier than the electrons and the physical phenomena of interest occur in a region where the density of states for the ionic degrees of freedom is extremely high [8], a classical description of these degrees of freedom seems more than reasonable. On the other hand, a quantum description of the electronic degrees of freedom is unquestionably the right approach. This view is supported by the experimental evidence of pure quantum phenomena, reminiscent of the similar nuclear phenomena: relative abundances of different atomic clusters, odd–even particle effects, geometrical shapes of the clusters (as indirectly inferred from the study of their electromagnetic and optical properties), occurrence of the so called supershells; as well as by simple theoretical estimates of the relevant electronic energy scales in such finite objects [4, 5, 6, 7].

We attempt to elucidate to some extent the role of a finite temperature in sodium clusters. The approach chosen by us is not irreproachable. In choosing one or another description, various authors emphasize different dominant physical aspects. One can distinguish roughly two dominant trends in the literature: *i)* pure adiabatic picture with an explicit treatment of the ionic degrees of freedom, which can be subdivided in two subclasses *ia)* explicit treatment of the electronic degrees of freedom and *ib)* implicit treatment of the electrons via an effective many-body classical potential for the ions; and *ii)* featureless ionic background and explicit finite temperature treatment of the electronic degrees of freedom. We shall not discuss here the quantum chemistry calculations, which because of their rather ambitious goal to compute everything with essentially no approximation, are limited to relatively small clusters [9].

The approach *ia)* seems to be accepted as the most “fundamental” way to describe atomic clusters at zero as well as at finite temperatures and is often referred to as an *ab initio* calculation [10, 11]. It amounts to a classical description of the ionic degrees of freedom – which seems to be a very reasonable approximation, with the exception of very light atoms like hydrogen, helium and to some extent lithium – and a Density Functional Theory within the Local Density Approximation (DFT-LDA) for electrons, augmented with a pseudopotential interaction between ionic cores and valence electrons (which are the only ones usually treated explicitly) [10, 11, 12, 13]. From the point of view of a pure practitioner, the main drawback of this type of approach is the appalling amount of computer time required to extract relevant physical information. It is for this reason that several groups decided to simplify the treatment of the electronic degrees of freedom by using relatively old ideas, originated in condensed matter physics, like the tight-binding approximation (see Refs. [15, 16, 17, 18] for a sample of references), embedded atom [19, 20], etc. The “natural” extension of these

methods to finite temperatures still does raise some questions. Although one can accept this type of approach for the description of insulators, where the gap between the occupied and unoccupied electronic states is sufficiently large and the assumption that the electrons are at all times essentially at zero temperature seems reasonable, the applicability of the strict adiabatic approximation for metals or atomic metallic clusters is questionable. One possible approach seems to be the generalization of the DFT-LDA to finite temperatures [21]. However, this line of thought implies a relatively quick relaxation of the electronic degrees of freedom. At low temperatures the relaxation times in many-fermionic systems have a $1/T^2$ behaviour [22, 23] and ionic and electronic relaxation times can become comparable. Moreover, atomic clusters are likely rather floppy objects and level crossing phenomena can occur. In such a case nonadiabatic effects could prove to be quite important and in any event this seems to be yet a *terra incognita*.

A further simplification *ib)* relies on the use of an effective many-body interaction among atoms, derived as before in the Born-Oppenheimer approximation for the electrons [3, 24, 25, 26, 29]. In particular, the strongly delocalized character of the valence electrons in simple metallic systems is at the origin of the many-body character of this effective potential and it cannot be simulated by two-body forces only. In this way one loses some pure quantum features, like shell effects, odd-even effects, etc. However, one has the advantage, like in a Thomas-Fermi approximation, of describing the gross properties of the clusters, since volume and surface effects seem to be mimicked rather well by this type of model [25, 26, 27].

The last listed type of approach, *ii)*, emphasizes solely the role of electrons, while the ionic degrees of freedom form a simple featureless jellium background, without any dynamic or thermodynamic properties [1, 2, 3, 31, 33]. The main *raison d'être*

for such models is the hypothesis that the electron dynamics dominates completely the properties of simple metallic clusters, as manifested in abundances, odd-even effects, electromagnetic and optical properties, supershell effects, etc. While perfectly suited to explain this range of phenomena, the jellium approach has its own inherent limitations, especially when finite temperature properties of metallic clusters are concerned. The gross properties of metallic clusters are rather poorly described in such pure electronic models. For example the volume energy (total energy per particle) derived in a jellium model is about 2.26 eV [31, 32] as contrasted with the cohesive energy for sodium 1.113 eV. This fact alone sheds strong doubts on the treatment of the ions as a physically featureless background. In the pure jellium model the shape and stability of a cluster are totally governed by the electronic degrees of freedom. If the volume energy is so strongly affected by the ions, a similar strong effect for the surface tension, due to the ionic degrees of freedom, is plausible. As a result the whole concept behind the jellium model, seemingly so successful in describing a whole range of pure quantum effects, becomes to some extent questionable.

Moreover, a large series of molecular dynamics (MD) calculations [3, 5, 6, 7] point to the existence of a large number of isomers, which are absent in a pure jellium description, and their presence gives rise to the phase transitions occurring in atomic clusters. The phase space for the ionic degrees of freedom increases exponentially with increase of temperature (or equivalently excitation energy of the cluster, see Section 3), while at the same time the phase space for the electrons increases at a much smaller rate, since the electrons behave essentially like a degenerate Fermi gas. One can estimate the electronic density of states using Bethe's Fermi gas formula [34]

$$\rho_{el}(E) = \frac{\exp \left[\sqrt{\pi^2 N E / \varepsilon_F} \right]}{\sqrt{48 E}}, \quad (4.1)$$

where N is the number of valence (delocalized) electrons in the cluster, ε_F is their Fermi energy and E is the electronic excitation energy. For the ionic degrees of freedom an estimate from below (see Section 3) for their density of states can be obtained from the classical formula for $3N - 6$ intrinsic degrees of freedom in the harmonic approximation (Debye model) [8]

$$\rho_{ion}(E) = \frac{E^{3N-7}}{(3N-6)!} \prod_{i=1}^{3N-6} \frac{1}{\omega_i}, \quad (4.2)$$

where N is the number of atoms in the cluster and ω_i are the vibrational frequencies of the normal modes. For the Na_{20} cluster one obtains in this way $\rho_{el} \approx 4 \times 10^4 \text{ eV}^{-1}$ and $\rho_{ion} \approx 10^{58} \text{ eV}^{-1}$ at an excitation energy of 3 eV. Consequently, the finite temperature properties, the phase transitions in particular, should be dominated by the ionic degrees of freedom. Since the density of states is directly linked with the entropy, one can rephrase the above discussion in terms of entropic effects; the electronic entropy is much smaller than the ionic entropy.

Experimentally, sodium clusters are likely to be produced in a liquid state, with an estimated temperature around a few hundred degrees. This could serve as an explanation of the spectacular success of the jellium model. Being in a liquid state, the ions are rather mobile and therefore the cluster can be easily deformed. If the contribution to the surface tension, originating from the ionic degrees of freedom, is significantly smaller than the electronic part, one can expect that the electronic degrees of freedom (through the quantum shell effects) would play the major role in determining the shape and the stability of the cluster. The surface energy for liquid bulk sodium ($\sigma = [0.699 - 3.18 \times 10^{-4}(T - T_{melting})] \text{ eV}$) [35] seems to be in qualitative agreement with the value extracted from jellium calculations, $\sigma_{jellium}(T = 400 \text{ K}) = 0.5918 \text{ eV}$ [33] (The total surface energy is defined as $\sigma N^{2/3}$, where N is the number of atoms in the cluster). However, the surface tension for liquid bulk

sodium shows a relatively strong temperature dependence, while the jellium model seems to underestimate it by at least one order of magnitude in the temperature range $T = 0 \dots 600$ K, $d\sigma_{\text{jellium}}/dT \approx 2 \dots 8 \times 10^{-5}$ eV/K compared to 3.18×10^{-4} eV/K for liquid bulk sodium [35] (We have estimated the temperature dependence of the surface energy in the jellium model from the results for the liquid drop energy in Ref. [33]). This comparison seems to indicate that a combined treatment of the ionic and electronic degrees of freedom is desirable in order to understand the finite temperature properties of these clusters. The apparent agreement between the jellium prediction and the bulk value for the surface tension might very easily prove to be an accident.

MD calculations with effective many-body potentials definitely fail to describe the electronic shell effects. The amplitude of the so called shell-correction terms (computed in the spherical approximation, which overestimates them as a result, probably by as much as a factor of two) never exceeds 1 – 3 eV for clusters with up to a few hundred atoms and a little bit more for larger ones [3, 33]. When converted into energy per atom, the magnitude of the shell-corrections is relatively small, about 0.025 eV or 300 K for $N = 40$ (note however that this is still about 20% of the potential internal energy for Na_{40} around $T = 500$ K, see Section 3, and therefore a quite sizable correction). For larger clusters the contribution from these pure quantum effects becomes even smaller, smaller than, or at least of the same order of magnitude as, the uncertainty of the estimated temperatures of the clusters. Nevertheless, the rather fine details of the abundance distributions seem to correlate qualitatively well with the effects predicted on the basis of the shell-corrections [33, 36]. One might therefore conclude that, if one is not interested in rather fine details, a pure MD approach to these metallic clusters might provide a quite reasonable description.

There is one more argument in favour of using such a relatively simplified approach. A reasonable model for the description of thermodynamic properties of small metallic particles has been suggested by Kubo and Gorkov and Eliashberg (see Refs. [37, 38] for reviews of this approach and other relevant references). The specific heat at small temperatures for a many-fermion system, in an independent particle model, is shown to be determined essentially by the fluctuation properties of the single-particle spectra near the Fermi level. Assuming either a Poisson or GOE type of level spacing distribution, one can show that the electronic contribution to the specific heat at low temperatures, $T \ll 2\varepsilon_F/N$, for an even number of electrons, is either $C_{el} \approx 5TN/2\varepsilon_F$ or $C_{el} \approx 30T^2N^2/4\varepsilon_F^2$ respectively. Here T is the absolute temperature, $\varepsilon_F \approx 3.2$ eV is the Fermi energy and N is the number of electrons. Throughout the paper we shall use energetic units for the temperature ($k_B = 1$) unless otherwise explicitly mentioned. The mean level spacing is estimated as $2\varepsilon_F/N$. Even though these values represent averages over an ensemble of clusters and not values for individual clusters, they should provide a good estimate of the magnitude of the electronic specific heat. For temperatures of interest in sodium clusters, the ionic contribution to the specific heat is dominant, since $C_{ion} \geq (3N - 6) \gg C_{el}$ (see Refs. [39]). At relatively high temperatures the electronic contribution to the specific heat can become comparable to the ionic part (For $T \geq 2\varepsilon_F/N$ the specific heat for the electrons, in the leading $1/N$ approximation, is $C_{el} = 2\pi^2TN/6\varepsilon_F$, irrespective of the character of the fluctuations [37, 38]). Consequently, the structural changes (phase transitions) are likely to be caused by the ionic degrees of freedom for not too large and moderate sized clusters. This last argument is another way of comparing the electronic and ionic densities of states, see eqs. (4.1–4.2).

In spite of all these semi-quantitative or qualitative arguments which we have

presented in favor of dealing with mostly the ionic degrees of freedom in metallic clusters at finite temperatures, we do not mean to imply that the electronic degrees of freedom are unimportant. On the contrary, we believe that a combined treatment of both ionic and electronic degrees of freedom is warranted. In Refs. [13, 14] such a problem has been studied to a certain extent, however from those results one cannot make a judgement concerning the relative role of different degrees of freedom. The quite ambitious method chosen there (DFT-LDA in conjunction with the Carr-Parinello method), aimed at a complete description of the system, did not allow the authors to clearly disentangle the specific role played by ions and electrons. The relatively delicate interplay between these two types of degrees of freedom is likely to lead to interesting phenomena, some of them we have partially alluded to above (part of which seem to be beyond the present formulation of DFT at finite temperatures). Even though in the present paper we shall focus by default on the role of the ionic degrees of freedom, we plan to extend our studies in the near future to a comprehensive treatment of all degrees of freedom in these clusters.

In the following section we shall formulate explicitly our approach. In particular, we shall present an improved isothermal molecular dynamics scheme, based on a previous development [46, 41, 42] of the Nosé-Hoover method [43, 44]. Section 3 is devoted to the presentation of our results, followed by a short summary.

4.2 Isothermal Dynamics

The delocalized character of the valence s -electrons makes the alkali clusters quite different from noble gas clusters. In the case of argon clusters one need only introduce an effective two-body interaction among the atoms, typically the Lennard-Jones potential. Electron delocalization makes a two-body interaction among alkali atoms

physically unacceptable. Instead of treating the electrons explicitly we shall use a phenomenological interaction: the many-body alloy potential [24, 25, 26, 28, 30]. This potential has a many-body attractive part and a two-body repulsive part. The parameters of this potential were determined from *ab initio* calculations with no free parameters [25, 26, 27]. A similar type of interaction has been used in the description of other metal clusters as well [3, 28, 29, 30].

The Hamiltonian describing the properties of a sodium cluster used by us is

$$H = E_{kin} + V = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \frac{E_{coh}}{(1 - q/p)\sqrt{Z_b}} \times \sum_{i=1}^N \left\{ \sqrt{\sum_{\substack{j=1 \\ j \neq i}}^N \exp \left[-2q \left(\frac{r_{ij}}{r_0} - 1 \right) \right]} - \frac{q}{p\sqrt{Z_b}} \sum_{\substack{j=1 \\ j \neq i}}^N \exp \left[-p \left(\frac{r_{ij}}{r_0} - 1 \right) \right] \right\}, \quad (4.3)$$

where the following values for the constants have been adopted $E_{coh} = -1.113$ eV for the bulk cohesive energy, $Z_b = 10.4$ for the effective coordination number in the bulk, $p = 9$, $q = 3$ and $r_0 = 3.66$ Å for the nearest neighbor distance [25, 26, 27]. The second term in the rhs describes the attractive part of the interaction and has a many-body character, due to the delocalized valence *s*-electrons. The last term describes the short range repulsion between sodium atoms.

Since we are interested in the thermal behaviour of the clusters, we have to introduce the coupling to a thermal bath. In a recent study of Na_{7-9} clusters [39], a cubic coupling scheme suggested previously [46, 41, 42] was used. This scheme was an efficient algorithm to achieve ergodicity and also to allow a relatively fast exploration of the phase space [45] It works well for small clusters such as Na_{7-9} , but the cubic term introduced in the equations of motion makes the integration of the equations of motion rather difficult at high temperatures and for large clusters, since it requires a relatively small time step. For example, the choice of the time step ranged from 2.0

$\times 10^{-15}$ to 0.15×10^{-15} sec for different temperatures in the study of Na₇₋₉ clusters [39]. Another drawback of the cubic coupling scheme is that the optimal coupling coefficients are different for different temperatures and clusters [39]. This situation can be quite annoying, especially in the case of relatively large clusters. In this paper, we propose a new coupling scheme, similar to the one proposed for the description of a Brownian particle [46]. We will make the dependence of the coupling coefficients on the temperature and cluster size explicit. Furthermore, we can use the same integration time step for all cluster sizes and temperatures. In all our simulations, we used 1×10^{-15} sec as the time step and the simulations were carried out for 10^6 steps. Consequently the system was evolved for 1×10^{-9} sec for all temperatures. This makes the length of the simulation about 7 times longer than in the previous study [39] at high temperatures.

Our new coupling scheme to a thermal bath at temperature T is described by the following equations of motion for the coordinates x_i , momenta p_{xi} and pseudofriction coefficients ξ_x , ζ_x and ϵ_x (here for the x -components only)

$$\dot{x}_i = \frac{p_{xi}}{m} \quad (4.4)$$

$$\dot{p}_{xi} = -\frac{\partial V}{\partial x_i} - \frac{\alpha e_0}{NL_0} \xi_x^3 \frac{p_{xi}}{p_0} - \frac{\beta e_0}{NL_0} \zeta_x \left(\frac{p_{xi}^2}{p_0^2} - a_0 \right) - \frac{\gamma e_0}{NL_0} \epsilon_x \frac{p_{xi}^3}{p_0^3} \quad (4.5)$$

$$\dot{\xi}_x = \frac{\alpha T}{p_0 L_0} \left(\frac{\sum_{i=1}^N p_{xi}^2}{NmT} - 1 \right) \quad (4.6)$$

$$\dot{\zeta}_x = \frac{\beta T}{p_0 L_0} \left(\frac{\sum_{i=1}^N p_{xi}^3}{NmT p_0} - a_0 \frac{\sum_{i=1}^N p_{xi} p_0}{NmT} - \frac{2 \sum_{i=1}^N p_{xi}}{N p_0} \right) \quad (4.7)$$

$$\dot{\epsilon}_x = \frac{\gamma T}{p_0 L_0} \left(\frac{\sum_{i=1}^N p_{xi}^4}{NmT p_0^2} - \frac{3 \sum_{i=1}^N p_{xi}^2}{N p_0^2} \right) \quad (4.8)$$

Similar equations hold for the y - and z -components. In the equations above, $e_0 \sim mL_0^2 \omega_D^2$ is a constant with the dimension of energy, of the order of the energy cor-

responding to the highest frequency in the system (one can call it the Debye frequency, ω_D , for a cluster). L_0 is a constant with the dimension of length of order $\sim 1 \text{ \AA}$, $p_0 = \sqrt{2mT}$ is the average thermal momentum at temperature T and a_0 is a dimensionless constant of order one. α , β , γ are dimensionless constants, cluster independent and their temperature dependence is given by

$$\alpha \sim \beta \sim \gamma \sim \sqrt{\frac{mL_0^2}{Nt_0^2T}}, \quad (4.9)$$

where t_0 is the smallest characteristic time scale of the system, i.e. $t_0 \sim 2\pi/\omega_D$. In relations. (4.9) the number of particles N appears explicitly because the amplitude of fluctuations of the terms in parentheses in eqs. (4.6–4.8) is proportional to $\sqrt{N}$. All the constants, whose magnitude we have specified only by the order of magnitude, can be varied within reasonable limits, without critically affecting the quality of the simulation. However, relatively large variations of these constants might require significantly longer simulation times. This might not affect the ergodic properties of the equations of motion, and therefore in theory will lead to correct results, provided that the simulation is long enough.

A few clarifications, concerning the nature of this type of coupling to a thermostat, are in order. A complex system is always characterized by a rather wide range of characteristic frequencies (modes). In isothermal MD the thermostat is coupled mostly to some modes. In a 3-dimensional system the density of modes is largest at high frequency, like in the phonon density in a solid. Consequently, in order to have the most effective coupling to a thermostat, the characteristic frequencies of the thermostat should be comparable with the Debye frequency of the system under study. An analysis of the above equations of motion shows that this is indeed the case. A quick thermalization implies also that energy is exchanged at a reasonable rate among

all the modes of the system (i.e. relatively small apparent relaxation times). At the same time the thermalization of the slowest modes of the system is achieved only if the total time of the simulation is larger than the characteristic time of these slow modes and the intrinsic relaxation times of the system. It is possible to devise an isothermal MD in which coupling to all modes (both slow and fast) is achieved by a slight generalization of the type of couplings studied so far [47]. One may wonder as well, why we have introduced a relatively larger number of pseudofriction coefficients. Our experience [45, 46] shows that by increasing the number of pseudofriction coefficients one can ensure a more efficient rate of exploration of the system phase space (smaller apparent relaxation times) and hence avoid problems with lack of ergodicity. In particular one can achieve a better convergence in the case of phase transitions when the so called critical slowing down phenomenon sets in [45]. Moreover, in the case of isolated systems one wants to make sure that there are no conserved quantities (whose presence signals the absence of ergodicity), in particular neither the total angular momentum nor its direction is a constant of motion. The price one has to pay, the increased number of differential equations to be solved, is insignificant, especially for large systems. At the same time, a quicker decorrelation time among the generated phase space configurations (which is the essential element of any ensemble average procedure) ensures a much better overall quality of the simulation.

Provided that the equations of motion generate ergodic trajectories, one can replace the phase space average by the time average, which is much simpler to compute

$$\begin{aligned}
 \langle A(p, q) \rangle &= \frac{1}{Z(T)} \int d^{3N}p d^{3N}q \exp \left[-\frac{H(p, q)}{T} \right] A(p, q) \\
 &= \lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_0^{t_0} dt A(p(t), q(t))
 \end{aligned} \tag{4.10}$$

where p, q stand for the momenta and coordinates, $Z(T)$ is the partition function and

$A(p, q)$ is an arbitrary observable.

In this new coupling scheme, both the center of mass coordinate and momentum of the cluster are not constants of motion. When we discuss the thermal properties below, we will refer everything to the instantaneous center of mass of the cluster and present only the intrinsic thermodynamic properties of the cluster. In order to avoid evaporation at high T (around and above the “boiling” phase transition), we have added a linear restoring force every time a particular interparticle distance $r_{ij} > 3R$, where $R = r_0 N^{1/3}$ and N is the number of particles in the cluster.

4.3 Thermal Properties

We shall follow Refs. [39] to classify the cluster characteristics into two categories: thermodynamic properties (internal energy, specific heat, density of states, phase transitions) and geometric properties (shape, rms radius, momenta of inertia, relative bond length). The energetics and geometry of the cluster are strongly correlated and their analysis is extremely helpful in understanding the thermal behaviour of atomic clusters.

4.3.1 Thermodynamic Properties

During each time step we have monitored the kinetic, potential, rotational, vibrational and total energies of the cluster. The total kinetic energy carries no useful information about a system in the canonical ensemble and we have used it merely as a check of the quality of our simulation. However, the kinetic energy of a cluster can be separated in an unique way into two nontrivial parts, rotational and vibrational energies [48]. Although one might expect that the rotational energy could be different from that of a rigid body, since the clusters are to some extent floppy objects, in the whole

range of temperatures studied we have found that these clusters behave essentially like rigid bodies. In particular the rotational specific heat of the clusters is $C_{rot} = 3/2$ as for a rigid body. This is due to the fact that in this temperature range the thermal rotational motion is not fast enough to lead to any significant centrifugal stretching.

The only pertinent physical information comes from the analysis of the potential energy of the clusters. For each temperature, we bin the value of the potential energy at each time step, and construct the histogram $f(E_{pot}, T)$. This distribution of the potential energy at a given temperature T is

$$f(E_{pot}, T) = \frac{1}{Z_{pot}(T)} \rho(E_{pot}) \exp\left(-\frac{E_{pot}}{T}\right), \quad (4.11)$$

where $\rho(E_{pot})$ is the density of states originating from the potential energy only, and

$$Z_{pot}(T) = \int \rho(E_{pot}) \exp\left(-\frac{E_{pot}}{T}\right) dE_{pot} \quad (4.12)$$

is the potential energy partition function. The distribution $f(E_{pot}, T)$ is peaked near the average potential energy for the corresponding T , and drops off rapidly on both sides. This allows for a reconstruction of the density of states over an energy range comparable to the width of $f(E_{pot}, T)$ [39, 49]. By piecing together parts of $\rho(E_{pot})$ from simulations at different temperatures one can reconstruct the density of states over a significant energy interval, up to an undetermined multiplicative factor, which can in principle be determined as well. The logarithm of the densities of states of the potential energy for the clusters studied are shown in fig. 4.1 along with the logarithm of the corresponding Debye density of states, eq. (4.2), divided by $(3N - 8)/2$.

One can clearly see an increased density of states at higher excitation energies, which we associate with the softening of the clusters and which leads to the onset of the phase transitions. The internal energy and the specific heat can be determined

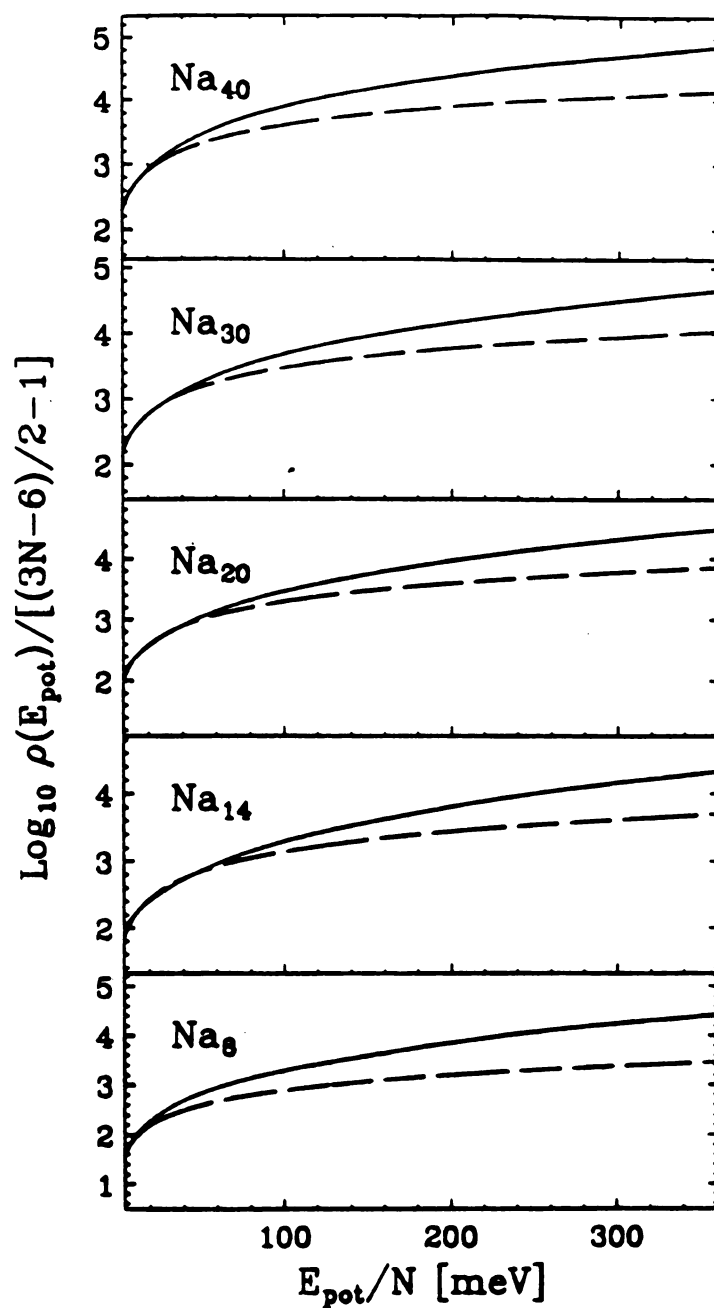


Figure 4.1: The decimal logarithm of the unnormalized density of states (potential energy only) as a function of the excitation energy per particle (solid line) and the Debye model expectation (dashed line), divided by $(3N - 8)/2$.

from the following standard relations

$$U(T) = \langle E_{pot} \rangle = \frac{1}{Z(T)} \int E_{pot} \rho(E_{pot}) \exp\left(-\frac{E_{pot}}{T}\right) dE_{pot}, \quad (4.13)$$

$$C(T) = \frac{\langle E_{pot}^2 \rangle - \langle E_{pot} \rangle^2}{T^2}, \quad (4.14)$$

once the density of states is known. We have computed these quantities using the above relations and checked them also against the corresponding averaged quantities obtained during each separate simulation, and the agreement between the two methods was satisfactory. However, in spite of the fact that our simulation time is rather long (1 nsec), the temperature dependence of some quantities is often not very smooth and some fluctuations are still present (their magnitude will be evident in some of the quantities presented in the following subsection, for which an equivalent of the density of states cannot be defined). This is indicative of the fact that even longer simulation times and/or an optimization of the coupling scheme to the thermostat are needed. The extracted density of states proved to be a rather smooth function of the energy (the inherent statistical fluctuations, due to finite simulation times, are indistinguishable in the plots). The internal energies presented here are calculated with respect to the ground state energy of each cluster. The temperature dependences of the internal energy and of the specific heat are displayed in figs. 4.2 and 4.3. Even though the change in the slope as a function of temperature is not so evident for $U(T)$, one can clearly identify the existence of two phase transitions in fig. 4.3. The lowest phase transition can be associated with the melting and the highest one with the boiling of the cluster. As expected, in finite systems the phase transitions are not sharp and not as well defined as in an infinite system. However one can unmistakably conclude that “something quite dramatic happened” to the cluster. As the cluster size increases, the two phase transitions become better defined and in the thermodynamic limit they

will likely correspond to the melting and boiling phase transitions for bulk sodium, with $T_{\text{melting}} = 371$ K and $T_{\text{boiling}} = 1156$ K. The reason for the appearance of these phase transitions is the dependence of the density of states on the excitation energy of the cluster. At low excitation energies, below the melting point, the density of states has a power law behaviour, characteristic for an ensemble of harmonic oscillators, see eq. (4.2). The cluster resembles a small crystal and the atoms perform only small amplitude oscillations near their equilibrium positions. This is reminiscent of the Einstein model for a solid. Note however that the finite number of ionic degrees of freedom leads to a finite number of vibration energies. Once the excitation energy is increased, the power law behaviour changes to an exponential one, see fig. 4.1, the available phase space increases at a tremendous rate and as a result so does the entropy of the cluster. At approximately $0.4 \times N$ eV excitation energy, the density of states for the cluster exceeds the Debye density of states, see eq. (4.2), by about $(3N - 6)/2$ orders of magnitude. The logarithm of the density of states is essentially the entropy of the system ($S(E) = \ln \rho(E)$). Our results shows that at this excitation energy the entropy per particle exceeds the Debye model estimate by approximately 3–4 units. One can see that the two transition temperatures go up with the cluster size and both melting and boiling occur at lower temperatures in a cluster than in the bulk [3, 5, 6, 7]. In finite systems these temperatures are obviously not sharply defined and both melting and boiling occur in a range of temperatures. A cluster has a significant part of its atoms (or perhaps better to say, most of them) at the surface. These atoms are not strongly bound, since their mean coordination number is lower than that for the inner atoms, and it is relatively easy to “shake them up”. For that reason atomic clusters “below the melting point” are in a rather unusual state, sometimes called the glassy, the molten or the fluctuating state [3, 28, 29, 30, 39]. “Above the melting point” they start behaving like liquids, as one can see more easily in the

behaviour of their pair correlation function (see the next subsection and Refs. [39].

As a side remark, we would like to stress the advantage of performing an MD calculation in the canonical rather than microcanonical ensemble. One finds often in the literature the statement that the two approaches are essentially equivalent with respect to the amount of physical information extracted and for that reason different authors rather often prefer microcanonical simulations to canonical ones. In a canonical simulation one can relatively easily extract the density of states, which is inaccessible in a microcanonical one, and the thermodynamic behaviour of the system can be easily inferred and understood. For a finite system, the density of states plays a similar central role as in statistical physics of large or infinite systems. In particular, it is much less expensive to perform a canonical MD and find structural isomers than in a straightforward search. If an isomer exists, its presence will show up at sufficiently high temperatures, as, in particular, a more careful analysis of the behaviour of the density of states shows (To some extent a similar ideology is behind the popular simulated annealing method).

In spite of the fact that we are dealing here with such small systems, we decided to estimate the latent heat of fusion for sodium from these simulations. Since the first phase transition occurs around 200–300 K, and the transition peak is very broad, we will simply take 500 K as the temperature at which we regard the clusters are completely in a liquid state. If there is no phase transition, the potential internal energy at temperature T would be $(3N - 6)T/2$, as for pure harmonic oscillators (note that the ionic degrees of freedom are treated classically). We shall identify the excess over the internal energy of pure oscillators as the energy necessary to melt the cluster, i.e. the energy needed to cause a structural change of the system. We estimate the heat of fusion to a value between 2.36 and 3.45 kJ/mole, which compares

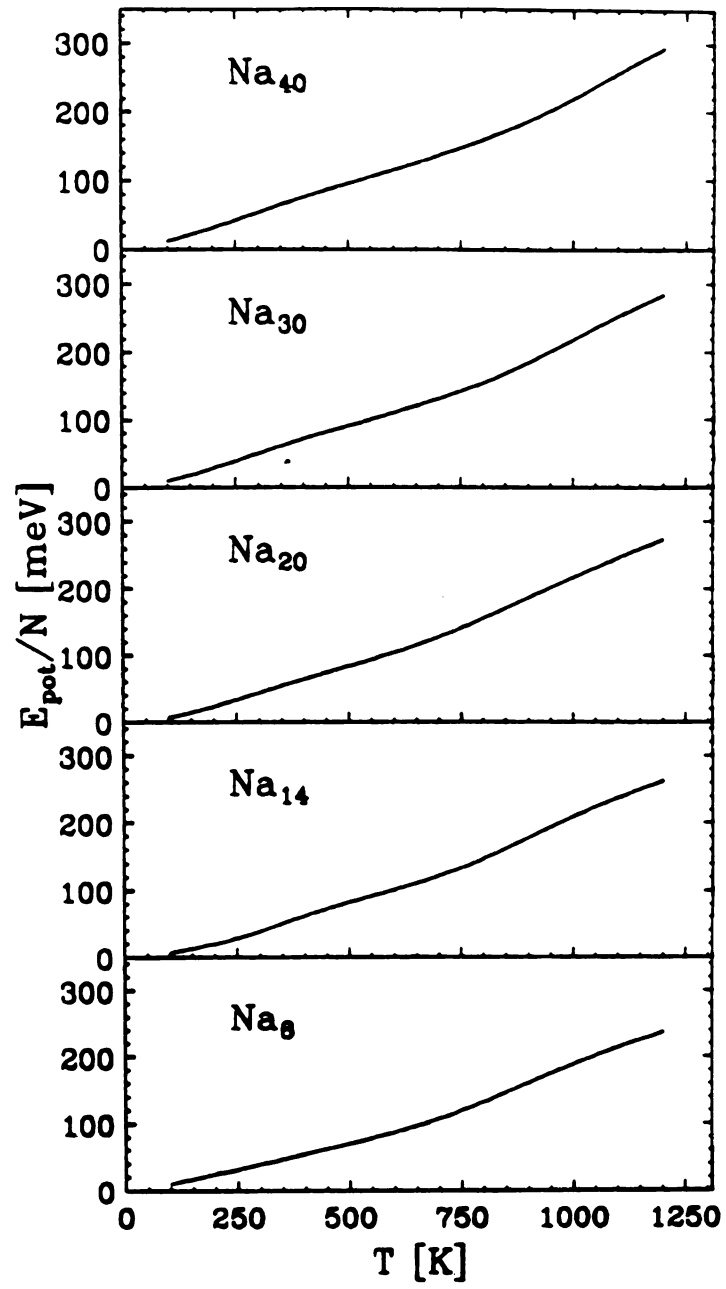


Figure 4.2: The temperature dependences of internal potential energies per particle.

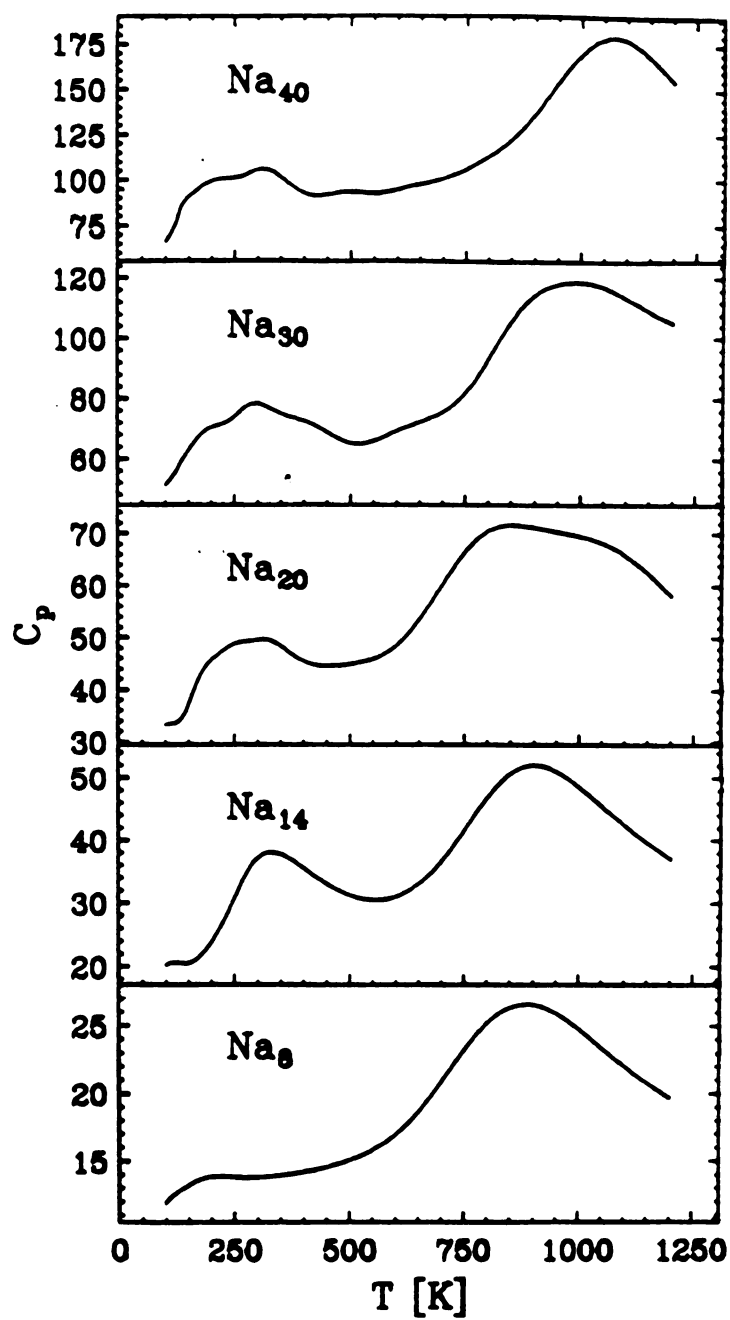


Figure 4.3: The temperature dependences of specific heat.

unexpectedly well with the value 2.6 kJ/mole for bulk sodium [35]. One can try to estimate in the same manner the heat of vaporization as well. At high temperatures the quality of our simulations is worse, due to significant evaporation. Nevertheless, we obtain a value which is approximately equal to the experimentally measured heat of vaporization for sodium 89.6 kJ/mol (within 15 – 20 %). This is not very surprising, since the effective interaction we are using has the correct asymptotic behaviour of the cohesive energy for large systems built in, and the heat of vaporization is almost equal to it.

4.3.2 Geometric Properties

A very sensitive indicator of structural changes in a cluster is the rms relative bond length [5, 6, 7, 39]

$$\delta = \frac{2}{N(N-1)} \sum_{i < j}^N \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle}. \quad (4.15)$$

The temperature dependence of the rms relative bond length is shown in fig. 4.4. As we have mentioned above, at low temperatures, “below the first phase transition”, the cluster behaves like a small crystal, with the atoms oscillating with small amplitudes around their equilibrium positions. At temperatures around 200 K the atoms are at their equilibrium positions for relatively long periods of time. However from time to time an atom jumps from one equilibrium position to another due to thermal fluctuations [3, 39]. The rms relative bond length changes drastically around this temperature, indicative of a structural change. At still higher temperatures, the atoms become extremely mobile and move across the entire cluster [39].

In the region of the second phase transition 850–1000 K, we observe a second increase in δ . This is partially linked with the fact that some atoms can evaporate,

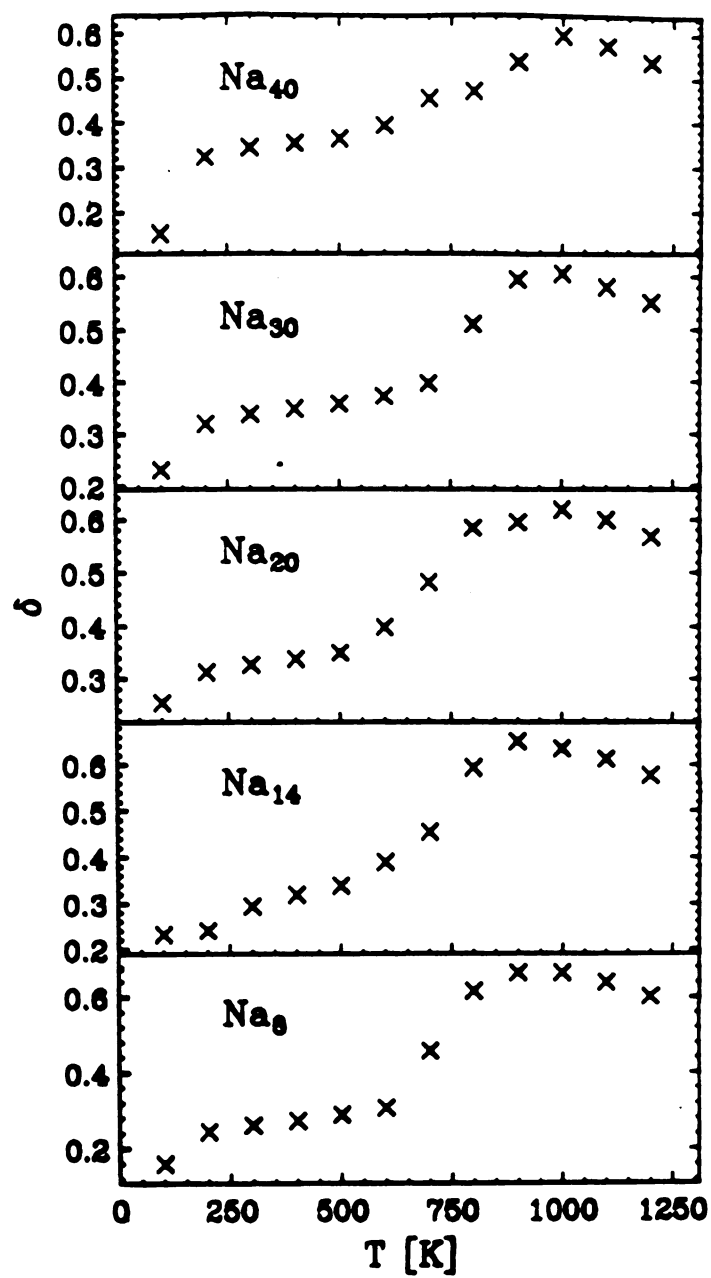


Figure 4.4: The temperature dependences of the relative bond length δ .

even though at a not very significant rate yet. At temperatures above 1000 K, the evaporation of atoms is significant and the precision of our results is therefore reduced. A better approach will be a grand canonical ensemble at these temperatures, suited for the description of the liquid–vapor coexistence. The structural transition in these sodium clusters can be seen also in the behaviour of the (unnormalized) pair correlation function $f(r_{ij})$, see figs. 4.5 and 4.6. Below the first phase transition the interparticle separations are rather well defined, as one would expect for a small crystallite. In the fluid phase, even though one can see a well defined short range correlation among particles, the long correlation is almost completely lost and at very high temperatures the presence of the vapor phase is obvious.

For each spatial configuration of the cluster, we have calculated three geometric quantities: the rms radius of the cluster, which characterizes the cluster size ; the shape parameter β , for the degree of asphericity of the cluster and the shape parameter γ ($0 \leq \gamma \leq \pi/3$), which describes the triaxiality of the cluster [39]. These parameters provide an average information about the size and shape of the clusters. The rms radius and shape parameters β and γ are related to the principal momenta of inertia ($I_1 \geq I_2 \geq I_3 \geq 0$) through the following relations

$$I_k = \frac{2}{3}r^2 \left[1 + \beta \sin \left(\gamma + \frac{(4k-3)\pi}{6} \right) \right] \quad k = 1, 2, 3, \quad (4.16)$$

where

$$r = \sqrt{\frac{1}{N} \sum_{i=1}^N \mathbf{r}_i^2} \quad \left(\sum_{i=1}^N \mathbf{r}_i = 0 \right) \quad (4.17)$$

is the rms radius of the matter distribution. The condition that the semiminor axis of the associated ellipsoid of the inertia is positive

$$a^2 = \frac{r^2}{3} [1 - 2\beta \sin(\gamma + \pi/6)] \geq 0 \quad (4.18)$$

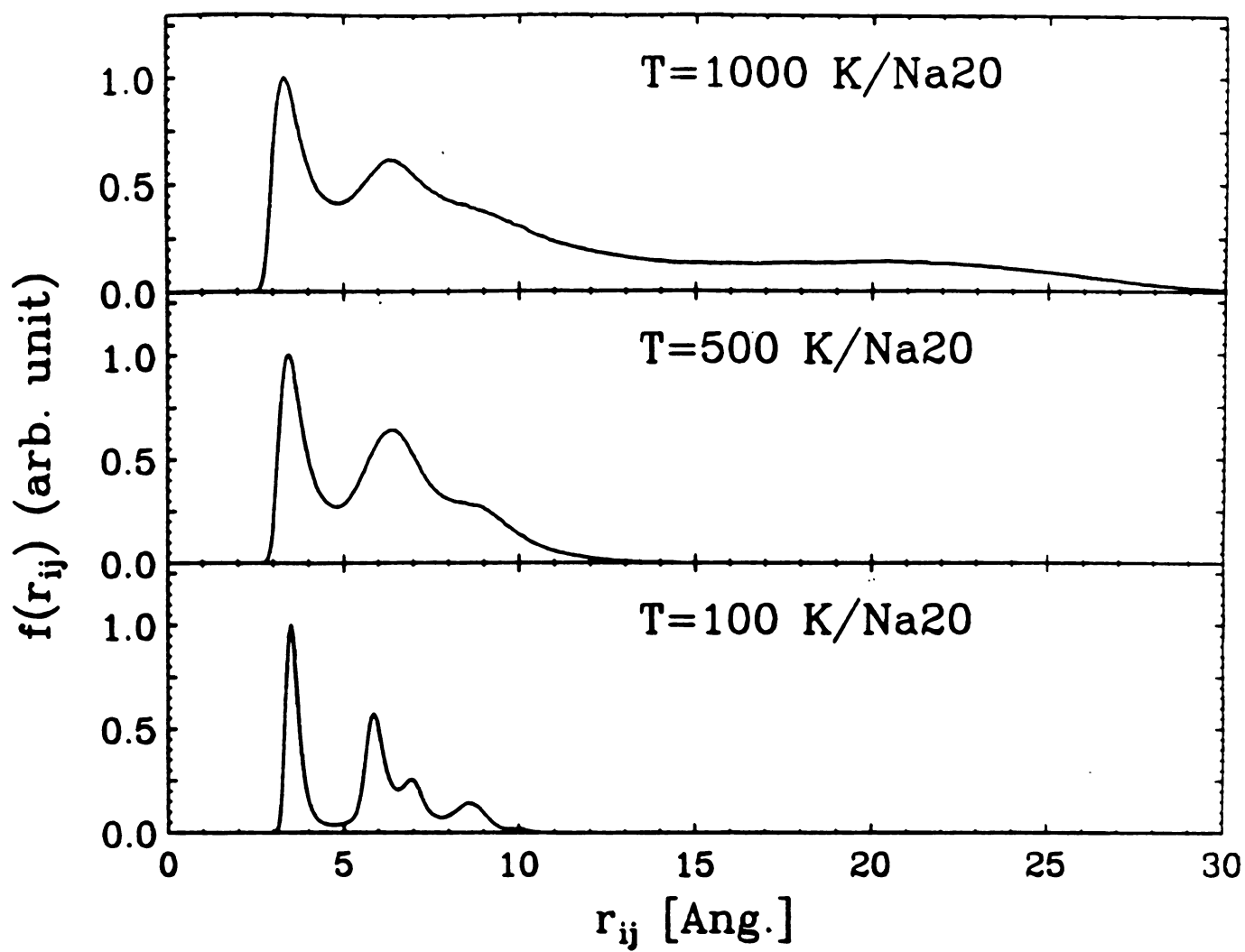


Figure 4.5: The pair correlation function for Na_{20} at several temperatures.

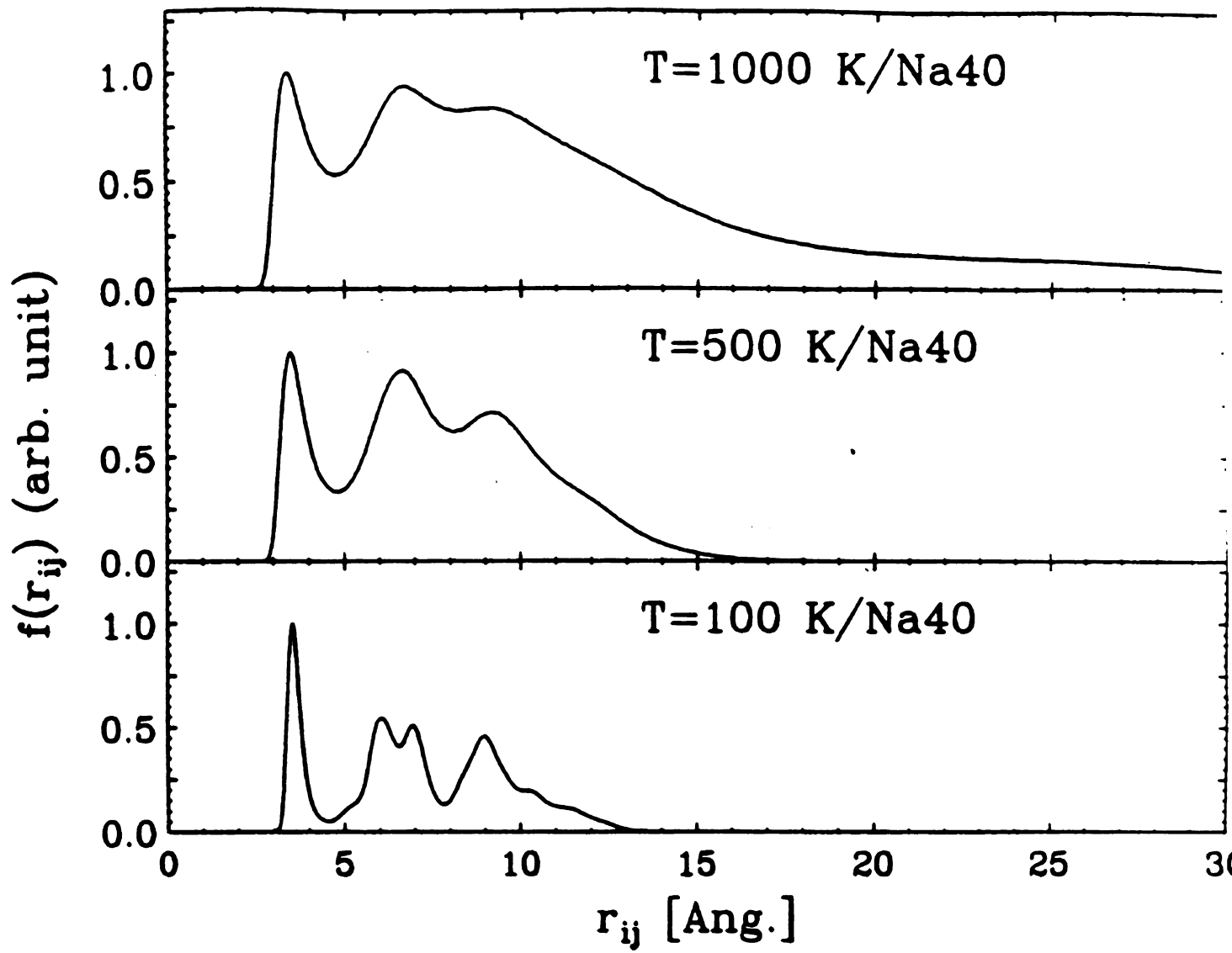


Figure 4.6: The pair correlation function for Na_{40} at several temperatures.

defines the region of allowed values for β and γ . If $\gamma = 0$, then $I_1 = I_2 > I_3$, and the shape of the cluster is an axially symmetric prolate ellipsoid (cigar) with $0 \leq \beta \leq 1$. For $\gamma = \pi/3$, $I_1 > I_2 = I_3$ and the shape corresponds to an axially symmetric oblate ellipsoid (pancake) and $0 \leq \beta \leq 1/2$. For all the remaining angles in between, the shape is a triaxial ellipsoid. For $\beta = 1/2$ and $\gamma = \pi/3$, the shape is a disk of zero thickness, while $\beta = 1$ and $\gamma = 0$ corresponds to a linear chain. The region of allowed values for β and γ has the shape of a triangle in the plane where β is the radial distance and γ is the angle at origin, see fig. 4.7.

The temperature dependence of the average principal momenta of inertia and its relative covariances are displayed in figs. 4.8–4.9, the rms radius of the cluster r , and the shape parameters β , γ along with their corresponding covariances, are displayed in figs. 4.10–4.12. From these plots, one can see that all these clusters tend to acquire a cigar-like shape at high temperatures. This might seem a bit peculiar, but is quite easy to understand. One can show that the shape space measure is proportional to $\beta^4 \sin 3\gamma d\beta d\gamma$ [52]. Consequently shapes with small values of β are strongly suppressed and for the same reason pure oblate or prolate shapes are suppressed as well. At the same time the shapes with as large values as possible for β are strongly favored by this measure and for this reason prolate-like shapes (for which large values of β , $1/2 \leq \beta \leq 1$, $0 \leq \gamma \leq \pi/6$ are possible) start dominating at high temperatures. For $0 \leq \beta \leq 1/2$ oblate-like ($\pi/6 \leq \gamma \leq \pi/3$) and prolate-like ($0 \leq \gamma \leq \pi/6$) shapes are equally probable, according to the shape measure only. One has to keep in mind that these distributions reflect the shape of the free energy of the cluster in the shape space, which takes into account both energetic and entropy properties of the system (the shape space measure is already included). We could have defolded the shape measure from these plots (this is the standard convention in nuclear

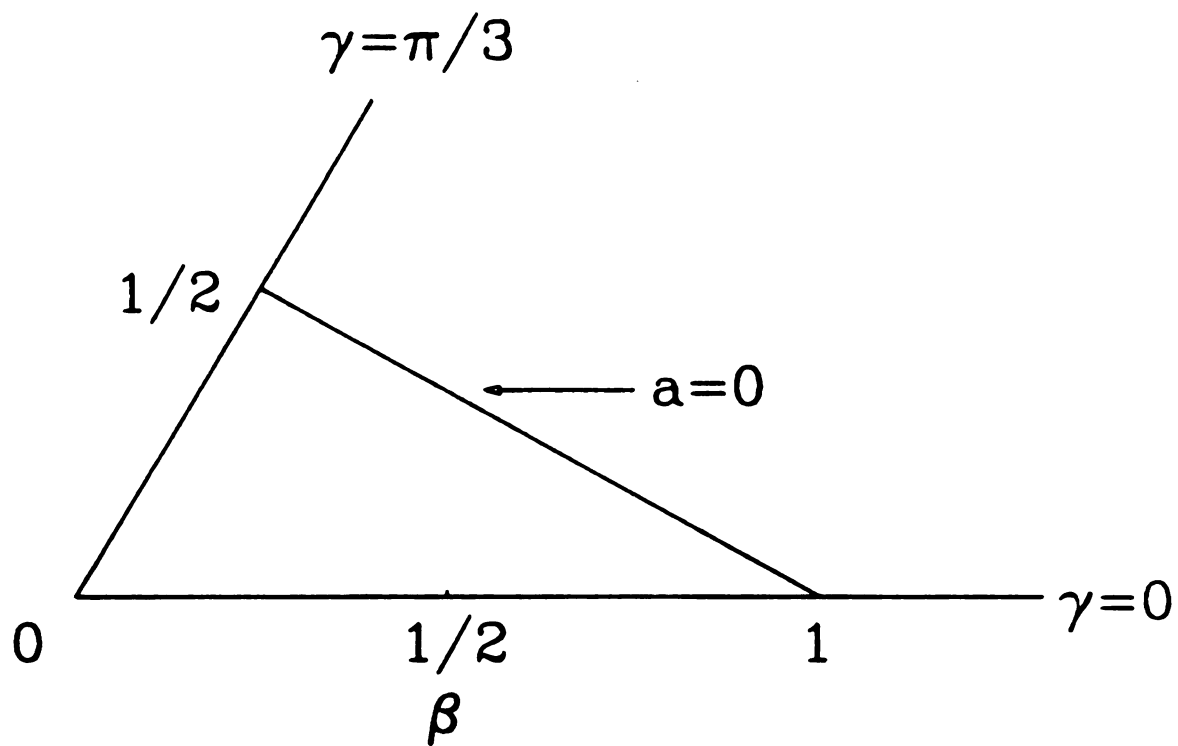


Figure 4.7: The allowed region for the shape variables β and γ .

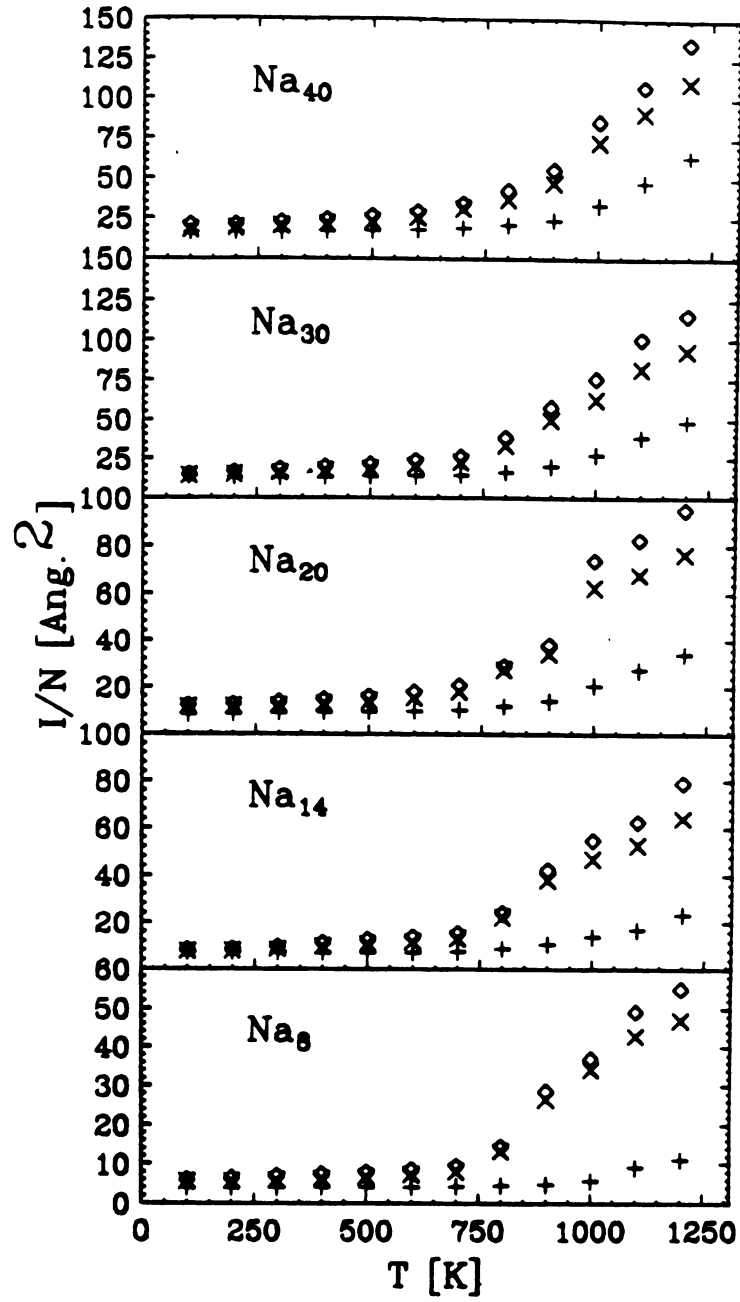


Figure 4.8: The temperature dependences of the average principal momenta of inertia per particle.



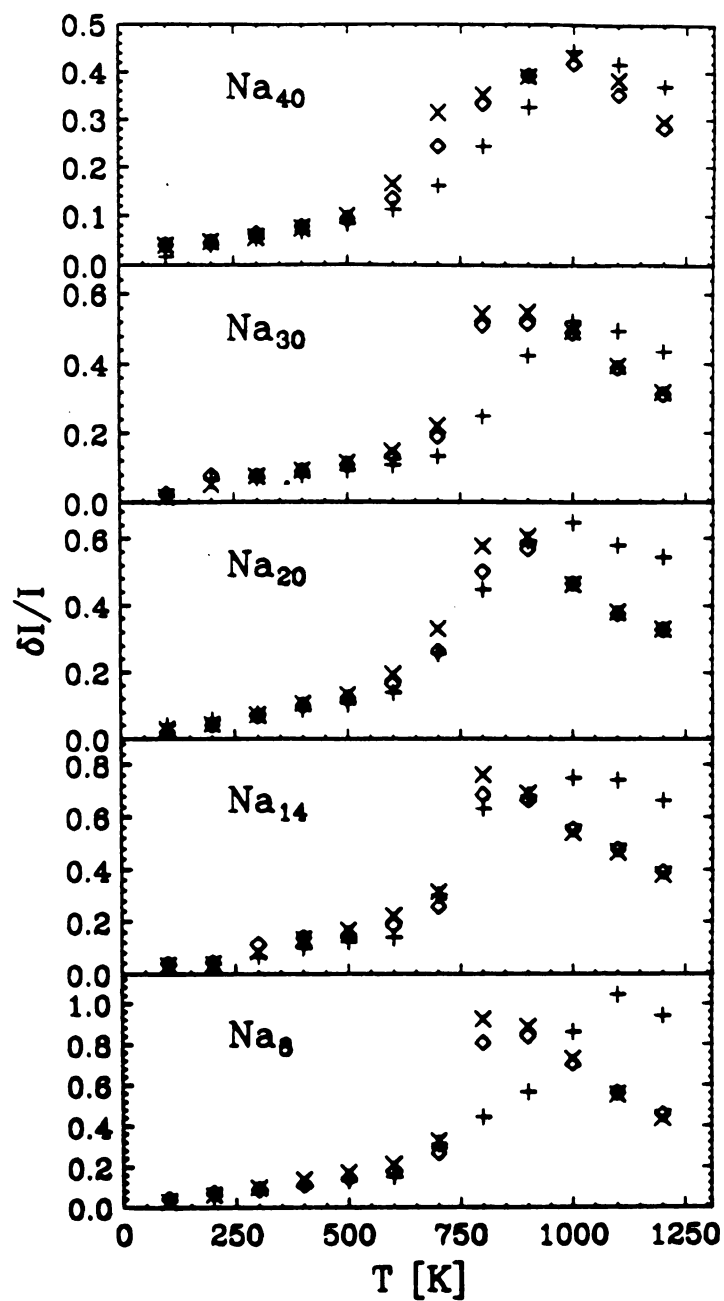


Figure 4.9: The temperature dependences of the relative covariances of the average principal momenta of inertia.

physics calculations of deformed nuclei [3, 52], but since any average will involve this measure anyway, such a way of displaying the shape properties of the cluster seems to us to a certain extent misleading. At low temperatures, these clusters are almost incompressible (their rms radii have relatively sharp distributions), but at the same time they can change their shape rather easily (the distributions for both β and γ have significant widths). At high temperatures, these clusters become apparently soft as well, having the characteristics of a compressible fluid. This apparent softness is to some extent an indirect indication of the presence of the vapor. In spite of the shape differences of their ground geometries, the high temperature behavior of their shapes is quite similar. The character of the shape parameters distributions changes dramatically in the vicinity of the phase transitions. The smallest principal momentum of inertia has the biggest fluctuations, since atoms evaporate more readily from the sides of the cigar for obvious reasons (more chances).

We have tried to extract the coefficient of thermal expansion from our results. Unfortunately we did not have enough statistics for a precise determination of the linear and quadratic expansion coefficients. Nevertheless, as one see from fig. 4.10 the clusters display a rather well defined nonlinear thermal expansion. This fact might play a quite significant role in explaining the red shift of the Mie plasmon in sodium clusters [1, 2]. In the jellium calculations, routinely used in describing the optical response of sodium clusters, the bulk density for the jellium is assumed. Besides melting and boiling in a quite different way than the bulk, sodium clusters seem to have also a rather distinct thermal expansion behaviour. Since the experiments are likely performed with liquid clusters, their larger volume can easily serve as an argument in favor of a lower plasmon energy. The classical Mie plasmon frequency will change approximately as $\delta\omega_{Mie}/\omega_{Mie} = -3\delta r/2r$ when the radius of the cluster

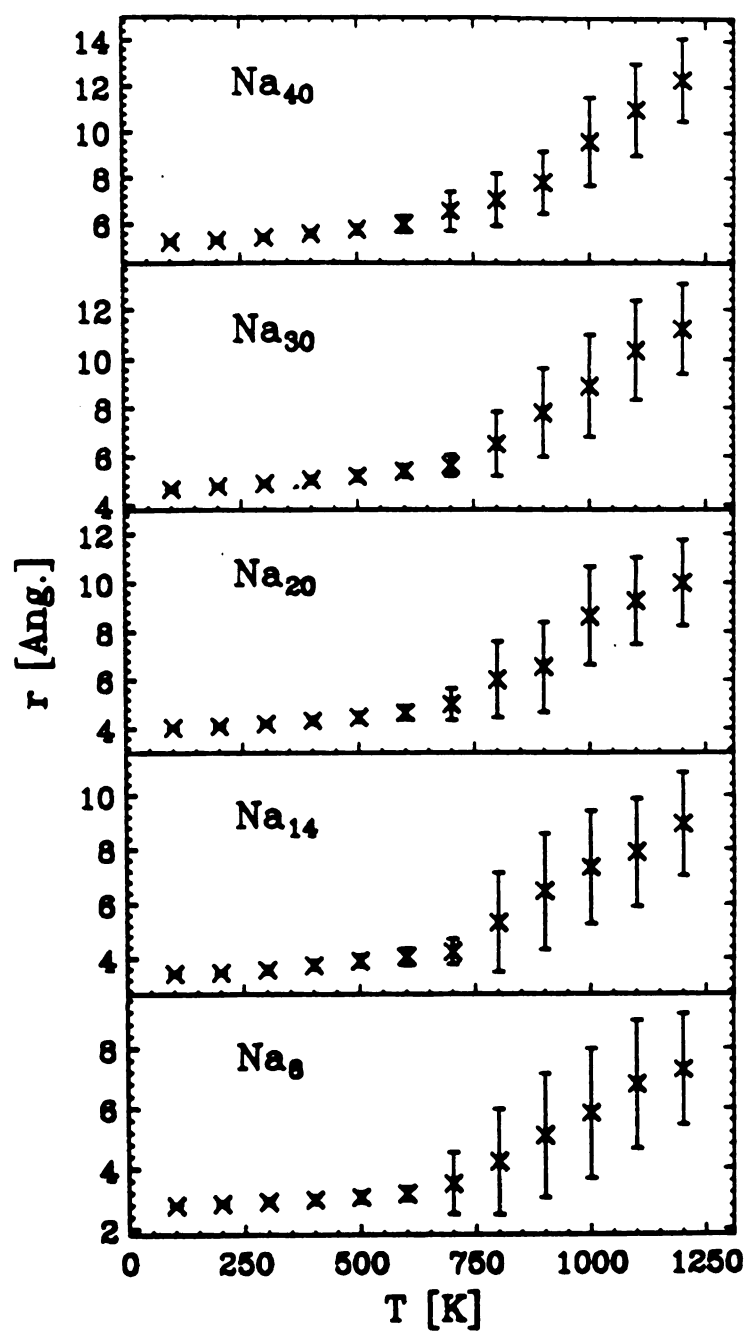


Figure 4.10: The temperature dependences of the rms radius and its covariance (error bars).

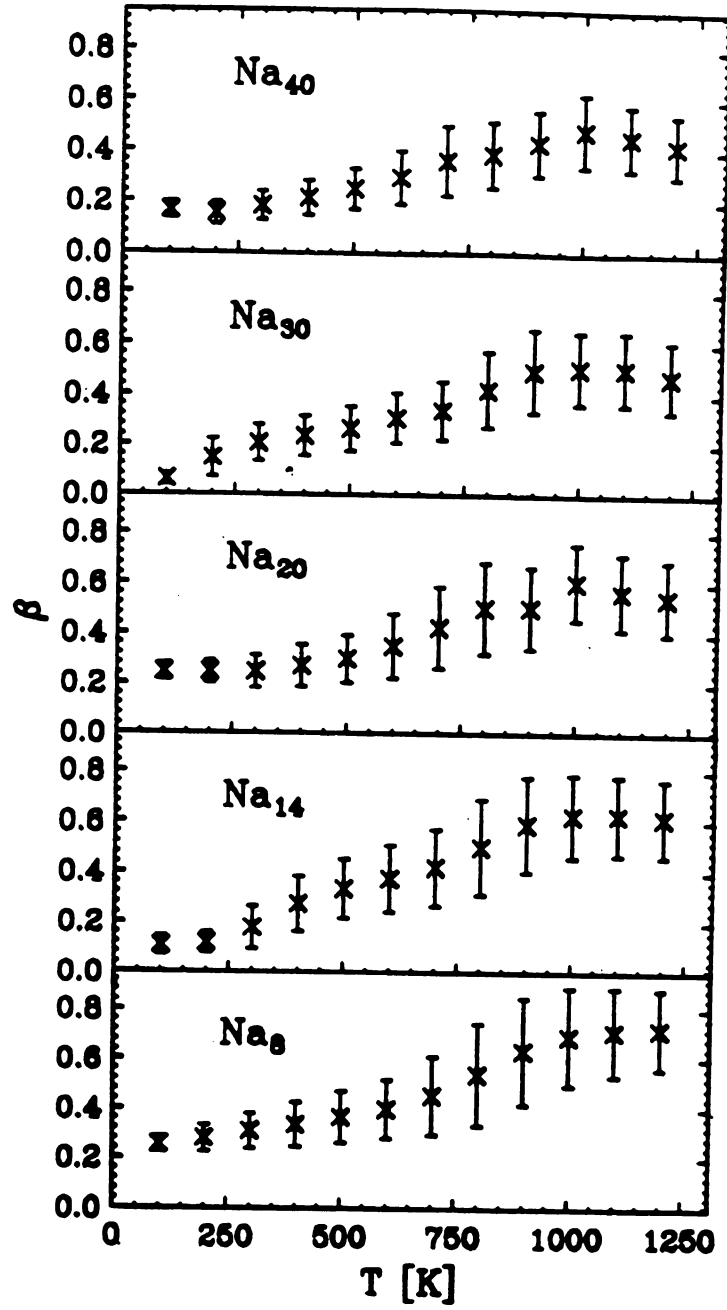


Figure 4.11: The temperature dependences of the shape parameter β and its covariance (error bars).

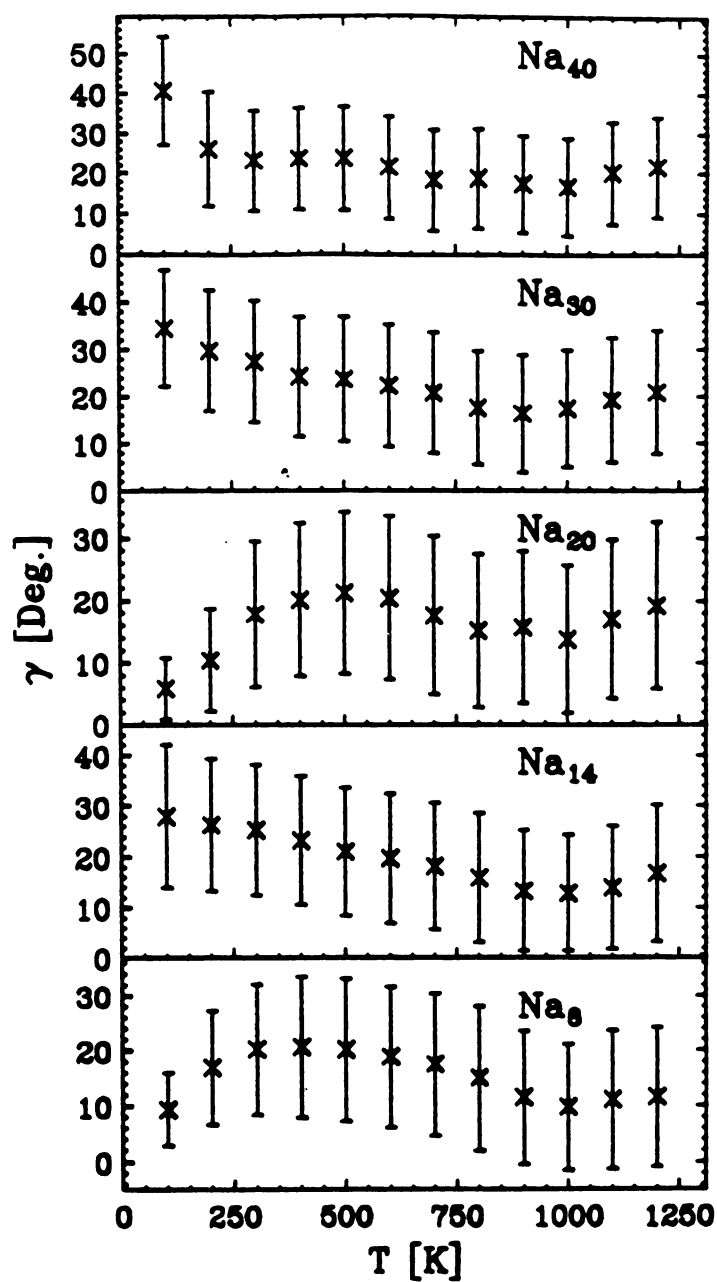
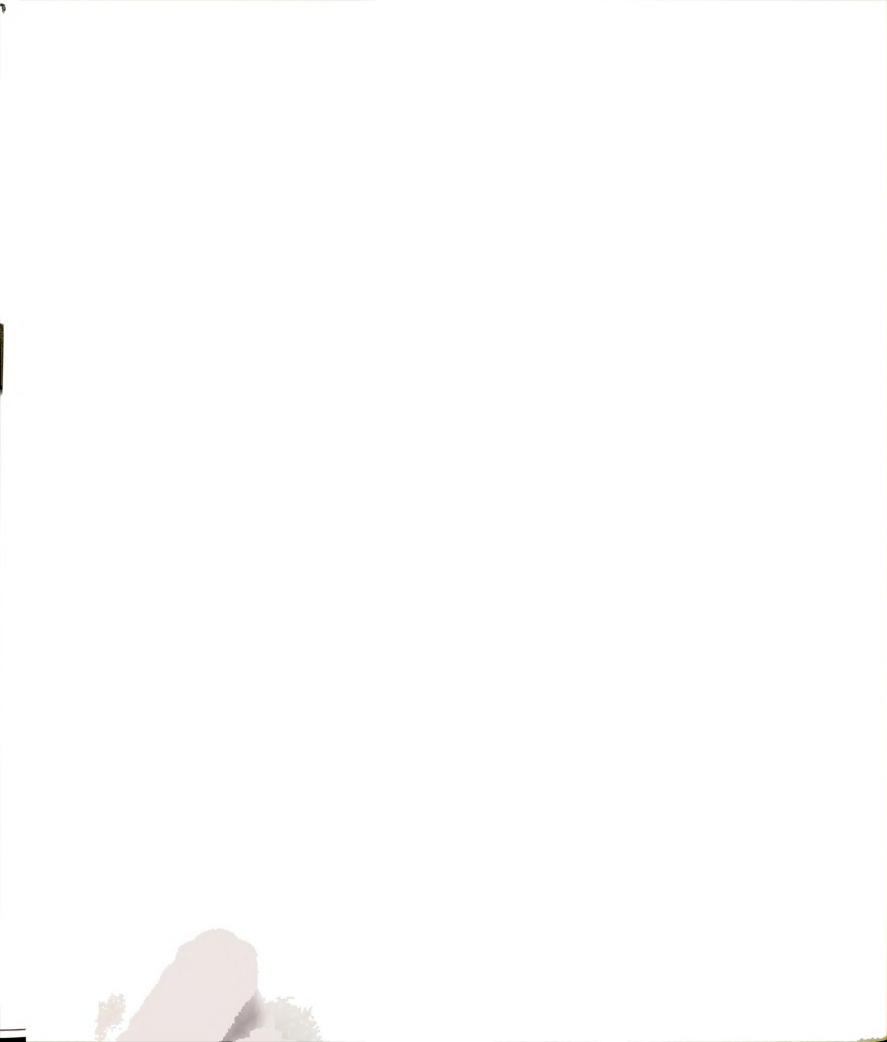


Figure 4.12: The temperature dependences of the shape parameter γ and its covariance (error bars).



changes. At 400–600 K (the estimated temperature of the clusters in nozzle experiments) the linear dimensions of a cluster seem to be about 6 – 15% larger than at $T=0$ K (and significantly larger for higher temperatures), already of the right order of magnitude to explain the observed red shift of the Mie plasmon. At the same time, at these temperatures the volume distribution of the clusters have a quite sizeable width $\Delta r/r \approx 0.04 - 0.07$ (and significantly larger at higher temperatures), which can explain at least part of the width of the plasmon. In figs. 4.13–4.13 we present the spherical part of the ionic density, extracted from our simulations at several selected temperatures (The relatively large fluctuations of $\rho(r)$ near the origin are due to obvious volume effects, near $r \approx 0$ the probability to find an ion at a distance r from the center of mass of the cluster is proportional to $r^2\rho(r)$ and correspondingly the statistics is lower). With increasing temperature this density becomes flatter. The radius of the cluster does not seem to vary significantly, however the surface diffuseness is greatly increased after the first phase transition, which explains the thermal behaviour of the rms radius discussed above. This relatively large apparent surface diffuseness is partially due to the fact that the cluster is rather strongly deformed as well. One can conclude that the anomalous thermal expansion of sodium clusters, when compared to the bulk, is mainly due to these surface effects.

An additional contribution to the width of the Mie plasmon in sodium clusters at finite temperatures will arise from shape fluctuations. The rough estimates we presented here should be looked upon only as order of magnitude effects. The shape of the cluster in its ground state and that with one Mie plasmon excited can be quite different and the ultimate shape and width of the plasmon should be estimated using a more detailed procedure [53].

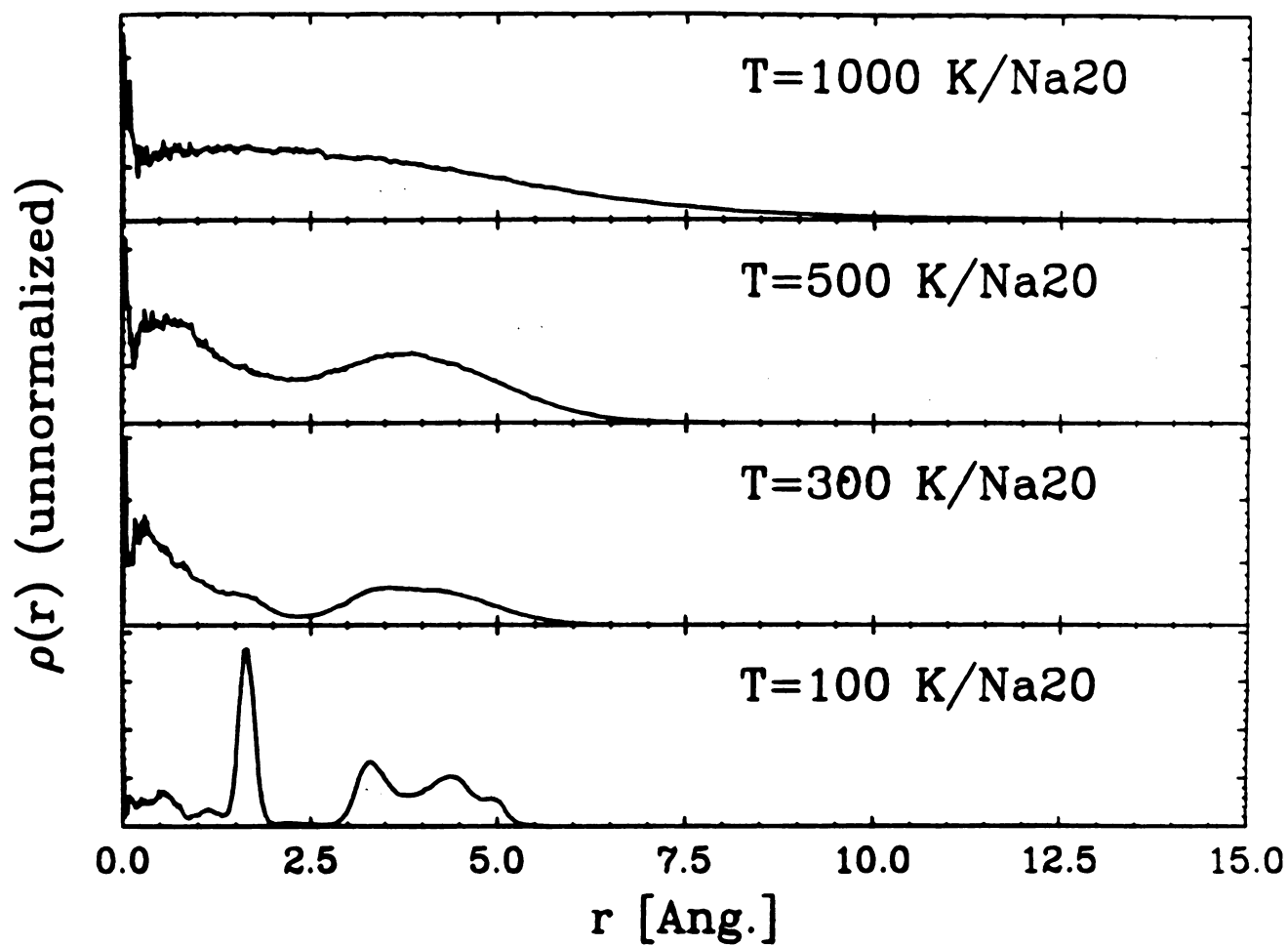


Figure 4.13: The extracted spherical part of the radial (unnormalized) ion density distribution for Na_{20} .

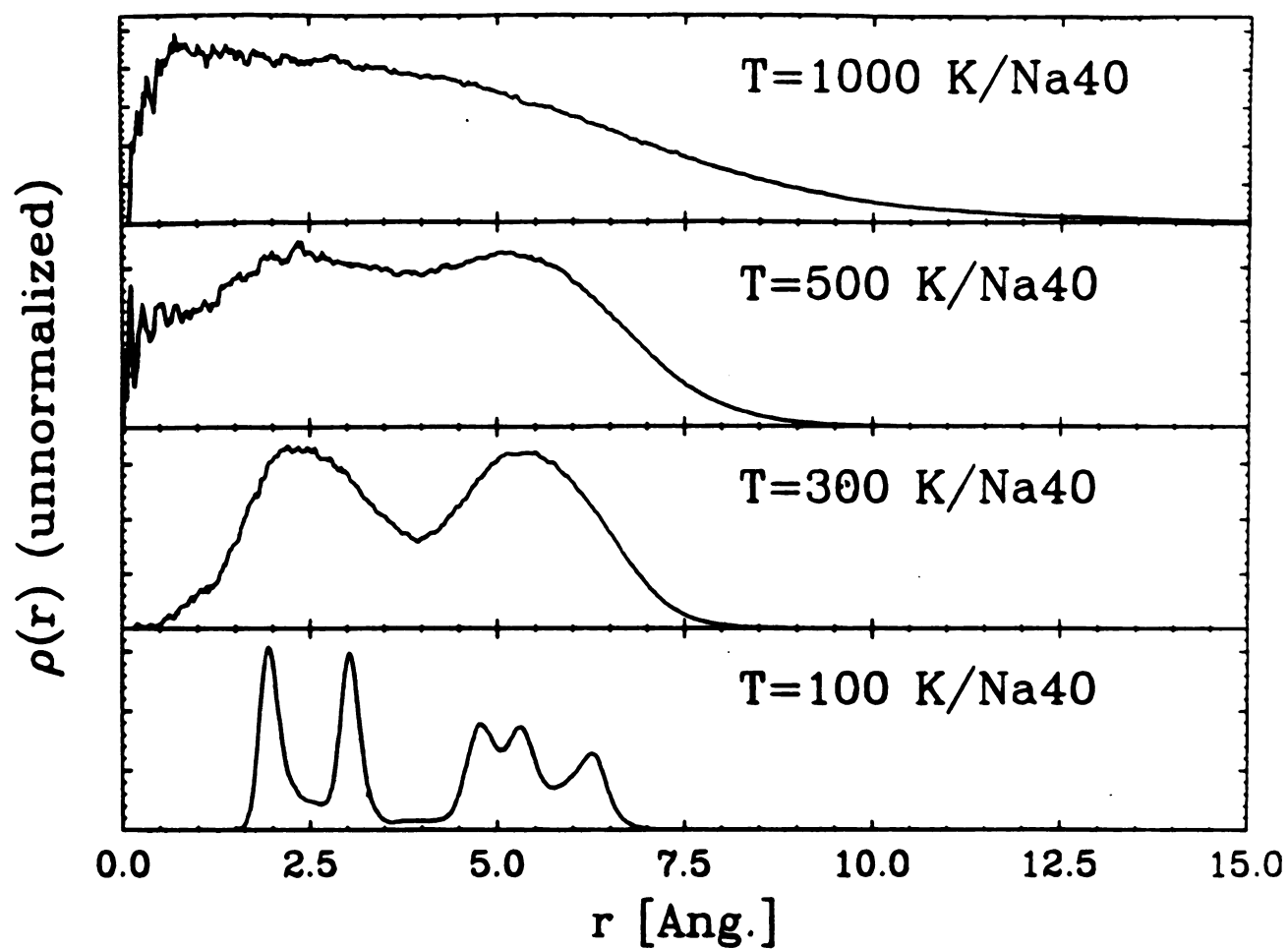


Figure 4.14: The extracted spherical part of the radial (unnormalized) ion density distribution for Na_{40} .

A comment concerning the potential use of such distributions in jellium-type calculations is in order. These distributions represent ensemble averages. The time scales for the ionic degrees of freedom are significantly lower than for the electronic degrees of freedom. If one would like to include such thermal effects in the calculations of the electronic properties and optical response of a cluster, one should perform the corresponding jellium calculations for one member of the ensemble at a time and take the ensemble average only afterwards. In particular, spill-out of the electron density can be more pronounced for some members of the ensemble.

4.4 Closing Remarks

Since the energy scale characteristic for the ionic degrees of freedom is relatively small, a huge phase space becomes available upon increasing the temperature of the cluster. These entropic effects show up in rather drastic structural changes and, without being extremely pedantic concerning the adequacy of the terminology, one can characterize these changes as phase transitions in finite systems. With increasing temperature, the clusters go first through a glassy/molten or fluctuating state (200–300 K) and eventually become totally liquid (above 300 K). In this temperature range they are almost incompressible, but highly deformable. At still higher temperatures (850–1000 K) they start boiling, vaporization sets in and they become rather soft/compressible. In contradistinction with noble gas clusters [5, 6, 7], the melting and boiling do not seem to be a geometric or particle number effect and the same behaviour is observed for all the clusters we have studied ($N = 7, 8, 9, 14, 20, 30$ and 40) [39]. The thermal expansion properties of these clusters seem to be more pronounced when compared to the bulk and it is mostly due to an increased surface diffuseness and deformation of the cluster. Thermally induced rotation is never fast enough to lead to any rotationally

induced effects and in the temperature range studied, one can safely characterize these sodium clusters as rigid bodies with respect to rotational degrees of freedom. The onset of the new phases can be observed in both thermodynamic and geometric properties of the clusters, which have a strong temperature dependence.

The present approach does not account for the electronic degrees of freedom explicitly and therefore electronic shell effects are not accounted for. We expect however that, due to the large ionic entropy effects we observe, similar behaviour should be observed in a more complete description of these clusters. The electronic shell effects should be rather important at relatively low temperatures, below melting. It will be extremely interesting to study the effects of the large geometric fluctuations on the electronic properties and on the optical response in particular (unless in a combined treatment the clusters do not become more stiff, which does not quite seem to happen [13, 14]).

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Chapter 5

Summary and Perspectives

5.1 Summary

Cluster physics is an exciting and young field, it has not only brought methods and concepts from different disciplines into new and unanticipated combinations, but also led to the development of new and advanced experimental techniques. Besides a few words about our work on the nuclear curvature energy problem, we have devoted most of chapter 1 to the review of the new developments in cluster physics, with special attention paid to the theoretical side.

Chapter 2 has been devoted to the calculation of the correlation energy of spherical nuclei using RPA method. We found that the correlation energy has a very different A -dependent behavior from that of the mean-field ground state energy. By finishing this project I learned the theoretical tools used for the study presented in chapter 3 even though by that time I did not know I would jump on the bandwagon of doing cluster physics research.

Chapters 3 and 4 are the main part of this thesis. We calculated the multipolar plasmon excitations in fullerenes in chapter 3. These calculations consist of two parts. One is concerned with the plasmons in C_{60} , its treatment, due to its spherical sym-

metry, is simpler than that of the nonspherical clusters. The other one is about the plasmons in other nonspherical fullerenes, their treatment is somewhat more complicated. With some manipulation of the RPA equation, we are able to completely solve the RPA problem within the framework of tight-binding description for the single particle spectrum and wave functions. The equivalents of both π and σ plasmons in graphite are predicted for these clusters. Good agreement is obtained between our calculations and available experimental data.

We addressed the finite temperature effects of clusters in chapter 4. Since clusters are produced at high temperatures, the study of clusters at finite temperatures is very important and absolutely warranted. We have computed rotational, vibrational and potential energies and corresponding specific heats, momenta of inertia, shapes parameters and bond lengths of $\text{Na}_{8, 14, 20, 30, 40}$ over a wide range of temperatures. The equivalents of both “melting” and “boiling” of the bulk are predicted for these clusters.

5.2 Perspectives

There are a number of directions along which the works presented in this thesis can be extended. First of all, the extremely large width of the σ plasmon in fullerenes is an important problem to be understood. Several possibilities come to mind. As we have remarked in chapter 3, because $2\omega_\pi$ and $3\omega_\pi$ are very close in energy to $3\omega_\sigma$, there may be a strong, essentially resonant coupling between them. This coupling of electronic excitations may lead to the large width of the σ plasmons. Another route one may take to improve the quality of the calculations in chapter 3 is to use a better Hamiltonian to describe the single spectrum and wave functions. Due to the limited Hilbert space of the tight-binding Hamiltonian, sum rule is severely violated (less

than one third of the dipole sum rule is accounted for). Since the RPA problem is completely solved in the framework of tight-binding, one may be tempted to use this method to study the dynamical responses of other clusters where a TB Hamiltonian is available, or at least for a rough idea of the system under study.

There are also many ways the work presented in chapter 4 can be extended. The most obvious one is probably to treat the electrons explicitly instead of being treated implicitly through the use of a many-body-alloy (MBA) potential. There are a couple of options one may take. The simplest and most computationally efficient approach is to use a tight-binding type Hamiltonian for the valence electrons. The most ambitious way is to use the *ab initio* methods like LDA. Although these *ab initio* methods as of now are computationally not practical to use in simulations to extract the density of states, which is the most useful statistical quantity as we did using the MBA potential, they can be used in molecular dynamics simulations to study other properties of finite systems. For example, one may use MD to generate a large number of configurations for clusters at finite temperatures, and then to take these configurations as input to study the optical properties like the plasmons. By using MD to generate a canonical ensemble of configurations and taking the average of different configurations, the effects of temperatures will be properly taken into account. For example, the finite temperature will increase the width of the plasmon. The molecular dynamics can also be used to study atom-cluster or cluster-cluster collisions. The study of cluster collision may lead to new structural as well as dynamical properties. It may also reveal how the energy is transferred from the projectile to the cluster target and how the energy is partitioned among the atoms in the target and how fast equilibration is achieved.

Appendix A

Multipolar Responses for C₆₀

The particle-hole state from chapter 3 is reproduced here,

$$\begin{aligned}
\langle \mathbf{r} | ph \rangle &= \sqrt{\frac{1}{4\pi}} \sum_i \left[f_p(\mathbf{R}_i) f_h(\mathbf{R}_i) \phi_0^2(r_i) + \mathbf{g}_p(\mathbf{R}_i) \cdot \mathbf{g}_h(\mathbf{R}_i) \phi_1^2(r_i) \right] Y_{00}(\hat{\mathbf{r}}_i) + \\
&\sqrt{\frac{1}{4\pi}} \sum_{im} (-1)^m \left[f_p(\mathbf{R}_i) g_{h,-m}(\mathbf{R}_i) + f_h(\mathbf{R}_i) g_{p,-m}(\mathbf{R}_i) \right] \phi_0(r_i) \phi_1(r_i) Y_{1m}(\hat{\mathbf{r}}_i) + \\
&\sqrt{\frac{3}{10\pi}} \sum_{im} (-1)^m \left[\mathbf{g}_p(\mathbf{R}_i) \times \mathbf{g}_h(\mathbf{R}_i) \right]_{2,-m} \phi_1^2(r_i) Y_{2m}(\hat{\mathbf{r}}_i) \\
&= \sum_{li} A_{ph}^l(i) \Phi_l(r_i)
\end{aligned} \tag{A.1}$$

The quantities $A_{ph}^l(i)$'s are defined as

$$\begin{aligned}
A_{ph}^0(i) &= \sqrt{\frac{1}{4\pi}} f_p(\mathbf{R}_i) f_h(\mathbf{R}_i) Y_{00}(\hat{\mathbf{r}}_i) \\
A_{ph}^0(i) &= \sqrt{\frac{1}{4\pi}} \mathbf{g}_p(\mathbf{R}_i) \cdot \mathbf{g}_h(\mathbf{R}_i) Y_{00}(\hat{\mathbf{r}}_i) \\
A_{ph}^1(i) &= \sqrt{\frac{1}{4\pi}} \sum_m (-1)^m \left[f_p(\mathbf{R}_i) g_{h,-m}(\mathbf{R}_i) + f_h(\mathbf{R}_i) g_{p,-m}(\mathbf{R}_i) \right] Y_{1m}(\hat{\mathbf{r}}_i) \\
A_{ph}^2(i) &= \sqrt{\frac{3}{10\pi}} \sum_m (-1)^m \left[\mathbf{g}_p(\mathbf{R}_i) \otimes \mathbf{g}_h(\mathbf{R}_i) \right]_{2,-m} Y_{2m}(\hat{\mathbf{r}}_i)
\end{aligned} \tag{A.2}$$

Note that there are two $A_{ph}^0(i)$'s for $l = 0$, they correspond to the two $\Phi_0(r_i)$'s, that is $\Phi_0(r_i) = \phi_0^2(r_i)$ and $\Phi_0(r_i) = \phi_1^2(r_i)$ respectively. $\Phi_1(r_i)$ and $\Phi_2(r_i)$ are obviously

given by $\Phi_1(r_i) = \phi_0(r_i)\phi_1(r_i)$ and $\Phi_2(r_i) = \phi_1^2(r_i)$. Now we consider the expansion of the Coulomb interaction. First we represent the Coulomb interaction through its Fourier representation

$$V = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2|} = \frac{e^2}{2\pi^2} \int \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2)] dk d\hat{\mathbf{k}} \quad (\text{A.3})$$

Now we expand the plane waves into spherical harmonics using the following formula

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_{lm} i^l j_l(kr) Y_{lm}(\hat{\mathbf{r}}) Y_{lm}^*(\hat{\mathbf{k}}). \quad (\text{A.4})$$

After we carry out the integration of the product of four spherical harmonics, we obtain the following formula for the Coulomb interaction

$$V = \sum_{JM} \left\{ \sum_{\substack{lL \\ l'L'}} V_{lL,l'L'}^J(r_1, r_2) [Y_l(\hat{\mathbf{r}}_1) \otimes Y_L(\hat{\mathbf{R}}_1)]_{JM} [Y_{l'}(\hat{\mathbf{r}}_2) \otimes Y_{L'}(\hat{\mathbf{R}}_2)]_{JM}^* \right\} \quad (\text{A.5})$$

with $V_{lL,l'L'}^J(r_1, r_2)$ defined by

$$V_{lL,l'L'}^J(r_1, r_2) = \frac{32\pi}{2J+1} \sqrt{(2l+1)(2L+1)(2l'+1)(2L'+1)} \\ C_{l0l0}^{J0} C_{l'0l'0}^{J0} i^{l+L-l'-L'} \int j_l(kr_1) j_L(kR_1) j_{l'}(kr_2) j_{L'}(kR_2) dk \quad (\text{A.6})$$

We have used the definition for the tensor product

$$[Y_{l_1}(\hat{\mathbf{r}}_1) \otimes Y_{l_2}(\hat{\mathbf{r}}_2)]_{JM} = \sum_{m_1 m_2} C_{l_1 m_1 l_2 m_2}^{JM} Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2). \quad (\text{A.7})$$

The quantities inside the curl bracket define the multipolar expansion of the Coulomb interaction. The quantum numbers JM define the multipolarity of the plasmons when we calculate the response functions. Since C_{60} has spherical symmetry, all the matrix elements are the same for a given J and different M 's. The matrices using (lL) and $(l'L')$ as their indices for different J 's are

$$\begin{array}{ll}
J = 0 & 4 \times 4 \\
J = 1 & 6 \times 6 \\
J \geq 2 & 7 \times 7
\end{array}$$

Now we will find the RPA Green's function G . First G^0 can be put in the following form

$$G_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{ph} \sum_{l_1 i} A_{ph}^{l_1}(i) \Phi_{l_1}(r_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \sum_{l_2 j} A_{ph}^{*l_2}(j) \Phi_{l_2}(r_j) \quad (\text{A.8})$$

Now we proceed to solve the RPA equation for a particular multipole JM by expansion.

$$\begin{aligned}
G^0 V G^0 &= \sum_{ph} \sum_{l_1 i} A_{ph}^{l_1}(i) \Phi_{l_1}(r_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \\
&\int \sum_{l_2 j} A_{ph}^{*l_2}(j) \Phi_{l_2}(r_j) \sum_{L_2 L_3} V_{l_2 L_2, l_3 L_3}^J(r_j, r_k) \left[Y_{l_2}(\hat{\mathbf{r}}_j) \otimes Y_{L_2}(\hat{\mathbf{R}}_j) \right]_{JM}^* \\
&\left[Y_{l_3}(\hat{\mathbf{r}}_k) \otimes Y_{L_3}(\hat{\mathbf{R}}_k) \right]_{JM} \sum_{p_1 h_1} \sum_{l_3 k} A_{p_1 h_1}^{l_3}(k) \Phi_{l_3}(r_k) dr_j dr_k d\hat{\mathbf{r}}_j d\hat{\mathbf{r}}_k \\
&\frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} \sum_{l_4 m} A_{p_1 h_1}^{*l_4}(m) \Phi_{l_4}(r_m) \\
&= \sum_{ph} \sum_{l_1 i} A_{ph}^{l_1}(i) \Phi_{l_1}(r_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \sum_{\substack{l_2 L_2 \\ l_3 L_3}} B_{ph}^{*l_1 2L_2} \\
&D^{l_2 L_2, l_3 L_3} B_{p_1 h_1}^{l_3 L_3} \frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} \sum_{p_1 h_1} \sum_{l_4 j} A_{p_1 h_1}^{l_4}(j) \Phi_{l_4}(r_j) \quad (\text{A.9})
\end{aligned}$$

Here

$$B_{ph}^{lL} = \sum_i \int A_{ph}^l(i) \left[Y_l(\hat{\mathbf{r}}_i) \otimes Y_L(\hat{\mathbf{R}}_i) \right]_{JM} d\hat{\mathbf{r}}_i \quad (\text{A.10})$$

for fixed JM and $D^{l_1 L_1, l_2 L_2}$ is defined by

$$D^{l_1 L_1, l_2 L_2} = \int \Phi_{l_1}(r_{i_1}) \Phi_{l_2}(r_{i_2}) V_{l_1 L_1, l_2 L_2}^J(r_1, r_2) dr_1 dr_2 \quad (\text{A.11})$$

Note that some arguments of the summation notation $\sum$ come before it, this is to ensure each block in the formulas has a clear meaning. Next we consider

$$\begin{aligned}
G^0 V G^0 V G^0 &= \sum_{ph} \sum_{l_1 i} A_{ph}^{l_1}(i) \Phi_{l_1}(r_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} B_{ph}^{*l_2 L_2} \\
D^{l_2 L_2, l_3 L_3} \sum_{p_1 h_1} B_{p_1 h_1}^{l_3 L_3} \frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} B_{p_1 h_1}^{*l_4 L_4} D^{l_2 L_2, l_3 L_3} \\
\sum_{p_2 h_2} \sum_{l_5 j} B_{p_2 h_2}^{l_5 L_5} \frac{2(\varepsilon_{p_2} - \varepsilon_{h_2})}{(\varepsilon_{p_2} - \varepsilon_{h_2})^2 - (\omega + i\eta)^2} A_{p_2 h_2}^{*l_6}(j) \Phi_{l_6}(r_j) = \\
\sum_{ph} \sum_{l_1 i} A_{ph}^{l_1}(i) \Phi_{l_1}(r_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} B_{ph}^{*l_2 L_2} D^{l_2 L_2, l_3 L_3} \\
E^{l_3 L_3, l_4 L_4} D^{l_4 L_4, l_5 L_5} \sum_{p_1 h_1} \sum_{l_6 j} B_{p_1 h_1}^{l_5 L_5} \frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} B_{p_1 h_1}^{l_6}(j) \Phi_{l_6}(r_j) \quad (A.12)
\end{aligned}$$

And $E^{l_1 L_1, l_2 L_2}$ is defined as

$$E^{l_1 L_1, l_2 L_2} = \sum_{ph} B_{ph}^{l_1 L_1} \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} B_{ph}^{*l_2 L_2} \quad (A.13)$$

Now the structure of the expansion is clear, in the middle we have

$$U_{eff} = D - DED + DEDED - \dots = D \frac{1}{1 + ED} \quad (A.14)$$

So we have

$$\begin{aligned}
G &= \sum_{ph} \sum_{l_1 i} A_{ph}^{l_1}(i) \Phi_{l_1}(r_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \sum_{l_2 j} A_{ph}^{*l_2}(j) - \\
&\sum_{ph} \sum_{l_1 i} A_{ph}^{l_1}(i) \Phi_{l_1}(r_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \sum_{\substack{l_2 L_2 \\ l_3 L_3}} B_{ph}^{l_2 L_2} U_{eff}^{l_2 L_2, l_3 L_3} \\
&\sum_{p_1 h_1} \sum_{l_4 j} B_{p_1 h_1}^{l_3 L_3} \frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} A_{p_1 h_1}^{*l_4}(j) \Phi_{l_4}(r_j) \quad (A.15)
\end{aligned}$$

When we look the response to an external field $F(r_i)$, we need to calculate

$$g(p, h) = \sum_i \int A_{ph}^l(i) \Phi_l(r_i) F(\mathbf{r}_i) d\mathbf{r}_i d\hat{\mathbf{r}}_i \quad (A.16)$$

Then the response is determined by

$$\begin{aligned}
\langle F(\mathbf{r})|G(\mathbf{r}, \mathbf{r}')|F(\mathbf{r}') \rangle &= \sum_{ph} g(p, h) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} g^*(p, h) - \\
&\sum_{ph} \sum_{\substack{l_1 L_1 \\ l_2 L_2}} \left[g(p, h) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} B_{ph}^{*l_1 L_1} \right] U_{eff}^{l_1 L_1, l_2 L_2} \\
&\sum_{p_1 h_1} \left[B_{p_1 h_1}^{*l_2 L_2} \frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} g^*(p_1, h_1) \right]
\end{aligned} \tag{A.17}$$

We use $\mathbf{r}'$ to denote the real coordinate, $\mathbf{R}$ the ion coordinate, $\mathbf{r}$ coordinate relative to the ion, i.e. $\mathbf{r}' = \mathbf{R} + \mathbf{r}$. Then the external field is denoted by $r'^J Y_{JM}(\hat{\mathbf{r}}')$ (for $J = 0$, we use $r'^2 Y_{00}(\hat{\mathbf{r}}')$). In order to do the integration over $\mathbf{r}$, we rewrite the multipolar field in terms of the ion coordinate R and the relative coordinate r .

$$\begin{aligned}
r'^J Y_{JM}(\hat{\mathbf{r}}') &= R^J Y_{JM}(\hat{\mathbf{R}}) + \sqrt{\frac{4\pi J(2J+1)}{3}} R^{J-1} r \sum_{m_1} C_{1m_1 J-1 M-m_1}^{JM} \\
&Y_{1m_1}(\hat{\mathbf{r}}) Y_{J-1, M-m_1}(\hat{\mathbf{R}}) + \sqrt{\frac{2\pi(J-1)J(2J-1)(2J+1)}{15}} R^{J-2} r^2 \\
&\sum_{m_1} C_{2m_1 J-2 M-m_1}^{JM} Y_{2m_1}(\hat{\mathbf{r}}) Y_{J-2, M-m_1}(\hat{\mathbf{R}}) + \dots
\end{aligned} \tag{A.18}$$

The terms with $l > 3$ have no contributions to the response function since the maximum angular momentum of site transition is $l = 2$. For $l = 0$, $F(\mathbf{r}') = r'^2 Y_{00}(\mathbf{r}')$ and the expansion is given by

$$\begin{aligned}
r'^2 Y_{00}(\mathbf{r}') &= \frac{1}{\sqrt{4\pi}} (R^2 + r^2 + 2\mathbf{R} \cdot \mathbf{r}) = \frac{1}{\sqrt{4\pi}} R^2 + \\
&\frac{1}{\sqrt{4\pi}} r^2 + \frac{2\sqrt{4\pi}}{3} Rr \sum_{\mu} Y_{1\mu}(\hat{\mathbf{R}}) Y_{1\mu}^*(\hat{\mathbf{r}})
\end{aligned} \tag{A.19}$$

Now the calculation of $g(p, h)$ is relatively simple, and we will not write down the formulas. In the Born approximation the differential cross section for inelastic electron scattering is

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{e^2 m}{\hbar^2} \right)^2 \frac{4p'}{pq^4} S(\omega, \mathbf{q}), \tag{A.20}$$

where p and p' are the initial and final linear momenta of the electron, $\mathbf{q} = \mathbf{p} - \mathbf{p}'$ is the transferred linear momentum, m the mass of the electron, ω the energy of the excited state and $S(\omega, \mathbf{q})$ is the spectral function (or the dynamical structure factor) of the cluster, which depends solely on the properties of the cluster and is given by

$$S(\omega, \mathbf{q}) = \frac{1}{\pi} \text{Im} \int \exp(i\mathbf{q} \cdot \mathbf{r}) G(\mathbf{r}, \mathbf{r}'; \omega) \exp(-i\mathbf{q} \cdot \mathbf{r}') dr d\Omega dr' d\Omega'. \quad (\text{A.21})$$

In order to do the integration, we expand $\exp(i\mathbf{q} \cdot \mathbf{r})$ and $\exp(-i\mathbf{q} \cdot \mathbf{r}')$ into spherical harmonics,

$$\exp(i\mathbf{q} \cdot \mathbf{r}) = 4\pi \sum_{lm} i^l j_l(qr) Y_{lm}(\hat{\mathbf{r}}) Y_{lm}^*(\hat{\mathbf{q}}). \quad (\text{A.22})$$

$$\exp(-i\mathbf{q} \cdot \mathbf{r}') = 4\pi \sum_{lm} (-i)^l j_l(qr') Y_{lm}^*(\hat{\mathbf{r}}') Y_{lm}(\hat{\mathbf{q}}) \quad (\text{A.23})$$

Now $j_l(qr) Y_{lm}(\hat{\mathbf{r}})$ acts as the external field in the calculation of the structure factor as $r'^J Y_{JM}(\hat{\mathbf{r}}')$ does in the calculation of the response function. Once again, we express $j_l(qr) Y_{lm}(\hat{\mathbf{r}})$ in terms of functions of coordinates of R and r using the following formula,

$$j_L(qr') Y_{LM}(\hat{\mathbf{r}}) = \frac{4\pi}{2L+1} \sum_{l_1 l_2=0}^{\infty} i^{l_1+l_2-L} \sqrt{(2l_1+1)(2l_2+1)} C_{l_1 m_1 l_2 m_2}^{l_2 m_2} j_{l_1}(qr) j_{l_2}(qR) [Y_{l_1}(\hat{\mathbf{r}}_1) \otimes Y_{l_2}(\hat{\mathbf{R}}_1)]_{LM} \quad (\text{A.24})$$

Now we can define a similar $g_L(p, h)$ for each multipole L , then $S(\omega, q, L)$ is defined by

$$\begin{aligned} S(\omega, q, L) &= \sum_{ph} g(p, h) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} g^*(p, h) - \\ &\sum_{ph} \sum_{\substack{l_1 L_1 \\ l_2 L_2}} g(p, h) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} B_{ph}^{*l_1 L_1} U_{eff}^{l_1 L_1, l_2 L_2} \\ &\sum_{p_1 h_1} B_{p_1 h_1}^{*l_1 L_1} \frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} g(p_1, h_1) \end{aligned} \quad (\text{A.25})$$

Since

$$\sum_{M=-L}^L 4\pi i^L Y_{LM}^*(\hat{\mathbf{q}}) 4\pi (-i)^L Y_{LM}(\hat{\mathbf{q}}) = 4\pi(2L+1) \quad (\text{A.26})$$

We may omit $4\pi i^L Y_{LM}(\hat{\mathbf{q}})$ and the summation over m everywhere in the formulas, and include a factor $4\pi(2L+1)$ in our final formula for the cross section. The differential cross section is given by

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{e^2 m}{\hbar^2}\right)^2 \frac{4p'}{pq^4} \sum_{L=0}^{Lmax} 4\pi(2L+1) S(\omega, q, L) \quad (\text{A.27})$$

We take $Lmax = 20$ in our calculations.

Appendix B

Multipolar Responses for C₂₀, 70, 100

Once again the particle-hole state is reproduced here,

$$\begin{aligned}
 \langle \mathbf{r} | ph \rangle = & \sqrt{\frac{1}{4\pi}} \sum_i \left[f_p(\mathbf{R}_i) f_h(\mathbf{R}_i) \phi_0^2(r_i) + \mathbf{g}_p(\mathbf{R}_i) \cdot \mathbf{g}_h(\mathbf{R}_i) \phi_1^2(r_i) \right] Y_{00}(\hat{\mathbf{r}}_i) + \\
 & \sqrt{\frac{1}{4\pi}} \sum_{im} (-1)^m \left[f_p(\mathbf{R}_i) g_{h,-m}(\mathbf{R}_i) + f_h(\mathbf{R}_i) g_{p,-m}(\mathbf{R}_i) \right] \phi_0(r_i) \phi_1(r_i) Y_{1m}(\hat{\mathbf{r}}_i) + \\
 & \sqrt{\frac{3}{10\pi}} \sum_{im} (-1)^m \left[\mathbf{g}_p(\mathbf{R}_i) \times \mathbf{g}_h(\mathbf{R}_i) \right]_{2,-m} \phi_1^2(r_i) Y_{2m}(\hat{\mathbf{r}}_i) \\
 = & \sum_{lmi} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i)
 \end{aligned} \tag{B.1}$$

The quantities $A_{ph}^{lm}(\mathbf{R}_i)$'s are defined as

$$A_{ph}^{00}(\mathbf{R}_i) = \sqrt{\frac{1}{4\pi}} f_p(\mathbf{R}_i) f_h(\mathbf{R}_i)$$

$$A_{ph}^{00}(\mathbf{R}_i) = \sqrt{\frac{1}{4\pi}} \mathbf{g}_p(\mathbf{R}_i) \cdot \mathbf{g}_h(\mathbf{R}_i)$$

$$A_{ph}^{1m}(\mathbf{R}_i) = (-1)^m \sqrt{\frac{1}{4\pi}} \left[f_p(\mathbf{R}_i) g_{h,-m}(\mathbf{R}_i) + f_h(\mathbf{R}_i) g_{p,-m}(\mathbf{R}_i) \right]$$

$$A_{ph}^{2m}(\mathbf{R}_i) = (-1)^m \sqrt{\frac{3}{10\pi}} \left[\mathbf{g}_p(\mathbf{R}_i) \times \mathbf{g}_h(\mathbf{R}_i) \right]_{2,-m}$$

Note that there are two $A_{ph}^{00}(\mathbf{R}_i)$'s for $(lm) = (00)$, they correspond to the two $\Phi_0(r_i)$'s, that is $\Phi_0(r_i) = \phi_0^2(r_i)$ and $\Phi_0(r_i) = \phi_1^2(r_i)$ respectively. In order to keep the number of indices in the formulas to a minimum, we did not introduce another index for this distinction, $\Phi_1(r_i)$ and $\Phi_2(r_i)$ are given by $\Phi_1(r_i) = \phi_0(r_i)\phi_1(r_i)$ and $\Phi_2(r_i) = \phi_1^2(r_i)$.

Using the notation in eq. (B.1) for the particle-hole state $< \mathbf{r}|ph >$, we can put the single particle Green's function in the following form,

$$G_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{ph} \sum_{\substack{lm \\ l'm'}} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} A_{ph}^{*l'm'}(\mathbf{R}_{i'}) \Phi_{l'}(r_{i'}) Y_{l'm'}^*(\hat{\mathbf{r}}_{i'}) \quad (\text{B.2})$$

The matrix elements of the Coulomb interaction are computed through its Fourier representation, but this time we treat $\mathbf{R}_1 - \mathbf{R}_2$ as a single vector instead of treating $\mathbf{R}_1$ and $\mathbf{R}_2$ as two separate vectors.

$$\begin{aligned} V &= \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2|} = \frac{e^2}{2\pi^2} \int \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_1 - \mathbf{R}_2)] dk d\hat{\mathbf{k}} \\ &= \frac{(4\pi)^3 e^2}{2\pi^2} \int \sum_{lm} i^l j_l(kr_1) Y_{lm}(\hat{\mathbf{r}}_1) Y_{lm}^*(\hat{\mathbf{k}}) \sum_{l'm'} i^{-l'} j_{l'}(kr_2) Y_{l'm'}^*(\hat{\mathbf{r}}_2) Y_{l'm'}(\hat{\mathbf{k}}) \\ &\quad \sum_{LM} i^L j_L(kR_{12}) Y_{LM}(\hat{\mathbf{R}}_{12}) Y_{LM}^*(\hat{\mathbf{k}}) dk d\hat{\mathbf{k}} \end{aligned} \quad (\text{B.3})$$

After the integration over $\hat{\mathbf{k}}$ of the product of three spherical harmonics is carried out, one obtains

$$\begin{aligned} V &= \sum_{\substack{l'l' \\ mm'M}} B_{lm,l'm'}^{LM} Y_{lm}(\hat{\mathbf{r}}_1) Y_{l'm'}^*(\hat{\mathbf{r}}_2) Y_{LM}(\hat{\mathbf{R}}_{12}) \\ &\quad \int j_l(kr_1) j_{l'}(kr_2) j_L(kR_{12}) dk, \end{aligned} \quad (\text{B.4})$$

where $B_{lm,l'm'}^{LM}$ is defined as

$$B_{lm,l'm'}^{LM} = i^{l+L-l'} 32\pi e^2 \sqrt{\frac{(2l+1)(2L+1)}{4\pi(2l'+1)}} C_{l0L0}^{l'0} C_{lmLM}^{l'm'}.$$

Now we will consider the expansion of the integral equation $G = G_0 - G_0 V G$. First we will consider

$$\begin{aligned}
G_0 V G_0 &= \sum_{\substack{ph \\ p'h'}} \sum_{\substack{lmi \\ l'm'i'}} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \\
&\sum_{\substack{l_1 m_1 i_1 \\ l_2 m_2 i_2}} A_{ph}^{*l_1 m_1}(\mathbf{R}_{i_1}) \sum_{LM} B_{l_1 m_1, l_2 m_2}^{LM} \int \Phi_{l_1}(r_{i_1}) j_{l_1}(kr_{i_1}) \Phi_{l_2}(r_{i_2}) j_{l_2}(kr_{i_2}) j_L(kR_{i_1 i_2}) \\
&dr_{i_1} dr_{i_2} dk Y_{LM}(\hat{\mathbf{R}}_{i_1 i_2}) A_{p'h'}^{l_2 m_2}(\mathbf{R}_{i_2}) \frac{2(\varepsilon_{p'} - \varepsilon_{h'})}{(\varepsilon_{p'} - \varepsilon_{h'})^2 - (\omega + i\eta)^2} \\
&A_{p'h'}^{*l'm'}(\mathbf{R}_{i'}) \Phi_{l'}(r_{i'}) Y_{l'm'}^*(\hat{\mathbf{r}}_{i'}) = \sum_{\substack{ph \\ p'h'}} \sum_{\substack{lmi \\ l'm'i'}} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \\
&\frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \sum_{\substack{l_1 m_1 i_1 \\ l_2 m_2 i_2}} A_{ph}^{*l_1 m_1}(\mathbf{R}_{i_1}) D_{l_1 m_1 i_1, l_2 m_2 i_2} A_{p'h'}^{l_2 m_2}(\mathbf{R}_{i_2}) \\
&\frac{2(\varepsilon_{p'} - \varepsilon_{h'})}{(\varepsilon_{p'} - \varepsilon_{h'})^2 - (\omega + i\eta)^2} A_{p'h'}^{*l'm'}(\mathbf{R}_{i'}) \Phi_{l'}(r_{i'}) Y_{l'm'}^*(\hat{\mathbf{r}}_{i'}), \tag{B.5}
\end{aligned}$$

where the quantities $D_{l_1 m_1 i_1, l_2 m_2 i_2}$ are defined as follows

$$\begin{aligned}
D_{l_1 m_1 i_1, l_2 m_2 i_2} &= \sum_{LM} B_{l_1 m_1, l_2 m_2}^{LM} Y_{LM}(\hat{\mathbf{R}}_{i_1 i_2}) \\
&\int \Phi_{l_1}(r_{i_1}) j_{l_1}(kr_{i_1}) \Phi_{l_2}(r_{i_2}) j_{l_2}(kr_{i_2}) j_L(kR_{i_1 i_2}) dr_{i_1} dr_{i_2} dk.
\end{aligned}$$

Next we consider

$$\begin{aligned}
G_0 V G_0 V G_0 &= \sum_{\substack{ph \\ p'h'}} \sum_{\substack{lmi \\ l'm'i'}} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \\
&\sum_{\substack{l_1 m_1 i_1 \\ l_2 m_2 i_2}} A_{ph}^{*l_1 m_1}(\mathbf{R}_{i_1}) D_{l_1 m_1 i_1, l_2 m_2 i_2} \sum_{p_1 h_1} A_{p_1 h_1}^{l_2 m_2}(\mathbf{R}_{i_2}) \frac{2(\varepsilon_{p_1} - \varepsilon_{h_1})}{(\varepsilon_{p_1} - \varepsilon_{h_1})^2 - (\omega + i\eta)^2} \\
&\sum_{\substack{l_3 m_3 i_3 \\ l_4 m_4 i_4}} A_{p_1 h_1}^{*l_3 m_3}(\mathbf{R}_{i_3}) D_{l_3 m_3 i_3, l_4 m_4 i_4} A_{p'h'}^{l_4 m_4}(\mathbf{R}_{i_4}) \frac{2(\varepsilon_{p'} - \varepsilon_{h'})}{(\varepsilon_{p'} - \varepsilon_{h'})^2 - (\omega + i\eta)^2} A_{p'h'}^{*l'm'}(\mathbf{R}_{i'})
\end{aligned}$$

$$\begin{aligned}
\Phi_{l'}(r_{i'})Y_{l'm'}^*(\hat{\mathbf{r}}_{i'}) &= \sum_{\substack{ph \\ p'h'}} \sum_{\substack{lm_i \\ l'm'i'}} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \\
&\sum_{\substack{l_1 m_1 i_1 \\ l_4 m_4 i_4}} A_{ph}^{*l_1 m_1}(\mathbf{R}_{i_1}) \left(\sum_{\substack{l_2 m_2 i_2 \\ l_3 m_3 i_3}} D_{l_1 m_1 i_1, l_2 m_2 i_2} E_{l_2 m_2 i_2, l_3 m_3 i_3} D_{l_3 m_3 i_3, l_4 m_4 i_4} \right) \\
&A_{p'h'}^{l_4 m_4}(\mathbf{R}_{i_4}) \frac{2(\varepsilon_{p'} - \varepsilon_{h'})}{(\varepsilon_{p'} - \varepsilon_{h'})^2 - (\omega + i\eta)^2} A_{p'h'}^{*l'm'}(\mathbf{R}_{i'}) \Phi_{l'}(r_{i'}) Y_{l'm'}^*(\hat{\mathbf{r}}_{i'}), \tag{B.6}
\end{aligned}$$

where $E_{l_2 m_2 i_2, l_3 m_3 i_3}$ are defined as

$$E_{l_2 m_2 i_2, l_3 m_3 i_3} = \sum_{ph} A_{ph}^{l_2 m_2}(\mathbf{R}_{i_2}) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} A_{ph}^{*l_3 m_3}(\mathbf{R}_{i_3}).$$

If one continues to calculate the successive terms in the expansion of $G_0 V G$, one can see that the expansion involves higher and higher powers of the matrix product of E and D . Once the rule of the expansion is clear, $G = G_0 - G_0 V G$ can be solved as

$$\begin{aligned}
G &= \sum_{ph} \sum_{\substack{lm_i \\ l'm'i'}} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \\
&A_{ph}^{*l'm'}(\mathbf{R}_{i'}) \Phi_{l'}(r_{i'}) Y_{l'm'}^*(\hat{\mathbf{r}}_{i'}) - \sum_{\substack{ph \\ p'h'}} \sum_{\substack{lm_i \\ l'm'i'}} A_{ph}^{lm}(\mathbf{R}_i) \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \\
&\frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} \sum_{\substack{l_1 m_1 i_1 \\ l_2 m_2 i_2}} A_{ph}^{*l_1 m_1}(\mathbf{R}_{i_1}) \left(D \frac{1}{1 + ED} \right)_{l_1 m_1 i_1, l_2 m_2 i_2} \\
&A_{p'h'}^{l_2 m_2}(\mathbf{R}_{i_2}) \frac{2(\varepsilon_{p'} - \varepsilon_{h'})}{(\varepsilon_{p'} - \varepsilon_{h'})^2 - (\omega + i\eta)^2} A_{p'h'}^{*l'm'}(\mathbf{R}_{i'}) \Phi_{l'}(r_{i'}) Y_{l'm'}^*(\hat{\mathbf{r}}_{i'}). \tag{B.7}
\end{aligned}$$

From here on, the procedure to calculate the response functions is exactly the same as that detailed in Appendix A for C_{60} . Since we have to take into account the different orientations of the nonspherical clusters, we outline how to average over the directions of $\mathbf{q}$ in the following. $S(\omega, \mathbf{q})$ is given by

$$S(\omega, \mathbf{q}) = \frac{1}{\pi} \text{Im} \int \exp(i\mathbf{q} \cdot \mathbf{r}) G(\mathbf{r}, \mathbf{r}'; \omega) \exp(-i\mathbf{q} \cdot \mathbf{r}') d\mathbf{r} d\Omega d\mathbf{r}' d\Omega'. \tag{B.8}$$



This amounts to the following calculation

$$\begin{aligned}
\int \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \exp(i\mathbf{q} \cdot \mathbf{r}') dr d\Omega &= \exp(i\mathbf{q} \cdot \mathbf{R}_i) \int \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) \\
\exp(i\mathbf{q} \cdot \mathbf{r}_i) dr d\Omega &= \exp(i\mathbf{q} \cdot \mathbf{R}_i) \int \Phi_l(r_i) Y_{lm}(\hat{\mathbf{r}}_i) 4\pi \sum_{l'm'} i^{l'} j_{l'}(qr_i) \\
Y_{l'm'}^*(\hat{\mathbf{r}}_i) Y_{l'm'}(\hat{\mathbf{q}}) dr d\Omega &= 4\pi i^{l'} Y_{lm}(\hat{\mathbf{q}}) \exp(i\mathbf{q} \cdot \mathbf{R}_i) \int \Phi_l(r_i) j_l(qr_i)
\end{aligned} \tag{B.9}$$

It is obvious that only $Y_{lm}(\hat{\mathbf{q}}) \exp(i\mathbf{q} \cdot \mathbf{R}_i)$ and $Y_{l'm'}^*(\hat{\mathbf{q}}) \exp(-i\mathbf{q} \cdot \mathbf{R}_j)$ (we have two plane waves in the formula for $S(\omega, \mathbf{q})$) depend on the directions of $\mathbf{q}$. To average over $\hat{\mathbf{q}}$ is fairly simple and amounts to do the following integral,

$$\begin{aligned}
&\int Y_{lm}(\hat{\mathbf{q}}) \exp(i\mathbf{q} \cdot \mathbf{R}_i) Y_{l'm'}^*(\hat{\mathbf{q}}) \exp(-i\mathbf{q} \cdot \mathbf{R}_j) d\hat{\mathbf{q}} = \\
&\int Y_{lm}(\hat{\mathbf{q}}) Y_{l'm'}^*(\hat{\mathbf{q}}) \sum_{LM} 4\pi i^L j_L(qR_{ij}) Y_{LM}(\hat{\mathbf{q}}) Y_{LM}^*(\hat{\mathbf{R}}_{ij}) d\hat{\mathbf{q}} = \\
&\sum_{LM} 4\pi i^L j_L(qR_{ij}) Y_{LM}^*(\hat{\mathbf{R}}_{ij}) \sqrt{\frac{(2l+1)(2L+1)}{4\pi(2l'+1)}} C_{l0L0}^{l'0} C_{lmLM}^{l'm'}
\end{aligned} \tag{B.10}$$

Note that we have treated $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ as one vector.





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