



133
787
THS

ENTROPY, STRAIN AND THE
FERMI-DIRAC STATISTICS

THESIS FOR THE DEGREE OF M. A.

Guy Berry

1931

MICHIGAN STATE LIBRARIES



3 1293 01771 2005

Thermodynamics

Physics
Mathematics

ACKNOWLEDGEMENT

To Doctor William Scribner Kimball
without whose aid and suggestions
this paper could not have been
completed.

ENTROPY, STRAIN AND THE
FERMI-DIRAC STATISTICS

A Thesis
submitted to the Faculty of

MICHIGAN STATE COLLEGE
of
AGRICULTURE AND APPLIED SCIENCE

In partial fulfillment of the
Requirements for the Degree of
Master of Arts

by

Guy Berry

1931

93909

ENTROPY, STRAIN AND THE FERMI-DIRAC STATISTICS

I Introduction

Boltzmann's famous relation between the entropy S of a gas and W the probability of its state is given by*

$$(1) \quad S = k \log W + C.$$

Here k is Boltzmann's constant and C is a constant depending upon the zero from which entropy is to be measured. The probability W of the gaseous state is calculated rigorously in statistical mechanics by counting the "complexions" or possible arrangements of molecules in phase space. The product of the number of complexions each raised to a suitable power measures the probability, being a physical quantity called (for the sake of definiteness) the weight. This weight represents the W of equation (1) and forms the basis of entropy calculations in statistical mechanics.

There has recently been developed** a "geometrical weight method" based on a physical concept called the "range" or volume occupied per molecule in phase space. The geometrical weight method has been extended*** to include the new statistical mechanics of Einstein, Bose, Fermi, and Dirac. Problems usually handled by the classical statistical mechanics all seem within the scope of this new method. One important advantage is that Stirling's approximations and associated

* E. Bloch; The Kinetic Theory of Gases, p. 69.

** W. S. Kimball; Entropy and Probability, Journal of Physical Chemistry, vol. 33 (1929) p. 1558, hereafter referred to as, Kimball, Entropy and Probability.

***S. Chandrasekhar; On the Probability Method in the New Statistics, Philosophical Magazine, vol. 9 (1930) p. 621, hereafter referred to as Chandrasekhar.

difficulties* do not enter at all into this direct geometrical treatment. (Since factorials never enter). Another advantage is the geometrical picture of weight** which the method affords. This contrasts favorably with counting complexions to find the measure of thermodynamic probability.

The most noteworthy achievement of this geometrical weight method is the new explanation, which it suggests, of the second law of thermodynamics. By using this method it has been shown*** that the equilibrium equations which (by the Lagrange method of conditional maxima and minima) determine a state of maximum entropy and probability are equilibrium equations between stress and strain. Entropy then appears as k times the total strain Y .

$$(2) \quad S = k \log W + C = kY.$$

The second law of thermodynamics is accounted for as being due to the operation of these internal forces or stresses in velocity or momentum as well as ordinary space. The equilibrium state of maximum entropy is really the state of maximum strain brought about by these forces.

Accordingly the known equilibrium**** equations that lead to the Maxwell-Boltzmann distribution law may be put in the form

$$(3) \quad -W \frac{f'}{f} du_i = -\lambda m u_i du_i = W \frac{dr_i}{r_i}$$

* J. Rice; Statistical Mechanics, p. 282.

** Kimball; Entropy and Probability, sec. 8, Fig. 3.

*** W. S. Kimball; Entropy, Elastic Strain, the Second Law of Thermodynamics; etc., Journal of Physical Chemistry, vol. 35 (1931) p. 611, sec. 5, hereafter referred to as Kimball; Elastic Strain.

****R. C. Tolman; Statistical Mechanics, Chap. 4.

wherein the λ is an undetermined constant and the f is the Maxwell-Boltzmann distribution function. The r_i 's in the right member are the ranges* or intervals between successive molecules in velocity or momentum space, and the u_i 's are the x velocity components for each molecule.

$$(4) \quad r_i = u_{i+1} - u_i = \frac{1}{f(u_i)}$$

When λ is given its value $-\frac{W}{kT}$ in terms of the absolute temperature T , determined from the distribution function in the usual way**, equations (3) take the form of equilibrium between stress and strain*** acting in velocity or momentum space,

$$(5) \quad kT = \frac{m u_1 du_1}{\frac{dr_1}{r_1}} = \frac{m u_2 du_2}{\frac{dr_2}{r_2}} = \frac{m u_i du_i}{\frac{dr_i}{r_i}}.$$

In this thesis we extend the geometrical weight method to include real gases in which the volume is restricted according to Van der Waal's equation and the energy of molecules obeys the Pauli exclusion principle****. We find that the isothermal bulk modulus of gases obeying these restrictions is the same as that of the classical perfect gas provided molecular attractions are neglected. This holds true both for momentum space and ordinary space. Also the state of

* Kimball; Entropy and Probability, sec. 8.

** L. B. Loeb; Kinetic Theory of Gases, Chap. 4.

*** Kimball; Elastic Strain.

**** J. Rice; Statistical Mechanics, p. 277.

maximum weight or entropy for a given internal energy, again corresponds to a state of equilibrium between stress and strain acting in momentum space as well as ordinary space just as was the case for the gas law. The entropy again appears as k times the total strain in phase space. The velocity distribution function which these equations represent is the same Fermi-Dirac distribution as usually derived by the statistical method, and which Chandrasekhar has shown* can be derived by the geometrical weight method.

Perhaps the most important result of the present investigation is that it affords a step toward a mechanical explanation of the Pauli exclusion principle. We show that forces acting in momentum space exclude particles from occupied cells with the same vigor as they are excluded from the occupied positions in ordinary space as represented by Van der Waal's constant b . Thus Pauli's exclusion principle is explained in exactly the same way as the second law of thermodynamics. Each is the result of the objections** which groups of particles have toward compression in phase space. The corrections introduced by the Pauli exclusion principle show the degree of objection which particles feel when compression tends to put additional ones in an occupied phase volume. The mechanical vigor of the objections is the same in momentum space as in ordinary space as measured by the gas law and Van der Waal's equation.

* Chandrasekhar.

** Kimball; Elastic Strain, p. 620.

II The Bulk Modulus and the Stress-Strain Relations For Real Gases In Ordinary Space

From the gas law we calculate the isothermal bulk modulus by differentiation at constant temperature.

$$(6) \quad p = - \frac{dp}{\frac{dV}{V}} = n k T$$

Here p is the pressure, V the volume, and n is the number of molecules per C.C. Multiplying both numbers of equation (5) by n gives the modulus for stress and strain in momentum space.

$$(7) \quad p = \frac{n m u du}{\frac{dr}{r}} = n k T$$

It is interesting to note by comparing (6) and (7) that the modulus of elasticity for change in volume is the pressure, p , the same as for change in momentum space.

For real gases obeying Van der Waal's equation,

$$(p + \frac{a}{V^2})(V - b) = R T$$

the isothermal bulk modulus calculated as above takes a modified form.

$$(8) \quad p' = (p + \frac{a}{V^2}) = - \frac{dp'}{\frac{dV}{V - b}}$$

If we consider only repulsive forces due to impact the potential energy term $\frac{a}{V^2}$ due to molecular attractions drops out and Van der Waal's equation simplifies to

$$p(V-b) = RT.$$

The simplified equation gives

$$(9) \quad p = - \frac{\frac{dP}{dV}}{\frac{V-b}{F}} = \frac{dP}{\frac{F}{F} \left(1 - \frac{b}{V}\right)}$$

for the bulk modulus instead of expression (8). In the right member of equation (9) we let $V = \frac{N}{F}$ and $\frac{b}{N} = \frac{1}{B}$ for sake of later comparisons (see (14)). The expression (9) shows that, if molecular attractions are neglected and account taken only of molecular size, the modulus of elasticity p is the same as for gases obeying the gas law. Hence the incorporation of what might be called "the Van der Waal exclusion principle" has no effect on the modulus of elasticity.

III Entropy Strain, and Weight for Real Gases in Ordinary Space.

If we use the gas law and restrict attention to isothermal changes, the first law of thermodynamics gives the relation between entropy change and the work term

$$(10) \quad ds = \frac{da}{T} = \frac{p dv}{T} = R \frac{dv}{V}$$

The right member shows the relation between entropy and strain.

If we consider real gases represented by Van der Waal's equation and again restrict attention to isothermal changes, the work term will be modified,

$$(11) \quad dS = \frac{dQ}{T} = \left(p + \frac{a}{V^2}\right) \frac{dV}{T} = R \frac{dV}{V-b}.$$

The entropy is equal to the sum of the strains Y multiplied by Boltzmann's constant k .

$$(12) \quad S = R \int \frac{dV}{V-b} = R \log(V-b) + C = kY$$

It has been shown* for a perfect gas, in which molecules are mere points, how the range in ordinary space, $\frac{1}{n}$, the volume occupied per molecule, is related to the weight which measures the thermodynamic probability for one out of N particles. The N is the number of molecules in a gram molecule, the amount considered.

$$(13) \quad w = N \frac{1}{n} = V$$

For real gases, following the idea of Van der Waal's equation and his constant b , we see that the range instead of being $\frac{1}{n}$, will be restricted by the effective volume attributed to each molecule by whatever method is used in calculating b .

* Kimball; Entropy and Probability, p. 1567.

Thus

$$(14) \quad r = \frac{1}{n} - \lambda_1 = \frac{1}{n} - \frac{\lambda_1}{N} = \frac{1}{F} - \frac{1}{B}$$

is the range or volume which each particle has to itself being the previous range reduced by λ_1 , the effective volume displaced by its physical size. In the right member we let F , a constant distribution function, represent the number of particles per unit volume in ordinary space just as f represents the number per unit volume in momentum space. Also $B = \frac{1}{\lambda_1}$ is evidently the number of particles that could be packed into a unit volume in case there is no free motion. Hence the weight per molecule is

$$(15) \quad w = Nr = \frac{N}{n} - N\lambda_1 = V - \lambda = \frac{N}{F} \left(1 - \frac{F}{B}\right).$$

For N molecules the weight is

$$(16) \quad W = (V - \lambda)^N = \left(\frac{N}{F}\right)^N \left(1 - \frac{F}{B}\right)^N$$

which when substituted in Boltzmann's equation gives

$$(17) \quad dS = Nk \frac{dV}{V - \lambda}$$

and

$$(18) \quad S = k \log W + C = Nk \log (V - b) + C = kY.$$

The expression (17) checks equation (11) and the entropy strain equation (2) shown* to hold for gases obeying the gas law. It will be observed that b and B represent the fact that only one particle at a time can occupy a volume displaced by its physical dimensions. We might refer to this as the Van der Waal exclusion principle by analogy with or perhaps a part of the Pauli exclusion principle which excludes extra particles from an occupied cell in phase space.

IV Entropy Strain, and Weight for Real Gases In Velocity and Momentum Space.

As in the classical statistics the number of particles in a unit volume of velocity or momentum space is also represented by a distribution function

$$(19) \quad \frac{dn}{d\omega} = f(u, v, w) = n_i = \frac{1}{v_i}$$

wherein $d\omega = du dv dw$ is a volume element in the space, and u , v , and w are the velocity components. The volume occupied by a particle at this place in velocity space is given by the reciprocal of this number as indicated. Where the gas law applies this volume equals the range $(\mathcal{V} = \mathcal{V}_i)$ that leads to the classical distribution law**. It has to be multiplied by N to give the weight per molecule, and the product for N molecules gives the total weight W being related to entropy

* Kimball; Elastic Strain.

** Kimball; Entropy and Probability.

and the Maxwell-Boltzmann law in the familiar way*.

For real gases we restrict the range given by (19) according to the Pauli exclusion principle. Thus

$$(20) \quad r_i = \frac{1}{n_i} - a_i = \frac{1}{f} - \frac{1}{A} = v_i - a_i = \frac{1}{g_i}$$

is the free empty range left to a particle at that place in velocity or momentum space after deducting a_i , the minimum range it can occupy. Here $A = \frac{1}{a_i}$ is evidently the number of such minimum ranges or cells in a unit volume of momentum space, being the usual symbol** used to represent the Pauli exclusion principle. Equation (20) is seen to be identical with (14) except that it applies to velocity or momentum space instead of ordinary space, and suggests possible physical relationship between the Pauli exclusion principle and the Van der Waal exclusion principle".

A causal relationship between these two has already been considered*** and then dismissed**** by Ehrenfest. The present treatment, shows that both are due to same cause, i.e. modus operandi of elastic forces in a restricted phase space. This of course merely takes us another step forward in explanation towards the ultimate "1st cause".

* Kimball; Entropy and Probability.

** Chandrasekhar.

*** P. Ehrenfest; Relation between the Reciprocal Impenetrability of Matter and Pauli's Exclusion Principle, Nature, vol. 119 (1927) p. 196.

**** P. Ehrenfest; Relation between the Reciprocal Impenetrability of Matter and Pauli's Exclusion Principle, Nature, vol. 119 (1927) p. 602.

Thus we see that $G_i = \frac{1}{A}$ is like $\mathcal{V}_i = \frac{V}{N} = \frac{1}{\rho}$, the latter being the volume in ordinary space that a particle must occupy to the exclusion of other particles by virtue of its very physical existence.

Having obtained the expression for range we multiply this by N to give the weight per molecule which measures the probability that any one of N molecules may occupy this particular range, thus

$$(21) \quad w = N r_i = \frac{N}{f_i} \left(1 - \frac{f_i}{A}\right) = \frac{N}{g_i}$$

and for N molecules the weight is

$$(22) \quad W = N^N (r_1 r_2 \dots r_N) = N^N \left(\frac{1 - \frac{f_1}{A}}{f_1}\right) \left(\frac{1 - \frac{f_2}{A}}{f_2}\right) \dots = \frac{N^N}{g_1 g_2 \dots g_N}$$

where the g 's are the reciprocals of the ranges. Substitution in Boltzmann's equation as before gives the entropy.

$$(23) \quad S = k \log W + C = k \left(\log N^N + \sum_{i=1}^N \log r_i \right) + C = k \int \frac{d r_i}{r_i} = k Y$$

Equations (21) and (22) have been given by Chandrasekhar*. They are here shown in terms of the free range (20) left to a particle after the volume $G_i = \frac{1}{A}$ which it displaces in momentum space is deducted according to Pauli's exclusion principle. It is significant that the weight is still N^N times the product of the free ranges reserved to the particles

* Chandrasekhar.

in momentum space, and the entropy is the sum of the corresponding strains exactly as it was in the case of a gas obeying the gas law.

Although the argument of this section refers to velocity or momentum space it may be generalized to include phase space (action space) and leads to formulas of the same form as (21) (22) and (23).

V The Equilibrium Equations for Stress and Strain in the Fermi-Dirac Statistics.

To find the maximum value of W subject to a constant energy, E , we use the method of Lagrange. The function ϕ is formed by adding E times an undetermined constant λ , to W ; $\phi = W + \lambda E$. Take N partial derivatives of the now N independent u 's, and set each partial derivative equal to zero.

$$(24) \quad \frac{\partial \phi}{\partial u_i} = \frac{\partial W}{\partial u_i} + \lambda \frac{\partial E}{\partial u_i} = -W \frac{d}{du_i} \log f_i + \lambda m u_i = 0$$

But in view of (20)

$$(25) \quad W \frac{du_i}{u_i} + \lambda m u_i du_i = -W \frac{df_i}{f_i} + \lambda m u_i du_i$$

wherein the partial derivatives are taken with respect to the X velocity component of each molecule. Equation (25) shows that there is a constant ratio, namely,

$$(26) \quad -\frac{W}{\lambda} = \frac{m u_i du_i}{\frac{du_i}{u_i}} = \frac{m u_i du_i}{\frac{dr_i}{r_i}} = -\frac{m u_i du_i}{\frac{dr_i}{r_i} \left(1 - \frac{f_i}{A}\right)}$$

between energy change per molecule (between successive molecules) and the corresponding strain just as was shown to be the case for the Maxwell-Boltzmann distribution. This ratio is of course the elastic modulus per molecule. To find its value we substitute in (26) the value of the λ determined by the integrals

$$(27) \quad 2 \int_0^{\infty} f(u) du = 1, \quad 2 \int_0^{\infty} \epsilon_i f(u) du = E$$

wherein

$$(28) \quad f(u) = \frac{1}{C e^{-\frac{\lambda m u}{2W}} - \frac{1}{A}}$$

is determined from (25) and the ϵ_i is the energy associated with each molecule. The determination of C from these integrals presents difficulties which do not concern equation (26). The λ however which appears in the exponential term of equation (28) is required* by thermodynamics to have the value $-\frac{W}{KT}$. It follows that $f(u)$ given by (28) will have the same form as the Fermi-Dirac distribution law. This formula of the new statistics is thus derived by the geometrical weight method as already shown by Chandrasekhar**. Substituting $-\frac{W}{KT}$ for λ in equation (26) gives the elastic modulus in terms of mean values of u and r:

$$(29) \quad K = \frac{m u du}{\frac{dr}{r}} = - \frac{m u du}{\frac{dF}{T} \left(1 - \frac{F}{A}\right)}.$$

* J. Rice; Statistical Mechanics, p. 274.

**Chandrasekhar.

Multiplying both members of equation (29) by n gives

$$(30) \quad p = nkT = \frac{n m u \, du}{\frac{d\tau}{\tau}} = - \frac{n m u \, du}{\frac{df}{f} \left(1 - \frac{f}{A}\right)}$$

These formulas are like (6) and (7) and show that in the case of the Fermi-Dirac statistics as well as the classical law, the elastic modulus per molecule is kT . For a unit volume it is equal to the pressure ($nkT = p$). Likewise the elastic modulus appearing in equation (30) is the same as that in (9) which refers to real gases in ordinary space. Now (9) represents real gases in which the Van der Waal constant b restricts the volume and no intermolecular attractions are considered. Thus there appears a striking parallelism (as represented by (29) and (30) on the one hand and (9) on the other) between the behavior of molecules in velocity space and ordinary space. In both types of space molecules "object" to being crowded together with the same vigor (same modulus of elasticity) whether their range is curtailed by the Pauli exclusion principle or the Van der Waal exclusion principle. Furthermore this resistance to compression is the same in each case as for the simple theory in which the exclusion principles are neglected*.

VI Intermolecular Attractive Forces.

On the other hand the elastic modulus given by equation (7) is not the same as in the other cases, since here

* Kimball; Elastic Strain, p. 620.

intermolecular attractions are considered. It is recognized* in connection with the new statistics that the Fermi-Dirac distribution law, with the negative correction term $(-\frac{f}{A})$ appearing in (21) and (22), corresponds experimentally to the case of an extra repulsion between particles, and is well verified by a gas of electrons or protons. Where attractive forces exist as with neutral molecules, the Bose-Einstein statistics ought to hold. If we were to introduce attractive forces into equilibrium equations like (24) and (25), it seems likely that they would correspond to the new statistical expressions for weight like (21) and (22) except with a positive correction term $(+\frac{f}{A})$. Such changes** give the Bose-Einstein statistics which can probably be fitted into the stress-strain, ~~and~~ entropy theory. The present treatment, however, considers only the repulsions corresponding to the Pauli exclusion principle.

VII Experimental Verification.

The most important verification of the stress strain relations and the allied entropy strain equations (2), (18), and (23) is that they afford a natural and obvious explanation*** of the second law of thermodynamics. The "ergodic" hypothesis, on the other hand, has proven quite unsatisfactory to most physicists****.

* P. Ehrenfest and J. R. Oppenheimer; Note on the Statistics of Nuclei, Physical Reviews, vol. 33 (1931) p. 333.

** Chandrasekhar.

*** Kimball; Elastic Strain, sec. 7.

****R. C. Tolman; Statistical Mechanics, p. 39.

The present viewpoint illuminates the heretofore unexplained Pauli exclusion principle. Not only is there a striking analogy between the equilibrium equation (9) for ordinary space and (29) and (30) for momentum space, but the modulus of elasticity is the same for the two cases, indicating the operation of the same mechanical causes in the two realms. Even the exclusion of occupied regions in the two cases introduces the correction terms ($\frac{A}{N} = \frac{1}{B}$ for Van der Waal's equation, and $\frac{1}{A}$ for the Pauli exclusion principle) in an exactly analogous way. This shows that their mechanical effect in these force equations is of the same type.

The operation of the Pauli exclusion principle is explained in exactly the same way as the second law of thermodynamics. Each of these is mechanically accounted for by the operation of forces acting in momentum space. They are a measure of the force which excludes particles from occupied cells in momentum space. The correction term given by the Pauli exclusion principle expresses the degree of the objection to forces tending to put particles in occupied phase positions.

Furthermore it is worthy of mention that the fundamental relations of the Fermi-Dirac statistics are obtained without the usual technical rules for counting complexions and the associated difficulties. It is significant that the two points which the statistical method does not explain, namely, the second law of thermodynamics and the Pauli exclusion principle, are explained by the present mechanical stress strain theory.

Bibliography

- E. Bloch; The Kinetic Theory of Gases
- W. S. Kimball; Entropy and Probability, Journal of Physical Chemistry, vol. 33 (1929) p. 1558.
- W. S. Kimball; Entropy, Elastic Strain, the Second Law of Thermodynamics, etc., Journal of Physical Chemistry, vol. 35 (1931) p. 611.
- S. Chandrasekhar; On the Probability Method in the New Statistics, Philosophical Magazine, vol. 9 (1930) p. 621.
- J. Rice; Statistical Mechanics.
- R. G. Tolman; Statistical Mechanics.
- L. B. Loeb; Kinetic Theory of Gases.
- P. Ehrenfest; Relation between the Reciprocal Impenetrability of Matter and Pauli's Exclusion Principle, Nature, vol. 119 (1927) p. 196.
- P. Ehrenfest; Relation between the Reciprocal Impenetrability of Matter and Pauli's Exclusion Principle, a Correction, Nature, vol. 119 (1927) p. 602.
- P. Ehrenfest and J. R. Oppenheimer; Note on the Statistics of Nuclei, Physical Reviews, vol. 33 (1931) p. 333.

MICHIGAN STATE UNIV. LIBRARIES



31293017712005