

QUANTUM STATISTICAL MECHANICAL MODEL  
FOR POLARIZABLE FLUIDS

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## ABSTRACT

The quantum statistical mechanics of a polarizable fluid model is considered using a path-integral approach. The quantum mechanical partition function associated with the internal degrees of freedom of each molecule is approximated by a classical partition function of a polymer ring, while the center-of-mass motion of each molecule is treated classically. The resulting system of particles can be derived by an Ornstein-Zernike equation, which we solve analytically in the Mean Spherical Approximation. We give the dielectric constant, free energy, and internal energy of our model in both its continuum-fluid and lattice-gas versions. (In the former we assume hard-sphere cores; in both versions we take harmonically oscillating dipole moments as characterizing the internal degrees of freedom, with ideal dipole-dipole intermolecular coupling.)

## I. INTRODUCTION

The path-integral approach to quantum mechanics<sup>1</sup> enables one to think of quantum problems as corresponding to limiting cases of certain classical statistical mechanical problems, since a path-integral can be regarded as a limit of approximating sums that can be thought of as a classical configuration integrals.<sup>2-4</sup> In the case of nontrivial quantum problems the associated classical problems can be of much interest in their own right, but tend to be almost as conceptually and computationally formidable as the quantum problems with which they are associated. Nevertheless, for two reasons, there is growing interest in the path-integral approach. First, there is the ever-increasing computational capabilities of electronic computers that render the approach a more and more viable computational tool.<sup>3</sup> Second, there is a growing set of new approximation techniques to handle some of the corresponding classical problems.<sup>4</sup> This paper exploits the second development.

We show here how a simple molecular model of a fluid in which the internal molecular degrees of freedom are treated quantum mechanically can be solved through the application to the corresponding classical problem of an appropriately tailored lowest-order gamma-ordered approximation, which amounts to the use of an extension of the well known mean spherical approximation (MSA). The fluid model we treat as an illustrative example consists of polarizable monatomic particles, modeled as hard spheres with harmonic polarizability. It

is a nontrivial and useful paradigm of a simple fluid, since the hard-sphere cores reasonably approximate the steeply repulsive part of the pair interaction between real monatomics while the polarizability gives rise to the dispersion forces that represent the source of the attractive part of the pair interaction.

To our knowledge, our treatment is significantly different from any of the various approaches using path-integral techniques that have previously appeared. It is perhaps closest in aim to that of Chandler and Wolynes,<sup>4</sup> but of the three new perspectives those authors list as characterizing the novelty of their work -- connection between quantum influence function and a classical cavity distribution function, observation of a (quantum exchange)-(classical chemical equilibria) isomorphism, and realization that modern classical theories of polyatomic fluids provide a practical computational route to the quantum problem -- our article touches on only the third, and then only in a peripheral way. Because we treat the center-of-mass motion of our molecules classically, the repulsive cores of our classical particles are not those of flexible polymer rings of hard-core atoms, but are instead simple hard-sphere cores.

The model we consider here is the quantum version of the thermally fluctuating model of polarizable monatomics that we have discussed in detail in an earlier publication.<sup>5</sup> It is a simpler model of a polarizable fluid than a more general model we have subsequently described in classical terms;<sup>6</sup> we hope to ultimately describe the quantum analog of that more general model too.

In Section II we describe our model. In III we summarize the relations between a quantum mechanical propagator and its approximating sum viewed as classical partition function. In Section IV, we find the properties of the classical system described by our quantum mechanical problem in an appropriate version of the mean spherical approximation (MSA). In Sections V through VII we give the dielectric constant, free energy, and internal energy of our model in the MSA, in both its continuum-fluid and lattice-gas versions. In an Appendix we briefly discuss the partition function for a harmonic oscillator, to which we refer in Sections VI and VII.

## II. MODEL

The atoms or molecules of our dielectric fluid will consist of two masses  $M_e$  and  $M_n$  where  $M_e \ll M_n$ . These masses, which are of opposite charge with charge of magnitude  $e$ , are bound by a potential that we can write as  $\phi(s)$ , where  $s = |\vec{s}|$  and

$$\vec{s} = e\vec{r} \quad (1)$$

will be the dipole moment with the charges separated by a displacement  $\vec{r}$ . The relative motion of these two masses will be associated with the reduced mass

$$M = \frac{M_e M_n}{M_e + M_n} \quad (2)$$

while the center-of-mass motion is associated with the full mass

$$M_0 = M_e + M_n. \quad (3)$$

Since  $M \ll M_0$  we shall not perform full quantization. Instead we shall treat the center-of-mass motion classically while the internal relative motion and its dipolar interaction with other molecules will be quantized. This is a strategy relevant to most real molecules, where  $M_e$  can represent the mass of the electronic cloud around a much heavier nucleus of mass  $M_n$ .

Assuming that the internal relative motions are small compared to intermolecular distances, the electronic interactions between molecules can be expressed in terms of the dipolar pair interaction

$$\phi(12) = - \frac{s_1 s_2}{r^3} D(12) \quad (4)$$

with

$$D(12) = 3(\hat{r}\hat{s}_1)(\hat{r}\hat{s}_2) - \hat{s}_1\hat{s}_2$$

where hats denote unit vectors. The  $\vec{s}_1$  and  $\vec{s}_2$  are the dipole moments of molecules 1 and 2 respectively, and  $r$  is their relative distance. Besides this dipolar interaction, which will enter the quantization, the molecules feel a highly repulsive core interaction which will not be quantized, as it is not coupled to the internal motion of the molecules. In our model we take this core interaction to be a hard-sphere interaction, with hard-sphere diameter  $R$ .

The potential  $\phi(s)$  that binds the masses  $M_e$  and  $M_n$  can be fairly arbitrary. If, for instance,  $\phi(s)$  allows only a fixed value  $s = m$  then the system will be a quantized polar fluid. However, for our computations a harmonic  $\phi(s)$  will be the most suitable:

$$\phi(s) = \frac{1}{2\alpha} s^2 . \quad (5)$$

This latter case will represent an "ideal" polarizable non-polar fluid where the average polarization of a single molecule is strictly proportional to the applied electric field of any magnitude. As is then obvious, the  $\alpha$  will be the polarizability both in the classical as well as the quantum-mechanical case, because the dynamics of the single molecule will be that of a harmonic oscillator. With the potential given by (5) we can deal explicitly with the internal degrees of freedom of the equivalent classical polymer problem as far as we shall go in our approximation to the many-body problem.

[With anharmonic  $\phi(s)$ , however, we would also have to introduce some approximation for the internal degrees of freedom too. For example, one might use the same type of approximation in the full problem as in the single-polymer problem, which in this context will be one dimensional (along the polymer).]

The approximation we shall use is the LOGA (lowest order  $\gamma$ -ordered approximation)<sup>7</sup> which can conveniently be further approximated by the MSA (mean spherical approximation)<sup>8</sup> in its treatment of the hard-sphere reference system. Wertheim solved the MSA for the case of rigid dipolar spheres,<sup>9</sup> and we have already<sup>5</sup> extended his solution to the classical problem of spheres with thermally fluctuating polarizability. Here we extend it further to the problem of spheres with the fluctuating polarizability treated quantum mechanically.

The parameter  $\gamma$  in general characterizes the inverse range of the perturbing interaction, i.e., its  $r$ -dependence is parameterized as  $\gamma^d f(\gamma r)$ ,  $r = |\underline{r}_1 - \underline{r}_2|$ ,  $d = \text{dimensionality}$ . For dipolar interaction,  $\gamma$ -parameterization is a bit degenerate and the  $\gamma$  is simply the inverse range inside of which the dipolar interaction is cut off.<sup>10</sup> In terms of this ordering the LOGA gives the first-order contribution in  $\gamma$  beyond the reference-system hard spheres. It should then be noted that the LOGA becomes exact in two different limits. First of all, it becomes exact in the limit  $\gamma \rightarrow 0$ . Secondly it becomes exact in the Gaussian-model<sup>11</sup> limit too. The Gaussian model will be the case in which all the atoms are placed on the vertices of a regular lattice (with one atom at each vertex).<sup>12</sup>

### III. QUANTUM PARTITION FUNCTION

Consider the partition function  $Z$  of a quantum mechanical system

$$Z = \text{Tr} e^{-\beta H} = \sum_n \langle \psi_n | e^{-\beta H} | \psi_n \rangle . \quad (6)$$

Here the  $H$  is the Hamilton operator, and  $\psi_n$  are the eigenfunctions of the system or some other complete set of eigenfunctions that are normalized. Let the wave function at time zero be  $\psi(0)$ . At time  $t$  the wave function is then

$$\psi(t) = e^{-(it/\hbar)H} \psi(0) \quad (7)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ . In the Schrödinger representation the time evolution (7) may be expressed by means of the propagator  $K(x, x', t)$

$$\psi(x, t) = \int K(x, x', t) \psi(x', 0) dx' . \quad (8)$$

Here the  $x$  and  $x'$  stand for the spatial coordinates of the system. The propagator is the solution of the Schrödinger equation with boundary condition

$$K(x, x', 0) = \delta(x - x') . \quad (9)$$

By means of the propagator the partition function may now be written as

$$\begin{aligned}
Z &= \sum_n \int \psi_n^*(x) e^{-\beta H} \psi_n(x) dx \\
&= \sum_n \iint \psi_n^*(x) K(x, x', -i\hbar\beta) \psi_n(x') dx dx' \\
&= \int K(x, x, -i\hbar\beta) dx
\end{aligned} \tag{10}$$

where the completeness relation

$$\sum_n \psi_n^*(x) \psi_n(x') = \delta(x - x') \tag{11}$$

for complete sets of eigenfunctions has been utilized.

The propagator may be expressed in terms of a path integral.<sup>1</sup> For instance, for a single particle of mass  $M$  in a potential  $V(\vec{r})$ , the Schrödinger equation has the form

$$H\psi = \left[ -\frac{\hbar^2}{2M} \nabla^2 + V(\vec{r}) \right] \psi = i\hbar \frac{\partial}{\partial t} \psi \tag{12}$$

or

$$\left[ \frac{\hbar^2}{2M} \nabla^2 - V(\vec{r}) \right] \psi = \frac{\partial}{\partial \beta} \psi . \tag{13}$$

The propagator is then given by

$$\begin{aligned}
K(\vec{r}, \vec{r}', -i\hbar\beta) &= \lim_{N \rightarrow \infty} \int \exp \left\{ - \sum_{i=0}^{N-1} \left[ \frac{M}{2\eta\hbar^2} (\vec{r}_{i+1} - \vec{r}_i)^2 + \eta V(\vec{r}_i) \right] \right\} \\
&\quad \times \left( \frac{M}{2\pi\eta\hbar^2} \right)^{d/2} \prod_{i=1}^{N-1} \left[ \left( \frac{M}{2\pi\eta\hbar^2} \right)^{d/2} d\vec{r}_i \right]
\end{aligned} \tag{14}$$

where  $d$  is dimensionality and

$$\beta = \eta N, \quad \vec{r} = \vec{r}_0, \quad \vec{r}' = \vec{r}_N . \tag{15}$$

Here the interval  $\beta$  has been divided into  $N$  equidistant pieces of

length  $\eta$ . In (14) it is understood that the limit  $N \rightarrow \infty$  should be taken with  $\beta$  fixed, so  $\eta \rightarrow 0$ . [With  $V = 0$ , (14) is nothing but the solution of the diffusion equation.]

For a many-body system the path integral (14) generalizes in a straightforward way.

By use of (1), (10) and (14) we can easily write down the quantized partition function associated with the internal motion of one of our polarizable molecules when it is isolated. It is the limit, as  $N \rightarrow \infty$ ,  $\beta$  fixed, of the function

$$Z^{(N)} = \int \exp \left\{ - \sum_{p=0}^{N-1} \left[ \frac{1}{2} \frac{\sigma}{\eta} (\vec{s}_{p+1} - \vec{s}_p)^2 + \eta \phi(s_p) \right] \right\} \prod_{q=0}^{N-1} (A d\vec{s}_q) \quad (16)$$

with

$$\sigma = \frac{M}{(\hbar e)^2} \quad \text{and} \quad A = \left( \frac{\sigma}{2\pi\eta} \right)^{3/2} \quad (d = 3)$$

It is easy to see that this  $Z^{(N)}$  for the quantum system is nothing but the classical partition function for a polymer of segments bound to one another by a potential  $\phi(s)$ . The  $\vec{s}_p$  represent the positions of the individual particles (atoms) of the chain. Neighboring particles are separated by a distance  $\eta$  along the chain which is closed and of length  $\beta$ . It should be noted that the direction along the polymer acts as an additional spatial dimension in the problem. This will become clearer when interactions between polymers are turned on. Along the polymer there are nearest-neighbor interactions that give the polymer a certain flexibility. In the limit  $\beta \rightarrow 0$  the length of

the polymer goes to zero, and we obtain the usual classical partition function for the internal motion of a polarizable molecule. Likewise in the limit  $\hbar \rightarrow 0$  this classical limit is again obtained since then the flexibility of the polymer vanishes.

Now we consider the propagator for an arbitrary number of our polarizable molecules. If these molecules did not interact then the propagator would be nothing but the product of single-particle propagators given by (14). Likewise the partition function (16) would be a similar product. The classical analog of this partition function or path integral would then obviously be a system of non-interacting polymers.

When the two-body interaction is turned on it will enter the propagator in the same way that the  $V(\vec{r})$  does in (14). The only difference is that the two-body interaction will contain the coordinates of two different molecules. In this way we obtain a classical polymer problem with two-body interaction for the quantum partition function of the internal motion of the polarizable molecules. In addition we must integrate over the center-of-mass motion, which involves hard-sphere interaction, and which we shall treat classically.

## IV. METHOD OF SOLUTION: THE MSA

We have just seen that the many-body quantum problem is equivalent to a classical problem of interacting polymers. Now the question arises as to whether there is an adequate method for doing the statistical mechanics of this latter problem. We find that the  $\gamma$ -ordering idea for long-range forces may be applied in this case. Our reference system will be the (classical) hard spheres with the center-of-mass motions of the molecules. The perturbing interaction will be the dipole-dipole interaction due to the internal motion of the particles. We shall consider the  $\gamma$ -ordering to first order beyond the reference system (with quantization of the dipole interaction). Imposing the core condition (of the hard spheres) on the pair correlation function gives the MSA (mean spherical approximation), which we shall consider. To apply the MSA to the present polymer problem we have to extend our trick used in the classical case with fluctuating polarizability.<sup>5</sup> The trick consists of regarding polymers (or molecules) with different internal configurations as being polymers (or molecules) of different species. With this point of view one gets a classical mixture problem where each species no longer has internal degrees of freedom. The density of the different species will be determined via the chemical potentials.

To find the interaction between the polymers due to the dipole interaction (4), we note (as concluded before) that  $\phi(12)$  will enter the many-body path integral in the same way that  $\phi(s)$  does in (16).

Thus the perturbing polymer pair interaction becomes

$$\psi(12) = -\frac{1}{\beta} \frac{\eta}{r^3} \sum_{p=1}^N s_{p1} s_{p2} D^{pp}(12) = -\frac{\eta}{\beta r^3} \sum_{p,q=1}^N s_{p1} s_{q2} D^{pq}(12) \delta_{pq} \quad (17)$$

where

$$D^{pq}(12) = 3(\hat{r} \hat{s}_{p1})(\hat{r} \hat{s}_{q2}) - \hat{s}_{p1} \hat{s}_{q2} .$$

The MSA is the solution of the OZ (Ornstein-Zernike) equation

$$h(12) = c(12) + \sum_{\ell} \rho_{\ell} \int c(13) h(32) d\vec{r}_3 \quad (18)$$

with boundary conditions that are, for particles with hard-sphere cores,

$$\begin{aligned} c(12) &= -\beta\psi(12) & \text{for } r > R, \quad r = |\vec{r}_1 - \vec{r}_2|, \\ h(12) &= -1 & \text{for } r < R, \end{aligned} \quad (19)$$

where the condition on  $h(12)$  is the exact core condition for such particles. In our case the densities  $\rho_{\ell}$  will become  $\rho(\{\vec{s}_p\})$ , i.e., functions of the internal polarizations  $\vec{s}_p$  ( $p = 1, 2, \dots, N$ ) along the polymer chain. So in (18) there will be the change

$$\sum_{\ell} \rho_{\ell} \rightarrow \int \left[ \prod_{p=1}^N d\vec{s}_p \right] \rho(\{\vec{s}_p\}) . \quad (20)$$

By inspection of (17) - (19) it is seen that the solution must have the form  $(\vec{r} = \vec{r}_1 - \vec{r}_2)$ ,

$$\begin{aligned} c(12) &= c_0(\vec{r}) + \eta^2 \sum_{p,q=1}^N s_{p1} s_{q2} [c_{\Delta}^{pq}(\vec{r}) \Delta^{pq}(12) + c_D^{pq}(\vec{r}) D^{pq}(12)] \\ h(12) &= h_0(\vec{r}) + \eta^2 \sum_{p,q=1}^N s_{p1} s_{q2} [h_{\Delta}^{pq}(\vec{r}) \Delta^{pq}(12) + h_D^{pq}(\vec{r}) D^{pq}(12)] \end{aligned} \quad (21)$$

with  $\Delta^{pq}(12) = \hat{s}_{p1} \hat{s}_{q2}$ . The  $c_0(\vec{r})$  and  $h_0(\vec{r})$  decouple from the remaining quantities and we shall regard them as given by the well-known MSA solution (identical to the Percus-Yevick solution) for hard spheres,<sup>13</sup> which constitute our reference system. The boundary conditions (19) with use of (17) then become

$$\begin{aligned} c_0(\vec{r}) &= 0, & c_{\Delta}^{pq}(\vec{r}) &= 0, & \text{and} & & c_D^{pq}(\vec{r}) &= \frac{1}{\eta r^3} \delta_{pq} & \text{for } r > R \\ h_0(\vec{r}) &= -1, & h_{\Delta}^{pq}(\vec{r}) &= 0, & \text{and} & & h_D^{pq}(\vec{r}) &= 0 & \text{for } r < R \end{aligned} \quad (22)$$

With insertion of (21) into the Fourier-transformed OZ equation (18) there will be integrals such as

$$\rho \langle s_{pi} s_{qj} \rangle = \int \left( \prod_{m=1}^N d\vec{s}_m \right) s_{pi} s_{qj} \rho(\{\vec{s}_n\}) = \frac{1}{3} \delta_{ij} R_{pq}, \quad \langle s_{pi} \rangle = 0 \quad (23)$$

Here the  $s_{pi}$  means the  $i$ -th component of  $\vec{s}_p$ . So far in our development the  $R_{pq}$  are unknown while the factor  $\frac{1}{3} \delta_{ij}$  follows from the symmetry of the problem, consistent with the  $\rho(\{\vec{s}_n\})$  that we shall find later. Fourier transformed, Eq. (21) has the form

$$\begin{aligned} \tilde{c}(12) &= \tilde{c}_0(\vec{k}) + \eta^2 \sum_{p,q=1}^N s_{p1} s_{q2} [\tilde{c}_{\Delta}^{pq}(\vec{k}) \Delta^{pq}(12) + \tilde{c}_D^{pq}(\vec{k}) \tilde{D}^{pq}(12)] \\ \tilde{h}(12) &= \tilde{h}_0(\vec{k}) + \eta^2 \sum_{p,q=1}^N s_{p1} s_{q2} [\tilde{h}_{\Delta}^{pq}(\vec{k}) \Delta^{pq}(12) + \tilde{h}_D^{pq}(\vec{k}) \tilde{D}^{pq}(12)] \end{aligned} \quad (24)$$

where

$$\tilde{D}^{pq}(12) = 3(\hat{k} \hat{s}_{p1})(\hat{k} \hat{s}_{q2}) - \hat{s}_{p1} \hat{s}_{q2}. \quad (25)$$

For the fluid under consideration, the  $c_0$ ,  $c_{\Delta}^{pq}$ ,  $c_D^{pq}$ ,  $h_0$ ,  $h_{\Delta}^{pq}$ ,  $h_D^{pq}$  and their transforms depend upon  $\vec{r}$  and  $\vec{k}$  only through  $|\vec{r}|$  and  $|\vec{k}|$  respectively.

However to accommodate the lattice gas in discussions below, we use the more general vector notation.

It will be convenient to introduce

$$\begin{aligned}
 J_1 &= D + \Delta & \Delta &= \frac{1}{3} (J_1 + J_2) \\
 J_2 &= -D + 2\Delta & D &= \frac{1}{3} (2J_1 - J_2) \\
 \tilde{c}_1 &= \frac{1}{3} (\tilde{c}_\Delta + 2\tilde{c}_D) & \tilde{c}_\Delta &= \tilde{c}_1 + 2\tilde{c}_2 \\
 \tilde{c}_2 &= \frac{1}{3} (\tilde{c}_\Delta - \tilde{c}_D) & \tilde{c}_D &= \tilde{c}_1 - \tilde{c}_2
 \end{aligned} \tag{26}$$

along with the same equations in which  $c$  is replaced by  $h$ . Here

$$D = \tilde{D}^{pq}(12), \quad \Delta = \tilde{\Delta}^{pq}(12), \quad \tilde{c}_\Delta = \tilde{c}_\Delta^{pq}(\vec{k}), \quad \text{and} \quad \tilde{c}_D = \tilde{c}_D^{pq}(\vec{k}).$$

With this, (24) becomes

$$\tilde{c}(12) = \tilde{c}_0(\vec{k}) + \eta^2 \sum_{p,q=1}^N s_{p1} s_{q2} [\tilde{c}_1^{pq} J_1^{pq} + \tilde{c}_2^{pq} J_2^{pq}] \tag{27}$$

with an analogous expression for  $h(12)$ . By insertion into the Fourier-transformed OZ equation one then finds the "multiplication" table

$$J_1 J_1 = J_1, \quad J_1 J_2 = 0, \quad \text{and} \quad J_2 J_2 = J_2, \tag{28}$$

i.e.,

$$\int \left( \prod_{m=1}^N d\vec{s}_m \right) J_1^{pu}(13) \rho(\{\vec{s}_{n3}\}) J_1^{vq}(32) = R_{uv} J_1^{pq}(12) \tag{29}$$

etc. The OZ equation thus results in the following set of equations

$$\tilde{h}_i^{pq}(\vec{k}) = \tilde{c}_i^{pq}(\vec{k}) + \eta^2 \sum_{u,v=1}^N \tilde{c}_i^{pu}(\vec{k}) R_{uv} \tilde{h}_i^{vq}(\vec{k}), \quad (i = 1, 2) \tag{30}$$

Since the polymer chains are closed rings they possess translational invariance. This will reflect itself in Eq. (30) in the way that the

quantities involved will depend only upon relative distances along the chain. Thus we can Fourier transform (30) along the chain to obtain

$$\tilde{h}_i^K(\vec{k}) = \tilde{c}_i^K(\vec{k}) + R_K \tilde{c}_i^K(\vec{k}) \tilde{h}_i^K(\vec{k}) \quad (i = 1, 2) \quad (31)$$

where  $K$  is the discrete scalar transform variable,

$$K = 2\pi \frac{n}{\eta N} = 2\pi \frac{n}{\beta} \quad (n = 1, 2, \dots, N) . \quad (32)$$

Here

$$R_K = \eta \sum_{n=1}^N R_{pq} e^{iKx} \xrightarrow{\eta \rightarrow 0} \int R_{pq} e^{iKx} dx \quad (33)$$

where  $n = p - q$  and  $x = n\eta$ . Inverted ( $N\eta = \beta$ ), we have

$$R_{pq} = \frac{1}{N\eta} \sum_K R_K e^{-iKx} . \quad (34)$$

The definitions of  $\tilde{c}_i^K(\vec{k})$  and  $\tilde{h}_i^K(\vec{k})$  are analogous.

Applying this latter Fourier transform to the boundary conditions (22) we find

$$\begin{aligned} c_{\Delta}^K(\vec{r}) = 0 \quad \text{and} \quad c_D^K(\vec{r}) = \frac{1}{r^3} & \quad \text{for } r > R \\ h_{\Delta}^K(\vec{r}) = 0 \quad \text{and} \quad h_D^K(\vec{r}) = 0 & \quad \text{for } r < R . \end{aligned} \quad (35)$$

Now consider Eqs. (31) and (35) for a fixed  $K$ . It is then seen that these equations are nothing but the equations that solve the corresponding problem of classical dipolar hard spheres, whose solution is well known.<sup>9</sup> From (31) and (35) the density  $\rho_K$  and the dipole moment  $m$  of these classical spheres are given by

$$\rho_K = R_K \quad \beta m^2 = 1 . \quad (36)$$

The  $R_K$  are to be determined later via the chemical potential. This result is the quantized generalization of our classical model with fluctuating polarization.<sup>5</sup> There we also had an effective dipole moment  $m = m_e$  for the equivalent polar-fluid problem to be determined. The generalization here in going to the quantized problem gives an infinite set of classical polar-fluid problems associated with the different values of  $K$ .

The explicit MSA solution of the classical dipolar hard-sphere problem thus gives<sup>9</sup>

$$1 - R_K \tilde{c}_i^K(0) = [1 + R_K \tilde{h}_i^K(0)]^{-1} = q_i \quad (i = 1, 2)$$

$$q_1 = q(2\xi) \quad \text{and} \quad q_2 = q(-\xi)$$

$$q(x) = \frac{(1+2x)^2}{(1-x)^4} \quad \text{with} \quad y = \frac{4\pi}{9} \beta m^2 \rho_K = \frac{4\pi}{9} R_K = \frac{1}{3} (q_1 - q_2)$$

$$c_{\Delta}^K(0) = -2K(q_1 - q_2) , \quad \xi = \frac{\pi}{6} K R_K R^3 , \quad 3K = \int h_D(r) r^{-3} dr . \quad (37)$$

Or by substitution

$$c_{\Delta}^K(0) = -16\xi . \quad (38)$$

To determine  $R_K$  we need the  $\rho(\{\vec{s}_n\})$  which we get via the chemical potentials. Considered as a mixture problem these will be by use of Eq. (16)

$$\beta\mu(\{\vec{s}_n\}) = \beta\mu + N\ell nA - \sum_{p=1}^N \left[ \frac{1}{2} \frac{\sigma}{\eta} (\vec{s}_{p+1} - \vec{s}_p)^2 + \eta\phi(s_p) \right] \quad (39)$$

where the last term has the same effect as an external field. The  $\mu$  is a common constant which is the proper thermodynamic chemical potential for the fluid under consideration. Equation (39) is the generalization of Eq. (4a) of ref. [5].

The chemical potentials must be related to the densities. Previously we have found this relation in general for the MSA.<sup>14</sup> The relevant equations we again find in ref. [5]. In referring to these equations we shall preface them with an I. Noting that in our case  $\sum_i \rho_i [\tilde{c}_{i\ell}(0) - \tilde{c}_{0i\ell}(0)] = 0$  or  $\langle \vec{s}_p \rangle = 0$  the excess chemical potential from Eq. (I.18) becomes

$$\beta\mu_\ell^E = \frac{1}{2} [c_{\ell\ell}(0) - c_{0\ell\ell}(0)] \quad (40)$$

or in our present notation, using (21) [ $c_D^{pq}(0) = 0$ ],

$$\beta\mu^E(\{\vec{s}_n\}) = \frac{1}{2} \sum_{p,q=1}^N s_p s_q c_\Delta^{pq}(0) . \quad (41)$$

This should be added to the reference-system piece to obtain in analogy with (I.21)

$$\beta\mu(\{\vec{s}_n\}) = \ln[\rho(\{\vec{s}_n\})/\rho] + \beta\mu_0 + \frac{1}{2} \sum_{p,q=1}^N s_p s_q c_\Delta^{pq}(0) , \quad (42)$$

where  $\mu_0 = \mu_0(\rho)$  is the chemical potential for reference-system hard spheres at density  $\rho$ ,

$$\rho = \int \rho(\{\vec{s}_n\}) \left( \prod_{q=1}^N d\vec{s}_q \right) . \quad (43)$$

Equation (39) combined with (42) gives the MSA density distribution

$$\rho(\{\vec{s}_n\}) = C \exp\left\{- \sum_{p=1}^N \left[ \frac{1}{2} \frac{\sigma}{\eta} (\vec{s}_{p+1} - \vec{s}_p)^2 + \eta\phi(s_p) \right] - \frac{\eta^2}{2} \sum_{p,q=1}^N \vec{s}_p \vec{s}_q c_{\Delta}^{pq}(0) \right\} \quad (44)$$

where  $C$  is a constant independent of  $\vec{s}_p$ .

The  $R_{pq} = \rho\langle \vec{s}_p \vec{s}_q \rangle$  [of Eq. (23)] is to be determined from (44). In this respect the  $R_{pq}$  represents the spin-correlation function of a one-dimensional spin problem, which in general is not exactly solvable. With  $c_{\Delta}^{pq}(0) = 0$  this reduces to the one-particle quantum problem, [Eq. (16)] which in (44) means nearest-neighbor interaction, and which may be treated more explicitly. (We note that we can apply the MSA to this one-dimensional problem too, along with our MSA of the full many-body problem. The details of this MSA for the single chain we shall not consider here.) However, with harmonic  $\phi(s)$ , as given by (5), this one-dimensional problem can be solved explicitly in a straightforward way since it becomes a Gaussian model. (This explicit and exact result would also come out of the MSA computation of the single chain.)

With  $\phi(s)$  given by (5), Fourier transformed coordinates may be introduced

$$\begin{aligned} \vec{a}_K &= \frac{1}{\sqrt{N}} \sum_{p=1}^N e^{iKx} \vec{s}_p \\ \vec{s}_p &= \frac{1}{\sqrt{N}} \sum_{K=1}^N e^{-iKx} \vec{a}_K \end{aligned} \quad (45)$$

with  $x = p\eta$  and  $K = 2\pi \frac{n}{\eta N}$ . With this transformation, (44) turns into

$$\rho(\{\vec{s}_n\}) = C \exp\left\{-\frac{\eta}{2} \sum_{n=1}^N \left[2[1 - \cos(k\eta)] \frac{\sigma}{\eta^2} + \frac{1}{\alpha} + c_{\Delta}^K(0)\right] \vec{a}_K \vec{a}_{-K}\right\} \quad (46)$$

where

$$\vec{a}_{-K} = \vec{a}_K^* \quad (K = 2\pi \frac{n}{\eta N}) .$$

Since

$$\prod_{p=1}^N d\vec{s}_p = \prod_{n=1}^N d\vec{a}_K$$

we now easily compute that ( $m = p - q_1$  and  $x = m\eta$ )

$$\begin{aligned} R_K &= \eta \sum_{m=1}^N R_{pq} e^{iKx} = \eta \rho \frac{1}{N} \sum_{p,q=1}^N \langle \vec{s}_p \vec{s}_q \rangle e^{iKx} \\ &= \eta \rho \langle \vec{a}_K \vec{a}_{-K} \rangle = \frac{3\rho}{2[1 - \cos(k\eta)] \frac{\sigma}{\eta^2} + \frac{1}{\alpha} + c_{\Delta}^K(0)} \\ &\xrightarrow{\eta \rightarrow 0} \frac{3\rho}{\sigma K^2 + \frac{1}{\alpha} + c_{\Delta}^K(0)} . \end{aligned} \quad (47)$$

This, combined with Eqs. (37) and (38), gives the explicit MSA solution for harmonic  $\phi(s)$ .

## V. THE DIELECTRIC CONSTANT

To find the dielectric constant  $\epsilon$  of our quantum fluid, we have to generalize previously known expressions for  $\epsilon$  of classical fluids. We shall employ a method used by Høye and Stell.<sup>10</sup> The method consists of adding two test charges to the dielectric fluid and computing the correlation function for large separation. This will give the resulting effective force between the charges and thus the dielectric constant.

Like Eq. (19) in ref. [10], the pair correlation function for the test particles again is given by the direct interaction between these particles plus interaction via one polar particle of the medium plus interaction via two polar particles correlated by the fluid's pair correlation function. We will thus need the Fourier transforms of the charge-charge interaction  $1/r$  and the charge-dipole interaction  $-(\hat{s}\hat{r})/r^2$ , which are respectively (with  $k = |\vec{k}|$ )

$$\frac{4\pi}{k^2} \quad \text{and} \quad -\frac{4\pi i}{k} (\hat{k}\hat{s}) . \quad (48)$$

By quantization the test charges should also become equivalent to polymers. But they may be regarded as stiff rods since the distance between the test particles is large. With charge  $q$  on each of the test particles their direct interaction, Fourier transformed, will be ( $\beta = N\eta$ )

$$\tilde{\phi}_{CC}(12) = \frac{4\pi q^2}{k^2} = \frac{1}{N} \sum_{p=1}^N \frac{4\pi q^2}{k^2} = \frac{1}{\beta} \eta \sum_{p=1}^N \frac{4\pi q^2}{k^2} . \quad (49)$$

Likewise, the interaction between one of the test charges and one of the "polymer" dipoles will be

$$\tilde{\phi}_{CD}(12) = -\tilde{\phi}_{DC}(21) = \frac{1}{\beta} \eta \sum_{p=1}^N - \frac{4\pi i}{k} (\hat{k}\hat{s}_{p2}) . \quad (50)$$

The effective interaction  $\tilde{\phi}_{CC}^E(12)$  between the two test charges now becomes

$$\begin{aligned} -\beta\tilde{\phi}_{CC}^E(12) &= -\beta\tilde{\phi}_{CC}(12) + \int [-\beta\tilde{\phi}_{CD}(13)]\rho(\{\vec{s}_{n3}\})[-\beta\tilde{\phi}_{DC}(32)] \\ &\quad \times \prod_{p=1}^N (d\vec{s}_{p3}) + \iint [-\beta\tilde{\phi}_{CD}(13)]\rho(\{\vec{s}_{n3}\})h(34) \\ &\quad \times \rho(\{\vec{s}_{n4}\})[-\beta\tilde{\phi}_{DC}(42)] \prod_{p=1}^N (d\vec{s}_{p3}) \prod_{q=1}^N (d\vec{s}_{q4}) \end{aligned} \quad (51)$$

or

$$\begin{aligned} \tilde{\phi}_{CC}^E &= \frac{4\pi q^2}{k^2} \left[ 1 - \frac{4\pi}{3\beta} \eta^2 \sum_{\ell,p=1}^N R_{\ell p} - \frac{4\pi}{3\beta} \eta^4 \sum_{\ell,v,u,p=1}^N R_{\ell v} \right. \\ &\quad \left. \times \left( \frac{2}{3} \tilde{h}_D^{vu} + \frac{1}{3} \tilde{h}_\Delta^{vu} \right) R_{up} \right] \\ &= \frac{4\pi q^2}{k^2} \left[ 1 - \frac{4\pi}{3} R_0 (1 + \tilde{h}_1^0 R_0) \right] \end{aligned} \quad (52)$$

when equations (26) and (33) are utilized.

The dielectric constant  $\epsilon$  is now determined by the macroscopic law ( $r \rightarrow \infty$  or  $k \rightarrow 0$ )

$$\phi_{CC}^E = \frac{1}{\epsilon} \phi_{CC} \quad (53)$$

which when combined with (52) yields ( $k \rightarrow 0$ )

$$\epsilon = \left[ 1 - \frac{4\pi}{3} R_0 (1 + \tilde{h}_1^0 R_0) \right]^{-1} . \quad (54)$$

Thus for our polarizable hard spheres we obtain the explicit result

$$\epsilon = \frac{q(2\xi)}{q(-\xi)} \quad (55)$$

with

$$\begin{aligned} \frac{4\pi}{3} R_0 &= q(2\xi) - q(-\xi) = \frac{4\pi\rho\alpha}{1 - 16\xi\alpha} \\ q(x) &= (1 + 2x)^2 / (1 - x)^4 . \end{aligned} \quad (56)$$

Here Eqs. (37), (38), and (47) have been used.

It is seen that the  $\epsilon$  in the MSA with harmonic  $\phi(s)$  of Eq. (5) is precisely the same in the quantum mechanical case, considered here, as in the classical case for the same model.<sup>5</sup> As is obvious from our computations here this would not be the case for anharmonic  $\phi(s)$  -- see Eq. (44) and our comments below.

As in the classical case we can put the particles on the vertices of a regular cubical lattice here too. In this case the hard-sphere results (37) and (38) are of course not valid. As  $[1 + \tilde{h}_1^0 R_0]^{-1} = 1 - \tilde{c}_1^0 R_0$  we have to know more precisely  $\tilde{c}_1^K(0) = \frac{1}{3} [\tilde{c}^K(0) + 2\tilde{c}_D^K(0)]$  [Eq. (26)]. For a cubic lattice with cells that may be chosen to have unit volume,  $\vec{r} = 0$  and  $\vec{r} \neq 0$  replace  $r < R$  and  $r > R$  in (22). One has

$$\tilde{c}_\Delta^K(k) = \tilde{c}_\Delta^K(0) = c_\Delta^K(0) , \quad (57)$$

since according to the resulting (22),  $c_\Delta^{Pq}(\vec{r}) = 0$  and thus  $c_\Delta^K(\vec{r}) = 0$  for  $\vec{r} \neq 0$ . From (35)  $c_D^K(\vec{r}) = 1/r^3$  ( $\vec{r} \neq 0$ ). Multiplying this with the angular dependence of the dipolar interaction [Eq. (17)] it is

found that<sup>5</sup>

$$\tilde{c}_D^{\mathbf{K}}(0) = -\frac{4\pi}{3}. \quad (58)$$

(For  $\vec{k} \rightarrow 0$  it makes no difference whether a system of cubical symmetry or one of spherical symmetry is considered.) Equations (57) and (58) used in (54) give

$$\frac{\epsilon-1}{\epsilon+2} = \frac{\frac{4\pi}{9} R_0}{1 + \tilde{c}_1^0 R_0 - \frac{8\pi}{3} R_0} = \frac{\frac{4\pi}{9} R_0}{1 - \frac{1}{3} R_0 c_{\Delta}^0(0)}. \quad (59)$$

Equation (47) means

$$R_0 = 3\rho\alpha \left[ 1 - \frac{R_0 c_{\Delta}^0(0)}{3\rho} \right] \quad (60)$$

which inserted in (59) gives

$$\frac{\epsilon-1}{\epsilon+1} = \frac{4\pi}{3} \rho\alpha \frac{1 - \frac{1}{3} \frac{R_0 c_{\Delta}^0(0)}{\rho}}{1 - \frac{1}{3} \rho \frac{R_0 c_{\Delta}^0(0)}{\rho}}. \quad (61)$$

Again comparing with the corresponding classical model it is seen that the MSA results are the same.<sup>5</sup> The equivalence follows from the fact that the  $c_{\Delta}(0)$  in Eq. (I.39) (of ref. [5]) is the same as our  $R_0 c_{\Delta}^0(0)/\rho$ . This is clear from Eq. (31) where  $R_{\mathbf{K}}$  enters instead of  $\rho$  ( $\mathbf{K} = 0$ ), and there are corresponding appropriate changes in boundary conditions (35) and in relation (47) compared to ref. [5].

If we let the lattice be close packed, i.e.,  $\rho = 1$ , then the MSA result (61) becomes the exact result

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3} \rho\alpha . \quad (62)$$

This is the well known Clausius-Mossotti relation for polarizable cubic crystals.

## VI. FREE ENERGY

Thermodynamic quantities can be obtained by use of the general MSA expressions obtained by Høye and Stell in ref. [15]. Its Eq. (38) for a mixture gives for the excess Helmholtz free energy  $f^E$  per particle

$$\begin{aligned}
 -\beta\rho f^E = I = & \frac{1}{2} \sum_{ij} \rho_i \rho_j [\tilde{c}_{ij}(0) - \tilde{c}_{0ij}(0)] \\
 & - \frac{1}{2} \frac{1}{(2\pi)^3} \text{Tr} \int \left\{ \ln[1 - \rho\tilde{c}(\vec{k})] + \rho\tilde{c}(\vec{k}) \right. \\
 & \left. - \ln[1 - \rho\tilde{c}_0(\vec{k})] - \rho\tilde{c}_0(\vec{k}) \right\} d\vec{k} \quad (63)
 \end{aligned}$$

where  $\rho\tilde{c}(\vec{k})$  is a matrix with elements  $(\rho_i\rho_j)^{1/2} \tilde{c}_{ij}(\vec{k})$ , and likewise for the reference-system piece  $\rho\tilde{c}_0(\vec{k})$ . In our case here  $\rho_i \rightarrow \rho(\{\vec{s}_n\})$  and  $\sum_i \rightarrow \int \prod_{p=1}^N (d\vec{s}_p)$ . The first term in (63) vanishes since  $\langle \vec{s}_p \rangle = 0$ , and the  $\rho\tilde{c}_0(\vec{k})$  terms cancel against similar pieces in  $\rho\tilde{c}(\vec{k})$ , which is clear from the form (27) [ $\tilde{c}(\vec{k}) \rightarrow \tilde{c}(12)$ ]. Inserting (27) into (63) we thus find  $K = 2\pi \frac{n}{N\eta} = \frac{2\pi}{\beta} n$ ,  $n = 1, 2, \dots, N$  and  $N \rightarrow \infty$ )

$$\begin{aligned}
 I = & - \frac{1}{2} \frac{1}{(2\pi)^3} \sum_{\mathbf{K}} \int \left\{ \ln[1 - R_{\mathbf{K}} \tilde{c}_1^{\mathbf{K}}(\vec{k})] + 2\ln[1 - R_{\mathbf{K}} \tilde{c}_2^{\mathbf{K}}(\vec{k})] \right\} d\vec{k} \\
 & - \frac{1}{2} \sum_{\mathbf{K}} R_{\mathbf{K}} c_{\Delta}^{\mathbf{K}}(0) . \quad (64)
 \end{aligned}$$

The factor 2 in front of the second  $\ln$  term is there because the  $J_2$  averaged over orientations is 2 while  $J_1$  so averaged is 1 [Eqs. (26) and (28)]. Due to integrals like (23) we get factors  $R_{pq}$  between  $\tilde{c}_i^{\ell p}(\vec{k})$  and  $\tilde{c}_i^{qj}(\vec{k})$ . Summations with respect to  $\dots\ell pqj\dots$  correspond

to convolutions. Thus Fourier transforms [Eqs. (33) and (34)] may be utilized, replacing all the summations with a single one in  $k$ .

To obtain the full free energy the reference-system piece  $f^R$  must be added to  $f^E$ . We have

$$\begin{aligned}
 -\beta\rho f^R = I^R = I_0 - \int \rho(\{\vec{s}_n\}) \ln[\rho(\{\vec{s}_n\})/\rho] \prod_{q=1}^N d\vec{s}_q + \rho N \ln A \\
 - \int \rho(\{\vec{s}_n\}) \sum_{p=1}^N \left[ \frac{1}{2} \frac{\sigma}{\eta} (\vec{s}_{p+1} - \vec{s}_p)^2 + \frac{\eta}{2\alpha} s_p^2 \right] \prod_{q=1}^N d\vec{s}_q .
 \end{aligned}
 \tag{65}$$

Here the  $I_0$  is the result for the reference-system hard spheres at density  $\rho$ . The second term is the ideal-mixture term. This enters because we regard the different "polymer" configurations of the internal motion as being different species of a mixture. The third term plus the last term represent an energy correction associated with the last two terms in expression (39) for the chemical potential [with  $\phi(s)$  given by (5)]. This arises because in our mixture picture we regard this term as an external potential. However, thermodynamically it does not have this status, so that its presumed partition function adds an artificial contribution to the energy. This term in (65) compensates for this mixture-picture assessment of energy contributions. In this way the resulting chemical potential will be the proper thermodynamic one. [This is the same correction as the one made in Eq. (94) of ref. [16].] Note that without the perturbing dipolar interaction the last two terms of (65) will give the contribution from the quantized internal motion

of the free molecules. When the perturbation is turned on, the  $I^R$  will change since the  $\rho(\{\vec{s}_n\})$  will change, i.e., the mixture reference-system changes.

With density distribution (44) used in (65) we find

$$I^R = I_0 - \rho \ln(C/\rho) + \frac{1}{2} \sum_{\mathbf{K}} R_{\mathbf{K}} c_{\Delta}^{\mathbf{K}}(0) + \rho N \ln A \quad (66)$$

The  $C$  is determined by the normalization (43). Except for the last term in (44), and the dimensionality of the vector  $\vec{s}_p$  this would give the quantized partition function of the single oscillator considered in the Appendix. Utilizing the methods applied in the Appendix to obtain (A1) and (A4) we find

$$N \ln A - \ln(C/\rho) = \frac{3}{2} \sum_{\mathbf{K}} \ln \left( \frac{\sigma_{\mathbf{R}_{\mathbf{K}}}}{3\rho\eta^2} \right) \quad (\mathbf{K} = 2\pi \frac{n}{N\eta}, n = 1, 2, \dots, N) \quad (67)$$

Altogether, adding (64) and (66) the Helmholtz free energy  $f$  per particle becomes

$$\begin{aligned} -\beta\rho f = & \frac{3}{2} \rho \sum_{\mathbf{K}} \ln \left( \frac{\sigma_{\mathbf{R}_{\mathbf{K}}}}{3\rho\eta^2} \right) - \frac{1}{2} \frac{1}{(2\pi)^3} \sum_{\mathbf{K}} \int \left\{ \ln(1 - R_{\mathbf{K}} \tilde{c}_1^{\mathbf{K}}(\vec{k})) \right. \\ & \left. + 2 \ln[1 - R_{\mathbf{K}} \tilde{c}_2^{\mathbf{K}}(\vec{k})] \right\} d\vec{k} + I_0 \quad (68) \end{aligned}$$

Here we can also specialize to a regular cubic lattice. We shall further let the lattice be close packed, i.e.,  $\rho = 1$  with cells of unit volume. With that,  $\int d\vec{k} = (2\pi)^3$ , and (68) becomes (with  $I_0 = 0$ )

$$\begin{aligned} -\beta f = & - \frac{1}{2} \frac{1}{(2\pi)^3} \sum_{n=1}^N \int \left[ \ln\{2[1 - \cos(K\eta)]\} + [\eta\hbar\omega_1(\vec{k})]^2 \right] \\ & + 2 \ln\{2[1 - \cos(K\eta)]\} + [\eta\hbar\omega_2(\vec{k})]^2 \Big] d\vec{k} \quad (69) \end{aligned}$$

when (47) is used for  $R_K$ . Use of (26) for  $\tilde{c}_1(\vec{k})$  and (57) for the lattice-gas case yields

$$\begin{aligned}\omega_1(\vec{k})^2 &= \frac{e^2}{M} \left[ \frac{1}{\alpha} - 2\tilde{c}_D^K(\vec{k}) \right] \\ \omega_2(\vec{k})^2 &= \frac{e^2}{M} \left[ \frac{1}{\alpha} + \tilde{c}_D^K(\vec{k}) \right]\end{aligned}\quad (70)$$

with (16) inserted for  $\sigma$ . For a lattice gas,  $c_D^K(0) = 0$ , which from boundary condition (35) means that  $\tilde{c}_D^K(\vec{k})$  is independent of  $K$ . From this one sees that the sum in (69) is precisely the same as that of (A4), which is evaluated in our Appendix (for fixed  $\vec{k}$ ). The result is given by (A16). Using this we find

$$\begin{aligned}-\beta f &= - \frac{1}{(2\pi)^3} \int \left[ \ln\{2\sinh[\frac{1}{2} \beta \hbar \omega_1(\vec{k})]\} \right. \\ &\quad \left. + 2\ln\{2\sinh[\frac{1}{2} \beta \hbar \omega_2(\vec{k})]\} \right] d\vec{k} .\end{aligned}\quad (71)$$

This is precisely the Helmholtz free energy for a set of quantized harmonic oscillators; one subset having frequencies  $\omega_1(\vec{k})$ , and two subsets having frequencies  $\omega_2(\vec{k})$ . Furthermore this is the result one would obtain by evaluating the eigenmodes of the lattice. These eigenmodes will have the frequencies  $\omega_1(\vec{k})$  and  $\omega_2(\vec{k})$ , and quantization of the resulting set of oscillators yields (71).

## VII. INTERNAL ENERGY

The internal energy  $u$  per particle may be obtained by differentiation of (68), utilizing Eq. (31) with conditions (35), since

$$u = \frac{\partial}{\partial \beta} (\beta f) . \quad (72)$$

The  $u$  may alternatively be obtained from the general MSA expressions. For the excess energy  $u^E$ , Eq. (37) of ref. [15] yields

$$-\beta \rho_i u_i = \frac{1}{2} \rho_i [h_{ii}(0) - c_{ii}(0)] + \frac{1}{2} \sum_j \rho_i \rho_j \tilde{c}_{ij}(0) \quad (73)$$

such that

$$\rho u^E = \sum_i \rho_i u_i .$$

For a hard-sphere reference system alone one has  $u_i = 0$ . Since  $\langle \vec{s}_p \rangle = 0$  the last term in (73) drops out. In analogy with (64) we thus get

$$\beta \rho u^E = \frac{1}{2} \sum_K R_K c_{\Delta}^K(0) . \quad (74)$$

This should be added to the internal energy  $u^R$  of the reference system which follows from (65) (with  $\beta = N\eta$ ).

$$\begin{aligned} \beta \rho u^R &= \eta \frac{\partial}{\partial \eta} (\beta \rho f^R) = \beta \rho u_0 + \int \rho(\{\vec{s}_n\}) \sum_{p=1}^N \left[ -\frac{1}{2} \frac{\sigma}{\eta} (\vec{s}_{p+1} - \vec{s}_p)^2 \right. \\ &\quad \left. + \frac{\eta}{2\alpha} s_p^2 \right] \prod_{q=1}^N d\vec{s}_q + \rho \frac{3}{2} N = \beta \rho u_0 + \frac{3}{2} \rho N \\ &\quad + \frac{1}{2} \sum_K \sigma \{ -2[1 - \cos(k\eta)] \frac{1}{\eta^2} + \hbar^2 \omega^2 \} R_K \\ &= \beta \rho u_0 + \frac{1}{2} \sum_K [3\rho - \sigma(K^2 - \hbar^2 \omega^2) R_K] \quad (\sigma \hbar^2 \omega^2 = \frac{1}{\alpha}) . \quad (75) \end{aligned}$$

The  $u_0$  is the classical kinetic energy of hard spheres. The  $\frac{3}{2} \rho N$  arises upon differentiation of the  $\rho N \mathcal{L} n A$  term of (65). Adding (74) and (75), the full internal energy per molecule is obtained:

$$\begin{aligned} \beta \rho u &= \beta \rho (u^R + u^E) = \beta \rho u_0 + \sum_{\mathbf{k}} [3\rho - \sigma \mathbf{k}^2 R_{\mathbf{k}}] \\ &= 3\rho \sum_{\mathbf{k}} \frac{\sigma \hbar^2 \omega^2 + c_{\Delta}^{\mathbf{k}}(0)}{\sigma (\mathbf{k}^2 + \hbar^2 \omega^2) + c_{\Delta}^{\mathbf{k}}(0)}, \end{aligned} \quad (76)$$

where expression (47) for  $R_{\mathbf{k}}$  has been used.

For a lattice gas the core condition  $h^{\mathbf{k}}(0) = 0$  may be used to put (76) into a different form. From (26)  $h_{\Delta}(\vec{k}) = h_1(\vec{k}) + 2h_2(\vec{k})$ .

So by use of (31)

$$\begin{aligned} 0 &= \frac{1}{(2\pi)^3} \int \frac{\tilde{c}_1^{\mathbf{k}}(\vec{k})}{1 - R_{\mathbf{k}} \tilde{c}_1^{\mathbf{k}}(\vec{k})} d\vec{k} + 2 \frac{1}{(2\pi)^3} \int \frac{\tilde{c}_2^{\mathbf{k}}(\vec{k})}{1 - R_{\mathbf{k}} \tilde{c}_2^{\mathbf{k}}(\vec{k})} d\vec{k} \quad (77) \\ 3R_{\mathbf{k}} &= \frac{1}{(2\pi)^3} \int \frac{d\vec{k}}{R_{\mathbf{k}}^{-1} - \tilde{c}_1^{\mathbf{k}}(\vec{k})} + 2 \frac{1}{(2\pi)^3} \int \frac{d\vec{k}}{R_{\mathbf{k}}^{-1} - \tilde{c}_2^{\mathbf{k}}(\vec{k})} \\ \frac{R_{\mathbf{k}}}{\rho} &= \frac{1}{(2\pi)^3} \int \left\{ \frac{1}{\sigma [\mathbf{k}^2 + \hbar^2 \omega^2] + (1-\rho) c_{\Delta}^{\mathbf{k}}(0) - 2\rho \tilde{c}_D^{\mathbf{k}}(\vec{k})} \right. \\ &\quad \left. + \frac{2}{\sigma [\mathbf{k}^2 + \hbar^2 \omega^2] + (1-\rho) c_{\Delta}^{\mathbf{k}}(0) + \rho \tilde{c}_D^{\mathbf{k}}(\vec{k})} \right\} d\vec{k}. \quad (78) \end{aligned}$$

For a close-packed lattice ( $\rho = 1$ ) this reduces to

$$R_{\mathbf{k}} = \frac{1}{(2\pi)^3} \int \left\{ \frac{1}{\sigma [\mathbf{k}^2 + (\hbar \omega_1(\vec{k}))^2]} + \frac{2}{\sigma [\mathbf{k}^2 + (\hbar \omega_2(\vec{k}))^2]} \right\} d\vec{k} \quad (79)$$

with  $\omega_1(\vec{k})$  and  $\omega_2(\vec{k})$  given by (70). Inserted in (76) with  $\rho = 1$  this gives (putting  $u_0 = 0$ )

$$\beta u = \sum_{\vec{k}} \frac{1}{(2\pi)^3} \int \left\{ \frac{(\hbar\omega_1(\vec{k}))^2}{k^2 + (\hbar\omega_1(\vec{k}))^2} + 2 \frac{(\hbar\omega_2(\vec{k}))^2}{k^2 + (\hbar\omega_2(\vec{k}))^2} \right\} d\vec{k} . \quad (80)$$

Again comparing with the Appendix, this is the sum evaluated in (A17).

Comparing we find

$$u = \frac{1}{(2\pi)^3} \int \left\{ \frac{1}{2} \hbar\omega_1(\vec{k}) \coth(\hbar\omega_1(\vec{k})) + 2 \cdot \frac{1}{2} \hbar\omega_2(\vec{k}) \coth(\hbar\omega_2(\vec{k})) \right\} d\vec{k} . \quad (81)$$

Corresponding to (71), this is nothing but the average quantized energy of the eigenmodes of the lattice.

## APPENDIX. PARTITION FUNCTION FOR A SINGLE HARMONIC OSCILLATOR

We want to compute the partition function (16) for a single oscillator with  $\phi(s)$  given by (5). This path integral is then the same as a Gaussian model and is exactly solvable by standard methods. Thus the normal modes as given by (45) may be introduced, and like (44), Eq. (16) assumes a simple form in terms of  $\cos(k\eta)$ ,  $a_K$  and  $a_{-K}$ .

$$Z = \int \exp \left\{ -\frac{\eta\sigma}{2} \sum_{n=1}^N \left[ [2(1 - \cos(k\eta)) \frac{1}{2} + \hbar^2 \omega^2] a_K a_{-K} \right] \right\} \times \prod_{n=1}^N (A^{1/3} da_K) . \quad (A1)$$

To have an oscillator with one degree of freedom only, for simplicity, the vector  $\vec{a}_K$  is replaced by the scalar  $a_K$  ( $K = 2\pi \frac{n}{\eta N}$ ) in this Appendix. The  $\omega$  is the eigenfrequency of the oscillator

$$\omega^2 = \frac{1}{\hbar^2 \sigma \alpha} = \frac{e^2}{M \alpha} . \quad (A2)$$

Equation (A1) integrated with  $\sigma$  and  $A$  as given by (16) leads to

$$Z = \prod_{n=1}^N \frac{1}{[2(1 - \cos(k\eta)) + (\eta \hbar \omega)^2]^{1/2}} \quad (A3)$$

or

$$\ln Z = N \ln \left( \frac{N}{2\pi} \right) - \frac{1}{2} \sum_{n=1}^N \ln \left[ \left( \frac{N}{2\pi} \right)^2 2(1 - \cos(k\eta)) + \epsilon^2 \right] \quad (A4)$$

where

$$\epsilon = \frac{N\eta}{2\pi} \hbar \omega = \frac{1}{2\pi} \beta \hbar \omega . \quad (A5)$$

We would like to identify the sum (A4) with the well-known result for the harmonic oscillator obtained by summation over the eigenstates. However, we are not able to sum (A4) directly so we shall use other methods to obtain the desired results. Differentiating (A4) with respect to  $\epsilon$  we obtain a series where only terms with  $n$  close to 1 or  $N$  are of importance. With that, the limit  $\eta \rightarrow 0$  may be taken before summation ( $K\eta = 2\pi n/N$ ), and the sum may be extended to all  $n$ .

$$\frac{\partial \ln Z}{\partial \epsilon} = - \sum_{n=-\infty}^{\infty} \frac{\epsilon}{n^2 + \epsilon^2} \quad (\text{A6})$$

This sum may be computed explicitly noting that, using residue calculus,

$$0 = \frac{1}{2\pi i} \oint \frac{dz}{(z^2 + \epsilon^2)(1 - e^{2\pi i z})} = \frac{1}{2i\epsilon(1 - e^{-2\pi\epsilon})} + \frac{1}{-2i\epsilon(1 - e^{2\pi\epsilon})} + \frac{1}{-2\pi i} \sum_{n=-\infty}^{\infty} \frac{\epsilon}{n^2 + \epsilon^2} \quad |z| = R \rightarrow \infty \quad (\text{A7})$$

or

$$\frac{\partial \ln Z}{\partial \epsilon} = -\pi \frac{\cosh(\pi\epsilon)}{\sinh(\pi\epsilon)} \quad (\text{A8})$$

which integrated means

$$\ln Z = -\ln[2\sinh(\pi\epsilon)] + C. \quad (\text{A9})$$

The remaining problem is to show that the constant of integration  $C$  equals zero. This requires additional investigation of (A4). For  $1 \ll \epsilon \rightarrow \infty$  the sum (A4) may be replaced by an integral, i.e., (with  $x = K\eta = 2\pi n/N$ )

$$\ell n Z = - \frac{1}{2} \frac{N}{2\pi} \int_0^{2\pi} \ell n \left[ 2(1 - \cos x) + \left( \frac{2\pi\epsilon}{N} \right)^2 \right] dx . \quad (\text{A10})$$

Because of the prefactor  $N \rightarrow \infty$  we must be a bit careful in going from (A4) to (A10). Equation (A4) may be considered as the trapezoidal-rule approximation to integral (A10). As the  $\cos(k\eta)$  runs through precisely one full period  $2\pi$  there will be no end-effect errors. The error connected to each term in the sum is thus proportional to the second derivative of the integrand times the step length  $\Delta x = 2\pi/N$  squared. The sensitive region is around  $x = 0$  where the integrand is almost singular ( $N \rightarrow \infty$ ). With  $2(1 - \cos x) \approx x^2$  we thus find for the error made with  $a = \frac{2\pi}{N} \epsilon$ ,

$$\frac{N}{2\pi} (\Delta x)^2 \int_{-\infty}^{\infty} \frac{x^2 - a^2}{(x^2 + a^2)^2} dx \sim \frac{N}{2\pi} (\Delta x)^2 \frac{1}{a} = \frac{1}{\epsilon} \xrightarrow{\epsilon \rightarrow \infty} 0 . \quad (\text{A11})$$

To compute (A10) we need consider

$$L = - \frac{1}{2\pi} \int_0^{2\pi} \ell n(1 - \sigma \cos x) dx . \quad (\text{A12})$$

We find ( $x = \text{tg } \frac{t}{2}$ )

$$\begin{aligned} \frac{dL}{d\sigma} &= \frac{1}{2\pi} \int_0^{2\pi} \frac{\cos x dx}{1 - \sigma \cos x} = \frac{1}{\sigma} \left[ -1 + \frac{1}{2\pi} \int_0^{2\pi} \frac{dx}{1 - \sigma \cos x} \right] \\ &= \frac{1}{\sigma} \left[ -1 + \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{1}{1 - \sigma + (1+\sigma)t^2} \right] = \frac{1}{\sigma} \left[ -1 + \frac{1}{\pi\sqrt{1-\sigma^2}} \int_{-\infty}^{\infty} \text{Arctg} \left( \sqrt{\frac{1+\sigma}{1-\sigma}} t \right) \right] \\ &= \frac{1}{\sigma\sqrt{1-\sigma^2}} - \frac{1}{\sigma} . \end{aligned} \quad (\text{A13})$$

Since obviously  $L = 0$  for  $\sigma = 0$ , (A13) integrated gives

$$L = -\ell n \left[ \frac{1}{2} \left( 1 + (1-\sigma^2)^{1/2} \right) \right] . \quad (\text{A14})$$

Applied to (A10), the above is to be used with

$$\sigma = \frac{1}{1 + \frac{1}{2} \left( \frac{2\pi\epsilon}{N} \right)^2} = 1 - \frac{1}{2} \left( \frac{2\pi\epsilon}{N} \right)^2 + \dots$$

$$(1 - \sigma^2)^{1/2} = \frac{2\pi\epsilon}{N}$$

$$\ell n Z = \frac{N}{2} [\ell n 2 + L] = -\pi\epsilon \quad (\epsilon \rightarrow \infty) . \quad (\text{A15})$$

This fixes the C in (A9) to zero, i.e.,

$$\ell n Z = -\ell n [2 \sinh(\pi\epsilon)]$$

or

$$Z = [2 \sinh(\pi\epsilon)]^{-1} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} \quad (\text{A16})$$

which is the well-known result for the harmonic oscillator.

By use of (A3) - (A8) the average energy or internal energy is found to be ( $k\eta = 2\pi n/N$ )

$$u = - \frac{\partial}{\partial \beta} (\ell n Z) = - \frac{1}{N} \frac{\partial}{\partial \eta} (\ell n Z)$$

$$= \frac{1}{N} \sum_{n=1}^N \frac{\eta \hbar^2 \omega^2}{2(1 - \cos k\eta) + \eta^2 \hbar^2 \omega^2} \xrightarrow[\substack{\eta \rightarrow 0 \\ N \rightarrow \infty}]{} \frac{1}{N\eta} \sum_{n=-\infty}^{\infty} \frac{\hbar^2 \omega^2}{k^2 + \hbar^2 \omega^2}$$

$$= - \frac{\hbar \omega}{2\pi} \frac{\partial}{\partial \epsilon} (\ell n Z) = \frac{1}{2} \hbar \omega \frac{\cosh \left( \frac{1}{2} \beta \hbar \omega \right)}{\sinh \left( \frac{1}{2} \beta \hbar \omega \right)} . \quad (\text{A17})$$

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