An attempt to separate the long and short range forces by Gaussian method

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In the study of phase transition problems, short range forces (SRF) play a dominant role. A constructive and rigorous study of the effects of short range forces has yet to be given. It is suggested in the present paper that by separating long range forces (LRF) from the short range forces, it would be possible to estimate contributions to the virial expansion of the collective oscillations due to short range forces. The method of Stratonovich *or* the functional integration technique is employed in the treatment of the interaction term of the partition function.

I. INTRODUCTION

In the present paper an explicit form of $V(r)$ is irrelevant since no particular physical system is under investigation. Our problem is concerned with the mathematics of this technique leading to an explicit expression of the SR and LR terms of the $V(r)$. From there on, it is hoped we shall be in a position to study specific physical problems with definite forms of $V(r)$ for solids, liquids, and gases leading to a new study of first and second order phase transition or order–disorder transitions.[1]

The problem of obtaining thermodynamic properties of a system with long range interaction (LRF) is confronted in many branches of physics, e.g., in plasma or in electrolyte theory.[2,3,4] Such forces cannot be treated in the same way as short range forces (SRF), since a straightforward calculation of the virial coefficients leads to a divergent answer so that either the divergent virial series has to be manipulated into a finite answer or a different approach has to be applied as in the Debye–Huckel electrolyte theory.[5,6] These methods have a number of setbacks especially when we need accuracy greater than 1st approximation and it is therefore necessary to produce or invent a method which gives the higher order corrections in a simple way and also present the possibility of investigating these systems at high densities, solids. A system with purely LRF has both mathematical and physical drawbacks since mathematically, the grand partition function will have an essential singularity when treated as a function of interaction terms or of temperature and will only exist in the absence of attractive forces. But physically, for example in an electrolyte, forces change their nature drastically at short distances.

The Gaussian method or the functional integration technique has application to a fairly wide class of statistical mechanics problems[7]; the great sucess of statistical mechanics is invariably associated with systems in which interaction between the particles is either neglected or can be transformed away.[8] Systems under conditions in which interaction plays an essential role are vastly more difficult to analyze rigorously and meaningful approximations are hard to

obtain. Unfortunately almost all phase transition problems—melting, condensation, ferromagnetic transition, order–disorder transition, and the like fall into this category. At present we do not have a complete understanding of any of these phase transitions as they occur in nature and it is interesting to note that we understand even less about boiling water than about liquid helium.

The immediate effect of interparticle interaction is that it will hinder the drift motion of the individual particles but contrary to this enhances their collective motion. The most direct method of studying the effects of intermolecular potentials between molecular systems that do not form stable compounds under ordinary conditions to date is the molecular beam scattering experiment (MBS).[9] However for studying effects of intermolecular potentials of stable systems, the MBS method cannot compete with optical spectroscopy (OS) which gives to a large extent only information on the attractive portion of the potential. It should however, be noted that the MBS is more universal and covers the entire energy range. Intermolecular potentials are of basic importance for the understanding of many macroscopic properties of matter. It is at the basis of all theories on the equation of state of gases, liquids and solids. In fact the two-body potential is the starting point of the theoretical description of gas kinetic processes. Thus once the potential curves (hypersurfaces) are available, nonequilibrium statistical mechanics–Boltzmann equation–or the simple equilibrium statistical mechanics can be used to compute all the transport properties or, when molecules are involved, relaxation times for rotational and vibrational degrees of freedom.[10,11] It is important to point out that previously information on the intermolecular potential has been obtained from measurements of these and other macroscopic properties. These experimental methods have the main disadvantage that since the observed values are averaged over the behavior of many molecular interactions, the data are frequently not sensitive to important details of the potential.

We believe that the method we are developing in this paper can prove to be very powerful in theoretical investigations of the problem of order–disorder transitions in alloys and lattice gas of Yang and Lee. The Ising model[12] which was initially developed as a model of ferromagnetism can be applied. It assumes that the energy of a lattice of spins is given,

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in the absence of an external magnetic field, by

$$H = \tfrac{1}{2} \sum_{ij}{}' V_{ij} \mu_i \mu_j,$$

where μ_i is the spin variable which the model assumes to be the only significant variable of the spin at the lattice site indexed i. μi assumes the values ± 1 (spin up and spin down); V_{ij} denotes the interaction energy between the particles i and j when their spins are parallel. The prime on the double sum indicates the constraint $i \neq j$. The partition function for an Ising model of N sites is therefore

$$Z_N = \sum_{\{\mu\}} \exp\!\left(-\beta \tfrac{1}{2} \sum_{ij}{}' V_{ij} \mu_i \mu_j \right),$$

where $\Sigma_{\{\mu\}}$ denotes summation over all spin configurations and $\beta = 1/kT$. The free energy per spin is given by

$$F = -kT \lim_{n \to \infty} \frac{1}{N} \log Z_N.$$

From the knowledge of this function we could compute all thermodynamic properties of the system.

The shape of a typical intermolecular potential in the radial region most effective at thermal energies is well known in literature. Scattering experiments indicate that this potential shape is typical for collision partners of which at least one has a closed shell. And for such systems, the potential minima are located between 3.0 and 6.0 Å while the depths lie between 1.10^{-3} and 60×10^{-3} eV. Thus the attraction at long distances can be attributed to the long range Coulomb coupling between the electrons in the two systems—London dispersion forces. Therefore, the electron motion are correlated in such a way as to reduce the potential energy. Theoretical calculations predict for ground state atom–atom interactions an R^{-6} behavior. The strong repulsion at short distances can be largely attributed to a repulsion of the electron clouds, due to the Pauli principle mutual exclusion of electrons, and to the electrostatic repulsion of the nuclei. In view of the difficulties encountered in calculation of potential surfaces and especially of the well location and depth, theoretical understanding is still based on aproximate methods. At long ranges, beyond the minimum $R \geqslant 2Rm$ reliable semiempirical methods[13,14] are available for obtaining constant C in the expression $V(R) = -C/R^6$. Unfortunately, there are no reliable methods available for estimating well location Rm and depth ϵ. However, at very short ranges (~ 2 Å) the Thomas–Fermi–Dirac method has been shown to give reliable results.[15]

II. CLASSICAL PARTITION FUNCTION
A. Thermodynamic properties

Let us consider a system of interacting particles with the following Hamiltonian,

$$H = \sum_i \frac{P_i^2}{2m_i} + \sum_{ij} V(r_i - r_j), \tag{II.1}$$

where P_i and m_i are the momentum and mass of the ith particle respectively. $V(r_i - r_j)$ is the interaction energy between particles at positions r_i and r_j.

The classical partition function for such a system is given by the following configuration integral,[16]

$$Z = \prod_i \int dP_i\, dr_i\, e^{-\theta H}$$

$$= \left(\frac{m}{2\pi KT}\right)^{3N/2} \prod_i \int dr_i\, e^{-\theta V(r_i)} \tag{II.2}$$

after carrying out integration on the kinetic energy term.

It is evident from Eq. (II.2) above that our problem reduces to the evaluation of the following integral,

$$Q = \prod_i \int dr_i\, e^{-\theta V(r_i)}. \tag{II.3}$$

The above integral involves both short and long range terms of the interaction potential. Our primary aim is to try and separate these two terms. In this way, we believe that we shall have introduced a new method for concrete and accurate investigation of the points of phase transitions.

Let us define a Fourier transform in a box Ω (periodic boundary condition),

$$f(x) = \frac{1}{\Omega} \sum_K e^{-iKx} f(K), \tag{II.4}$$

with the inverse

$$f(K) = \int_\Omega e^{iKx} f(x)\, dx \tag{II.5}$$

such that $f(K)$ is of order unity.

We note that

$$\frac{1}{\Omega} \sum_K e^{iKx} = \delta^3 x$$

and

$$\frac{1}{\Omega} \int_\Omega e^{iKx}\, d^3 x = \delta_{K,0}$$

the number density is $\rho(x)$. Its Fourier transform is

$$\rho_x = \frac{1}{\Omega} \sum_K \rho_K e^{-iKx} \tag{II.6}$$

with the inverse

$$\rho_K = \int_\Omega e^{iKx} \rho(x)\, d^3 x = \sum_n e^{iKx_n}. \tag{II.7}$$

Let us now consider the following potential,

$$\sum_{m,n} V(x_m - x_n) = \sum_{m,n} \sum_K \exp[iK(x_m - x_n)]\, \bar{V}(K), \tag{II.8}$$

and from the definition of the number density Eq. (II.6), we come to

$$\sum_{m,n} V(x_m - x_n) = \frac{1}{\Omega} \sum_K \bar{V}(K)\rho(K)\rho(-K)$$

$$= \left(\frac{1}{2\pi}\right)^3 \int d^3K\, \bar{V}_K \rho_K \rho_{-K}. \tag{II.9}$$

Putting the constraint $m \neq n$ we obtain

$$\sum_{m \neq n} V(x_m - x_n) = \left(\frac{1}{2\pi}\right)^3 \int d^3K \tilde{V}_K \rho_K \rho_{-K} + NV_0. \tag{II.10}$$

Here N is the number of particles in the system.

In this formalism, the expression for Q takes the form

$$Q = Q_0 \prod_n \int d^3x \exp\left(-\frac{\theta}{\Omega} \sum_{K \neq 0} \tilde{V}_K \rho_K \rho_{-K}\right), \tag{II.11}$$

where

$$Q_0 = \exp\left(\theta \frac{N}{2} V_0 + \theta \frac{N^2}{2\Omega} \tilde{V}_0\right)$$

which corresponds to the self energy part of the system.

We shall now introduce new variables by representing the number density in the form

$$\rho_K = C_K + iS_K, \quad \rho_{-K} = C_K - iS_K, \tag{II.12}$$

where

$$S_K = \frac{1}{2i} [\rho_K - \rho_{-K}] = \sum_n \sin Kx_n \tag{II.13}$$

$$C_K = \tfrac{1}{2}[\rho_K + \rho_{-K}] = \sum_n \cos Kx_n$$

and Eq. (II.11) takes the form

$$Q = Q_0 \prod_{n=1}^{N} \int d^3x_n \exp\left(-\frac{\theta}{2} \sum_{K \neq 0} \tilde{V}_K (C_K^2 + S_K^2)\right) \tag{II.14}$$

as evidenced by Eq. (II.12).

If we now call

$$\frac{\theta}{2} \tilde{V}_K = \lambda_K^2,$$

then Eq. (II.14) becomes

$$Q = Q_0 \prod_{n=1}^{N} \int d^3x_n \exp\left[-\tfrac{1}{2} \sum_{k \neq 0} \lambda_K^2 (C_K^2 + S_K^2)\right]. \tag{II.15}$$

Equation (II.15) is a standard form of integral and we shall now apply the following identity,

$$\exp(-\tfrac{1}{2} C_K^2 \lambda_K^2)$$
$$= \exp(\log\sqrt{\pi}) \int_{-\infty}^{\infty} \exp(-\alpha_K^2) \exp(i\alpha_K \lambda_K C_K \sqrt{2}) d\alpha_K, \tag{II.16}$$

and come directly to

$$Q = Q_0 \int \prod_K d\alpha_K d\beta_K \exp\left[-\sum_K (\alpha_K^2 + \beta_K^2 + \log\pi)\right]$$
$$\times \prod_n \int d^3x_n \exp\left[i \sum_K (C_K \alpha_K + S_K \beta_K)\lambda_K \sqrt{2}\right]. \tag{II.17}$$

Using Eq. (II.13) above, we can transform the last integral in Eq. (II.17) to be of the form

$$\prod_n^N \int \exp\left[i \sum_K (C_K \alpha_K + S_K \beta_K)\lambda_K \sqrt{2}\right] d^3x_n$$
$$= \left[\int d^3x \exp[iF(x)]\right]^N, \tag{II.18}$$

where

$$F(x) = \sum_{K \neq 0} \lambda_K \sqrt{2}(\alpha_K \cos Kx + \beta_K \sin Kx).$$

Now assuming that $F(x)$ is large only for a finite region about the origin and write

$$\left[\int_\Omega d^3x e^{iF(x)}\right]^N \underset{n \to \infty}{\Rightarrow} \Omega^N \exp\left(\frac{N}{\Omega} \int_\Omega d^3x\{e^{iF(x)} - 1\}\right). \tag{II.19}$$

Thus we have

$$Q = Q_0 \Omega^N \int \prod_K d\alpha_K d\beta_K \exp\left(-\sum_{K \neq 0} (\alpha_K^2 + \beta_K^2 + \log\pi)\right)$$
$$\times \exp\left(\frac{N}{\Omega} \int_\Omega \{e^{iF(x)} - 1\}d^3x\right). \tag{II.20}$$

The factor Ω^N occurs already for the free particles. It may be advantageous to remove the peculiar Ω dependence of λ_K assuming that

$$\tilde{\Phi}(K) = \sqrt{\theta\tilde{V}(K)} \sqrt{2}$$

and introducing new variables

$$\alpha_K = \alpha_K'/\sqrt{\Omega}, \quad \beta_K^+ = \beta_K'/\sqrt{\Omega},$$

Eq. (II.20) will thus be transformed to

$$Q = Q_0 \int \prod_K d\alpha_K d\beta_K$$

$$\times \exp\left(-\frac{1}{\Omega} \sum_{K \neq 0} (\alpha_K^2 + \beta_K^2 + \Omega \log\pi)\right)$$

$$\times \exp\left(\frac{N}{\Omega} \int_\Omega d^3x\{e^{iF(x)} - 1\}\right), \tag{II.21}$$

where we have dropped the primes and now

$$F(x) = \frac{1}{\Omega} \sum_{K \neq 0} (\alpha_K \cos Kx + \beta_K \sin Kx)\tilde{\Phi}_K.$$

To illustrate results obtainable in this formalism, we first expand,

$$e^{iF(x)} = 1 + iF(x) - \frac{F^2(x)}{2!} + \cdots. \tag{II.22}$$

Then

$$\int_\Omega d^3x F(x) = 0.$$

In order to compute $\int d^3x F^2(x)$ it is imperative to note that

$$F(x) = \frac{1}{\Omega} \sum_{K \neq 0} F(K) e^{-iKx}$$

with

$$F(K) = (\alpha_K + i\beta_K + \alpha_{-K} - i\beta_{-K}) \tfrac{1}{2} \Phi(K),$$

we have

$$\int d^3x F^2(x) = \left(\frac{1}{\Omega} \sum_{K \neq 0} F(K) F(-K) \right).$$

Thus the part of the partition function that is integrated over is the exponential of minus

$$\frac{1}{\Omega} \sum_{K \neq 0} (\alpha_K^2 + \beta_K^2) + \frac{N}{2\Omega^2} \sum_{K \neq 0} F(K) F(-K)$$

$$= \frac{1}{\Omega} \sum_{K \neq 0} \left((\alpha_K^2 + \beta_K^2) + \frac{N}{2\Omega} \Phi \tfrac{1}{4} (\alpha_K + \alpha_{-K})^2 \right.$$

$$\left. + \frac{N}{8\Omega} (\beta_K - \beta_{-K})^2 \Phi \right). \tag{II.23}$$

This is a Bogolyibov quadratic form. However we only need the Gaussian integral. Thus considering a pair K and $-K$ for α_K and β_K variables and performing all the necessary rearrangement and certain basic manipulations, we obtain the following result:

$$Q = Q_0 \exp\left(\sum_K \log\Omega \right)$$

$$\times \exp\left[-\tfrac{1}{2} \sum_K \log\left(1 + \frac{N}{\Omega} \Phi(K) \right) \right], \tag{II.24}$$

or finally

$$Q = \Omega^N \exp\left[-\left(\frac{N}{2} \theta V_0 + \frac{\theta}{2\Omega} \tilde{V}_0 N^2 \right) \right]$$

$$\times \exp\left[-\tfrac{1}{2} \sum_K \log\left(1 + \frac{N}{\Omega} \sqrt{2\theta V_K} \right) \right]. \tag{II.25}$$

From Eq. (II.25), we can now compute Helmholtz free energy for the system,

$$A(\Omega, \theta) = -KT \log Q + \text{free kinetic energy term.} \tag{II.26}$$

We can now write down expressions for certain thermodynamic properties of such a system. For example, pressure P will be given by

$$P = -\left(\frac{\partial A}{\partial \Omega} \right)_T, \tag{II.27}$$

$$P = \frac{N^2}{2\Omega^2} \tilde{V}_0 + \frac{N}{2\theta\Omega}$$

$$+ \frac{N}{2\theta\Omega^2} \sum_{K \neq 0} \frac{\sqrt{2\theta\tilde{V}_K}}{1 + (N/\Omega)(2\theta/\sqrt{\tilde{V}_K})},$$

and entropy S of the system will be of the form

$$S = -\left(\frac{\partial A}{\partial \theta} \right)_\Omega$$

$$= \frac{1}{2\theta^2} \left\{ \sum_{K \neq 0} \left[\log\left(1 + \frac{N}{\Omega} \sqrt{2\theta\tilde{V}_K} \right) \right. \right.$$

$$\left. \left. - \frac{2\theta(N/\Omega)\tilde{V}_K}{\sqrt{2\theta\tilde{V}_K}(1 + (N/\Omega)\sqrt{2\theta\tilde{V}_K})} \right] - \log\Omega^N \right\}. \tag{II.28}$$

From the knowledge of the free energy of the system as given by Eq. (II.26), one is, in principle, able to calculate all the thermodynamic properties of the system and compare the values with experimental results.

B. Change of variables

Here we shall use the relevant Gaussian quadrature formulas.[17] Let us introduce new variables:

$$\xi_K^{\pm} = \frac{\alpha_K \pm \alpha_{-K}}{\sqrt{2}}, \quad \eta^{\pm} = \frac{\beta_K \pm \beta_{-K}}{\sqrt{2}}.$$

The Jacobian of transformation will evidently take the form

$$\begin{vmatrix} \dfrac{\partial \xi_K^+}{\partial \alpha_K} = \dfrac{1}{\sqrt{2}} & \dfrac{\partial \xi_K^+}{\partial \alpha_{-K}} = \dfrac{1}{\sqrt{2}} \\ \dfrac{\partial \xi_K^-}{\partial \alpha_K} = \dfrac{1}{\sqrt{2}} & \dfrac{\partial \xi_K^-}{\partial \alpha_{-K}} = -\dfrac{1}{\sqrt{2}} \end{vmatrix} = -1. \tag{II.29}$$

In terms of the new variables, the Gaussian averaging becomes

$$\epsilon\langle \cdots \rangle$$

$$= \int \prod_{K \neq 0} d\alpha_K d\beta_K \exp\left[-\sum_{K \neq 0} (\alpha_K^2 + \beta_K^2 + \log\pi) \right] \langle \cdots \rangle$$

$$= \int \prod_{K \neq 0} d\xi_K^+ d\xi_K^- d\eta_K^+ d\eta_K^- \langle \cdots \rangle$$

$$\times \exp\left[-\sum_{K \neq 0} (\xi_K^2 + \xi_K^2 + \eta_K^2 + \eta_K^2 + 2\log\pi) \right], \tag{II.30}$$

where

$$\langle \cdots \rangle = \exp\left(\frac{N}{\Omega} \int_\Omega d^3x (e^{iF(x)} - 1) \right) \tag{II.31}$$

and

$$F(x) = 2 \sum_{K \neq 0} \lambda_K (\xi_K^+ \cos Kx + \eta_K^- \sin Kx).$$

We can thus get rid of ξ_K^- and η_K^+ by simply integrating

Eq. (II.30) and obtaining the following,

$$\epsilon\langle\cdots\rangle = \int \sum_{K\neq 0} d\xi_K^+ d\eta_K^- \langle\cdots\rangle$$

$$\times \exp\left[- \sum_{K\neq 0} (\xi_K^2 + \eta_K^2 + 2\log\pi)\right]. \qquad (II.32)$$

In an external field $U(x)$, the partition function Eq. (II.21) will take the form below,

$$Q = Q_0 \Omega^N \exp\left(\frac{N}{\Omega}\theta V_0\right)$$

$$\times \epsilon\left\langle \exp\left[\frac{N}{\Omega}\int d^3x (e^{iF(x)}e^{-\theta U(x)} - 1)\right]\right\rangle. \qquad (II.33)$$

C. Formal relations for external field response

By retracing the steps outlined earlier, we could write an expression for the partition function in the presence of an external potential $U(x)$ in the form

$$\frac{Q}{Q_0\Omega^N} = \exp\left(- \frac{N}{\Omega}U_0\right)$$

$$\times \epsilon\left\langle \exp\left[\frac{N}{\Omega}\int d^3x (e^{iF(x)}e^{-\theta U(x)} - 1)\right]\right\rangle. $$

$$(II.34)$$

On the other hand,

$$Q = \int \cdots \int dx_1 \cdots dx_n \exp\left(- \frac{\theta}{2}\sum_{i\neq j} V_{ij}\right)$$

$$\times \exp\left[- \theta \int U(x) \sum_{i=1}^{N} \delta(x_i - x)\, d^3x\right]. \qquad (II.35)$$

Now considering Q as a functional of $U(x)$ and noting that the local density is

$$n(x) = \sum_{i=1}^{N} \delta(x_i - x), \qquad (II.36)$$

then the variation Q with respect to $U(x)$ is

$$\frac{1}{Q}\frac{\delta Q}{\delta U(s)} = - \theta \,\overline{n(s)}, \qquad (II.37)$$

$$\frac{1}{Q}\frac{\delta^2 Q}{\delta U(s)\delta U(s')} = \theta^2\overline{n(s)n(s')}. \qquad (II.38)$$

But since

$$\overline{n(s)n(s')} = \overline{(\bar{n}(s) + \delta n)(\bar{n}(s') + \delta n)}$$

$$= \overline{n(s)}\,\overline{n(s')} + \overline{\delta n(s)\delta n(s')}, \qquad (II.39)$$

it follows then from Eq. (II.37), Eq. (II.38), and Eq. (II.39)

that

$$\theta^2\overline{\delta n(s)\delta n(s')} = - \theta\,\frac{\delta\overline{n(s')}}{\delta U(s)}. \qquad (II.40)$$

We recognize in Eq. (II.40) that $\overline{n(s')}$ is a functional of $U(s)$.

Next we consider Q as a functional of $\overline{n(s)}$ expecting this to be more correlated with it. Thus

$$\int \frac{\delta\bar{n}(s)}{\delta U(s')}\frac{\delta U(s')}{\delta\bar{n}(s')}\, ds' = \delta(s - s'') \qquad (II.41)$$

and

$$\frac{1}{Q}\frac{\delta Q}{\delta\bar{n}(s)} = - \theta \int \bar{n}(s'')\frac{\delta U(s'')}{\delta\bar{n}(s)}\, ds''. \qquad (II.42)$$

Expressions for higher order and mixed derivatives can be found if desired.

D. Separation of short and long range interactions

This paper sets out on an attempt to separate long and short range parts of interaction potential $V(xi - xj)$. In doing so we believe that it is necessary to define the regime and limits of the short range part of the potential. The region of long range forces includes certain aspects of short range interactions. So by determining the short range region, we aim at renormalizing the long range part of the interaction potential. Our Gaussian average denoted by ϵ was performed in reciprocal K space corresponding to the Fourier transform of function $F(x)$, see Eq. (II.23).

Now assuming that short range forces act in K space for values of $K\geqslant K_0$, then we could draw a sharp distiction between $K > K_0$ and $K < K_0$ the latter corresponding to purely long range interactions.

With the above in mind, let us denote by ϵ_L the average carried out over α_K and β_K for $K < K_0$ corresponding to long range forces. Then we write

$$\epsilon^W = \epsilon\left\langle \exp\left(\frac{N}{\Omega}\int d^3x (e^{iF(x)} - 1)\right)\right\rangle$$

$$= \epsilon\left\langle \exp\left(\frac{N}{\Omega}\int d^3x (e^{iF_L(x)} - 1)\right)\right.$$

$$\times \exp\left(\epsilon\frac{N}{\Omega}\int e^{iF_L(x)}(e^{iF_S(x)} - 1)d^3x\right)\right\rangle. \qquad (II.43)$$

We have inserted ϵ which is later set equal to 1. Here

$$F(x) = F_L(x) + F_S(x),$$

representing long $F_L(x)$ and short $F_S(x)$ range forces, respectively.

Let us now concentrate on the short range part of the potential by taking the average over α_K and β_K denoted by ϵ_S for $K > K_0$. Equation (II.43) can be written in the form

$$e^W = \epsilon_L\left\langle \exp\left(\frac{N}{\Omega}\int d^3x [e^{iF_L(x)} - 1]e^A\right)\right\rangle \qquad (II.44)$$

with the short range average

$$e^A = \epsilon_S \left\langle \exp\left(\epsilon \frac{N}{\Omega} \int e^{iF_L(x)}(e^{iF_S(x)} - 1)\, d^3x \right) \right\rangle. \quad \text{(II.45)}$$

Further we consider e^A and treat it by a virial development in ϵ in order to determine the contributions from different terms, linear etc. The $F_L(x)$ will remain and e^A is a function of α_K and β_K for $K < K_0$.

Develop

$$A = A_0 + \epsilon \left. \frac{dA}{d\epsilon} \right|_{\epsilon = 0} + \frac{\epsilon^2}{2!} \left. \frac{d^2A}{d\epsilon^2} \right|_{\epsilon = 0} + \cdots. \quad \text{(II.46)}$$

Here the constant term $A_0 = 0$ corresponds to a system with purely long range forces.

Considering the linear term in the expansion given by Eq. (II.46),

$$\left. \frac{dA}{d\epsilon} \right|_{\epsilon_0} = \frac{N}{\Omega} \mathcal{H}(K_0) \int e^{iF_L(x)}\, d^3x. \quad \text{(II.47)}$$

$$\mathcal{H}(K_0) = \epsilon_S \langle e^{iF_S(x)} - 1 \rangle$$

$$= \left\langle \exp\left(- \frac{1}{\Omega} \sum_{K \geqslant K_0} \frac{|\Phi(K)|^2}{4} - 1 \right) \right\rangle. \quad \text{(II.48)}$$

Equation (II.48) describes a system with purely short range forces. Since we will develop $\exp[iF_L(x)]$ up to $F_L^2(x)$ we see that the short range forces induce a renormalization of the quadratic form of the long range part.

In the quadratic approximation to the short range force, we need the following term,

$$\left. \frac{d^2A}{d\epsilon^2} \right|_{\epsilon_0}$$

$$= \frac{N^2}{\Omega^2} \int d^3x\, d^3y \exp\{i[F_L(x) + F_L(y)]\} Z(y - x), \quad \text{(II.49)}$$

where

$$Z(y - x)$$

$$= \exp\left[- \frac{1}{\Omega} \sum_{K \geqslant K_0} \frac{|\Phi_K|^2}{2} \right]$$

$$\times \left[\exp\left(- \frac{1}{\Omega} \sum_{K \geqslant K_0} \frac{|\Phi_K|^2}{2} \cos K(y - x) \right) - 1 \right]. \quad \text{(II.50)}$$

Thus to this order

$$A = \epsilon \frac{N}{\Omega} \mathcal{H}(K_0) \int e^{iF_L(x)} d^3x + \frac{\epsilon}{2!} \frac{N^2}{\Omega^2} \int d^3x\, d^3y$$

$$\times \exp\{i[F_L(x) + F_L(y)]\} Z(y - x). \quad \text{(II.51)}$$

Let us now go back and reexamine Eq. (II.44) by expanding it in powers of $F_L(x)$ up to quadratic term. Thus

$$W = W_0 + W_1 + W_2.$$

W_0 is the constant part of the exponential and corresponds to a system with purely short range interactions,

$$W_0 = \epsilon \frac{N}{\Omega} \mathcal{H}(K_0) + \frac{\epsilon^2}{2!} \frac{N^2}{\Omega} \int Z(y)\, dy. \quad \text{(II.52)}$$

The linear term $W_1 = 0$, simply because

$$\int F_L(x)\, d^3x = 0,$$

the absence of long range forces in the region $K > K_0$, i.e.,

$$W_1 = \frac{\epsilon^2}{2!} \frac{N^2}{\Omega^2} 2i$$

$$\times \int F_L(x) Z(|y - x|)\, d^3x\, d^3y = 0. \quad \text{(II.53)}$$

W_2 is the quadratic part and has the form

$$W_2 = - \frac{N}{2\Omega} \int F_L^2(x)\, d^3x \{1 + \epsilon \mathcal{H}(K_0)\}$$

$$+ \frac{\epsilon^2}{2!} \frac{N^2}{\Omega^2} \int d^3x\, d^3y [F_L(x) + F_L(y)]^2 Z(y - x). \quad \text{(II.54)}$$

The obvious physical intepretation of the quadratic term Eq. (II.54) is that a system with long range forces has a certain amount of short range interactions.

We could go on with this scheme and obtain higher order terms in W. However from what we have done above, the trend looks pretty obvious and in fact we already know what terms to choose from our expansions in order to deal with a system with purely short range or long range forces. Our next task would be to reexpress the partition function Q in terms of the short range and long range Gaussian averages.

Thus thermodynamic properties of a system with purely short range forces can be computed from the following partition function,

$$Q = Q_0 e^{W_0}, \quad \text{(II.55)}$$

where W_0 is given by Eq. (II.52). And similarly from

$$Q = Q_0 e^{W_2}, \quad \text{(II.56)}$$

for systems exhibiting long range interactions. W_2 is given by Eq. (II.54).

III. THE GRAND PARTITION FUNCTION
A. General remarks

It seems easier to make contact with the standard treatment (e.g., virial series) via the grand partition function. The grand partition function $\Xi(\theta, \Omega, z)$ is defined by

$$\Xi(\theta, \Omega, z) = \sum_{N > 0} Q_N(\Omega, \theta) \frac{z^N}{N!}. \quad \text{(III.1)}$$

Here

$$Q_N(\Omega, \theta) = \int_\Omega \cdots \int dx_1 \cdots dx_N e^{-\theta V} \quad \text{(III.2)}$$

and

$$z = \frac{e^{-\theta\mu}}{\Lambda^3}, \quad \Lambda = \left(\frac{h^2\theta}{2\pi m}\right)^{1/2}.$$

We go back to the beginning and express Q_N in terms of Gaussian quadratures. However, to include the $\tilde{V}(0)$ and $V(0)$ terms, we use variables α_0 and β_0. Extend $F(x)$ to include $K = 0$ terms and let $\epsilon\langle\cdots\rangle$ involve Gaussian averages over α_0 and β_0 as well. Then

$$Q_N = \epsilon\left\langle\left[\int d^3x e^{iF(x)}\right]^N\right\rangle\{e^{\theta V(0)/2}e^{\theta\tilde{V}(0)/2\Omega}\}^N \quad (III.3)$$

such that

$$\Xi(\theta,\Omega,z) = \epsilon\left\langle\exp\left(z_1\int d^3x e^{iF(x)}\right)\right\rangle \quad (III.4)$$

with

$$z_1 = z\exp\left(\frac{\theta}{2}V_{x=0}\right)\exp\left(\frac{\theta}{2\Omega}\tilde{V}_{K=0}\right)$$

and we expect the term $(\theta/2\Omega)V_K = 0$ to vanish since it comes from $N(N-1)/2$.

In what follows, we drop that term and Eq. (III.3) will take the form

$$Q_N = \epsilon\left\langle\exp\left(\frac{\theta}{2}V_{x=0}\right)\int d^3x e^{iF(x)}\right\rangle.$$

The ordinary virial development gives pressure in the form

$$p\theta = \frac{1}{\Omega}\log\Xi = b_1 z + b_2 z^2 + b^3 z^3 + \cdots, \quad (III.5)$$

where $b_1, b_2, \cdots$ are the virial coefficients. It follows from Eq. (III.1) above and Eq. (II.43) that

$$\frac{\omega}{\Omega} = \frac{1}{\Omega}\log\Xi$$

$$= z + \frac{z^2}{2!}\int f(x)\,d^3x + \cdots. \quad (III.6)$$

Here

$$f(x) = \{e^{-\theta V(x)} - 1\}$$

and z is determined from $\bar{N}/\Omega$.

It is well known from statistical thermodynamics that

$$\bar{N} = \theta\left(\frac{\partial\log\Xi}{\partial\mu}\right)_{\theta,\Omega}$$

$$= z\left(\frac{\partial\log\Xi}{\partial z}\right)_{\theta,\Omega}. \quad (III.7)$$

B. Separation of long range forces in the grand partition function

In this subsection we shall try to compare results obtainable in Sec. II by separating long and short range interactions in the grand partition function. From Sec. III A we

have

$$\Xi = \epsilon\left\langle\exp\left\{z\int d^3x \exp[iF(x)]\exp\left[\frac{\theta}{2}V(0)\right]\right\}\right\rangle \quad (III.8)$$

and putting

$$F = F_S + F_L,$$
$$R_S = \exp[\theta V_S(0)/2],$$
$$R_L = \exp[\theta V_L(0)/2],$$

we can show that

$$\Xi = \epsilon_L\left\langle\exp\left(z\int e^{iF_L(x)}R_L d^3x\right)\right\rangle$$

$$\times \epsilon_S\left\langle\exp\left[z\int R_L e^{iF_L}(e^{iF_S}R_S - 1)d^3x\right]\right\rangle. \quad (III.9)$$

Next we perform the cumulant expansion which is simple since

$$\epsilon_S\langle(e^{iF_S(x)}R_S - 1)\rangle = 0,$$

for all x. Thus

$$\epsilon_S\left\langle\exp\left[z\int e^{iF_L}R_L(e^{iF_S}R_S - 1)d^3x\right]\right\rangle$$

$$\equiv \frac{z^2}{2!}X_2 + \frac{z^3}{3!}X_3$$

$$= \exp\left(\frac{z^2}{2!}X_2 + \frac{z^3}{3!}X_3\right) \quad (III.10)$$

with

$$X_2 = \int\int dx\,dy\,R_L^2\exp\{i[F_L(x) + F_L(y)]\}f(x-y), \quad (III.11)$$

$$X_3 = \int\int\int dx\,dy\,dz\,R_L^3\exp\{i[F_L(x) + F_L(y) + F_L(z)]\}$$

$$\times[f(x-y)f(y-z)f(z-x) + 3f(x-y)f(y-z)].$$

Here

$$f(r) = e^{-\theta V(r)} - 1$$

refers to the short range part of the interaction potential.

Our next task is to carry the development of the long range part

$$e^{iF_L(x)}R_L,$$

and briefly mention the physics they represent.

As in Sec. II, the constant part corresponds to a system with purely short range forces

$$W_S = z\Omega R_L + \frac{z^2}{2!}\int f(x)R_L^2 d^3x$$

$$\times \frac{z^3}{3!}R_L^3\int\int\int dx\,dy\,dz\,(f_{12}f_{23}f_{31} + 3f_{12}f_{23}). \quad (III.12)$$

For the time being we have kept R_L unexpanded.

We therefore have

$$\frac{z^2}{2!} X_2$$

$$= \frac{z^2}{2!} R_L \left\{ \Omega \tilde{f}(0) + 2i \tilde{f}(0) \int F_L(x) \, d^3x \right.$$

$$\left. - \int \int F_L(x)[\tilde{f}(0)\delta(x-y) + f(x-y)]F_L(y) \, dx \, dy \right\} \quad \text{(III.13)}$$

for the short range forces, as can be seen in Eq. (III.10), and we could also write an expression for the next term $(z^3/3!)X_3$, which is rather long.

The linear part W_1 all refers to the α_0 and β_0 modes and can be treated separately.

The quadratic part of the expansion admittedly contains a lot of algebraic manipulations and we are not going to reproduce that here. We just mention that with

$$F_L(x) = \frac{1}{\Omega} \sum_K \tilde{F}_L(K) e^{-iKx}$$

we would split off the $K = 0$ term and the result would be essentially the same result we obtained in Sec. II. Namely, the long range forces involve some amount of short range interactions. So the contribution to the grand partition function from terms $K \neq 0$ are

$$\exp\left(-\tfrac{1}{2} \sum_{\substack{K \neq 0 \\ K < K_0}} \log[1 + \theta \tilde{V}_K \{A + 2\tilde{B}(K)\}] \right). \quad \text{(III.14)}$$

Here

$$\tilde{B}(K) = \int_\Omega B(x) e^{iKx} \, d^3x$$

and

$$A = \frac{z^2}{2} R_L^2 + \frac{z^2}{2} R_L^2 \tilde{f}(0)$$

$$+ \frac{z^3}{4} R_L^3 \left\{ 3\tilde{f}^2(0) + \frac{1}{\Omega} \sum_m \tilde{f}(m)\tilde{f}(-m)\tilde{f}(m) \right\}. \quad \text{(III.15)}$$

Now turning to the zero mode, the quadratic part is proportional to $1/\Omega$ and does not contribute. The linear part requires completing the square and gives

$$\exp\left(-\Omega \frac{\theta}{2} \tilde{V}(0)\{1 + zR_L \tilde{f}(0) \right.$$

$$\left. + \frac{z^2}{2} R_L^2 [f_3 + 3\tilde{f}^2(0)] \right\}^2 z^2 R_L^2 \Big). \quad \text{(III.16)}$$

Lastly, putting all these approximations together, we come to the following virial formula,

$$\frac{1}{\Omega} \log \Xi$$

$$= zR_L \left(1 + \frac{zR_L}{2} \int f(x) \, d^3x + zR_L^2 f_3 \right)$$

$$- \frac{1}{2} \frac{1}{\Omega} \sum_{\substack{K \neq 0 \\ K < K_0}} \log\{1 + 2\theta \tilde{V}(K)[A + \tilde{B}(K)]\}$$

$$- \frac{\theta}{2} \tilde{V}(0)\left(1 + zR_L \tilde{f}(0) + \frac{z^2}{2} R_L^2 [f_3 + 3\tilde{f}(0)] \right)^2$$

$$\times z^2 R_L^2, \quad \text{(III.17)}$$

which in effect gives the pressure of the system.

We have thus shown that for both the classical partition and the grand partition function, the constant term of expansion W_0 of Gaussian averages describes a system with purely short range forces while the quadratic term W_2 corresponds to a system with a mixture of short and long range interactions which is to be expected.

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APPENDIX: THE USE OF THE GRAND PARTITION FUNCTION

Let us consider a system with the following coordinate independent Hamiltonian,

$$\mathcal{H} = \sum_{i=1}^N \frac{P_i^2}{2m} + \frac{N(N-1)^2}{2\Omega} \tilde{V}(0)\varepsilon^2 - \frac{N}{2} V(0)\eta^2 \quad \text{(A1)}$$

The coefficient ε and η will be set equal to unity later. The classical partition function for such a system will take the form

$$Z_N = \left(\frac{m}{2\pi KT} \right)^{3N/2} \int dx_1 \cdots dx_N e^{-\theta V}$$

$$= \left(\frac{m}{2\pi KT} \right)^{3N/2} \Omega^N$$

$$\times \exp\left(-\frac{\theta N(N-1)}{2\Omega} \tilde{V}(0)\varepsilon^2 + \frac{\theta N}{2} V(0)\eta^2 \right). \quad \text{(A2)}$$

Thus the free energy for the canonical ensemble is given by

$$A = \frac{N}{\theta} \left(\log \frac{N}{\Omega} \Lambda^3 - 1 \right) - \frac{1}{\theta} \log\left(\frac{Z_N}{\Omega^N} \right), \quad \text{(A3)}$$

and therefore its variation is given by

$$\delta A = \frac{N(N-1)}{2\Omega} \tilde{V}(0) + \frac{N}{2} V(0). \quad \text{(A4)}$$

Pressure for such a system will be

$$P = \frac{N}{\Omega}\frac{1}{\theta} + \frac{1}{\theta}\left[\frac{\partial}{\partial\Omega}\log\left(\frac{Z_N}{\Omega^N}\right)\right]_{\theta,N} \tag{A5}$$

and its variation is

$$\delta_P = \frac{N(N-1)}{2\Omega^2}\tilde{V}(0). \tag{A6}$$

The chemical potential for the system is

$$\mu = \frac{1}{\theta}\log\left(\frac{N\Lambda^3}{\Omega}\right) - \frac{1}{\theta}\left[\frac{\partial}{\partial N}\log\left(\frac{Z_N}{\Omega^N}\right)\right] \tag{A7}$$

with a variation of

$$\delta\mu = \frac{N-\frac{1}{2}}{\Omega}\tilde{V}(0) - \frac{1}{2}V(0). \tag{A8}$$

The grand partition function for such a system is of the form

$$\Xi(\Omega,\theta,z) = \sum_{N\geqslant 0} Z_N(\Omega,\theta)z^N/N! \tag{A9}$$

and it is clear from the above that

$$Z_N z^N = \exp\left(-\frac{\theta}{2\Omega}\tilde{V}(0)\varepsilon^2 N^2\right)[\Omega,z_1]^N \tag{A10}$$

with

$$z_1 = z\exp\left(\frac{\theta}{2\Omega}\tilde{V}(0)\varepsilon\right)\exp\left(\frac{\theta}{2}V(0)\eta^2\right). \tag{A11}$$

Using Gaussian quadratures we can write the following,

$$\exp\left(-\frac{\theta}{2\Omega}\tilde{V}(0)\varepsilon^2 N^2\right)$$
$$= \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\exp(-\alpha_0^2)$$
$$\times\exp\left[i\alpha_0\sqrt{2}\left(\theta\frac{\tilde{V}(0)}{\Omega}\varepsilon^2\right)^{1/2}N\right]d\alpha_0 \tag{A12}$$

such that

$$Z_N z^N = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}e^{-\alpha_0^2}$$
$$\times\left\{\Omega z_1\exp\left[i\alpha_0\left(2\theta\frac{\tilde{V}(0)}{\Omega}\varepsilon^2\right)^{1/2}\right]\right\}^N d\alpha_0. \tag{A13}$$

Thus the grand partition function will be of the form

$$\Xi = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}e^{-\alpha_0^2}d\alpha_0\exp\left[\Omega z_1\exp\left(i\alpha_0\frac{\tilde{\Phi}}{\sqrt{\pi}}\right)\right], \tag{A14}$$

where

$$\tilde{\Phi}(0) = [2\theta\tilde{V}(0)\varepsilon^2]^{1/2}.$$

It follows readily from Eq. (A14) that the grand partition

function satisfies the following functional equation,

$$\frac{d\Xi(z_1)}{dz_1} = \Omega\exp\left(\frac{-\tilde{\Phi}^2}{4\Omega}\right)\Xi\left[z_1\exp\left(-\frac{\tilde{\Phi}^2}{2\Omega}\right)\right] \tag{A15}$$

with

$$\Xi(0) = 1.$$

Now to show how the grand partition works, we use the maximum term,

$$\frac{Z_{\bar{N}}z^{\bar{N}}}{\bar{N}!}.$$

On applying Stirling's approximation, we find that

$$\log\left(\frac{\Omega z_1}{\bar{N}}\right) = \frac{\bar{N}}{\Omega}\frac{\tilde{\Phi}^2}{2} \tag{A16}$$

and this yields

$$z_1(\bar{N}) = \frac{\bar{N}}{\Omega}\exp\left(\frac{\bar{N}}{\Omega}\frac{\tilde{\Phi}^2}{2}\right)$$

$$\Rightarrow\exp\left(-\frac{\theta}{2}\tilde{V}(0)\right)\frac{\bar{N}}{\Omega}\exp\left(\frac{\bar{N}}{\Omega}\frac{\tilde{\Phi}^2}{2}\right).$$

Thus the value of Ξ is

$$\Xi = \exp\left(\frac{\bar{N}_2}{\Omega}\frac{\tilde{\Phi}^2}{4}\right)e^{\bar{N}}. \tag{A17}$$

The equation

$$\bar{N} = z\left(\frac{\partial\log\Xi}{\partial z}\right)$$

is an identity and

$$\frac{\log\Xi}{\Omega} = \frac{\bar{N}^2}{\Omega^2}\frac{\tilde{\Phi}^2}{4} + \frac{\bar{N}}{\Omega}. \tag{A18}$$

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