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Analysis of Classical Statistical Mechanics by Means of Collective Coordinates*

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The three-dimensional classical many-body system is approximated by the use of collective coordinates, through the assumed knowledge of two-body correlation functions. The resulting approximate statistical state is used to obtain the two-body correlation function. Thus, a self-consistent formulation is available for determining the correlation function. Then, the self-consistent integral equation is solved in virial expansion, and the thermodynamic quantities of the system thereby ascertained. The first three virial coefficients are exactly reproduced, while the fourth is nearly correct, as evidenced by numerical results for the case of hard spheres.

INTRODUCTION

THE analysis of the state of a physical system for which an exact description is not feasible is generally facilitated by isolating predominant qualitative characteristics, and then arranging a quantitative formulation which exhibits these characteristics as directly as possible. In uniform many-body systems, the omnipresence of freely propagating sound waves is most striking, and suggests that harmonic fluctuations, spatially and temporally, of the system density be incorporated as an integral part of a many-body theory.

Following the above approach, we have, in a sequence of papers,[1] investigated the use of the Fourier components of the particle density as fundamental coordinates for the analysis of the classical many-body problem; in particular, the approximate validity of the dynamical independence of these collective coordinates and of their simple harmonic motion has been established. We have seen that the two-body correlation function plays a paramount role in determining the oscillation frequencies which characterize the lowest order approximation. Further, a method of computing the correlation function in terms of the approximate solution to the problem has been obtained, thereby affording a self-consistent method for the primitive collective coordinate treatment of the many-body problem.

In this paper, the analysis of the optimum oscillator frequencies required for the collective coordinate representation of the potential energy is extended to three dimensions, and is sharpened by explicit use of the knowledge that the system is to be in a statistical state. The expression for the correlation function in terms of the oscillator frequencies is found to be as in Paper IV and is given further credence by comparison with a thermodynamic relation of Ornstein and Zernike.

The stage is now set for a self-consistent computation of the two-body correlation function, a problem which is set up in the form of a simple nonlinear integral equation. First, however, the thermodynamic properties are obtained in terms of the correlation function by two approaches: via the isothermal compressibility, and through variation of the free energy. The leading virial coefficients are then determined for the approximate theory and compared with the exact coefficients; for a hard sphere gas, coefficients B_1-B_4 are numerically reproduced with negligible error. Finally, the complete cluster expansion for the pressure is obtained in our approximation, and compared with the exact cluster expansion.

It seems pertinent to mention at this point that the methods employed in the present paper may be regarded

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[1] G. J. Yevick and J. K. Percus, Phys. Rev. **101**, 1186 (1956), Paper I; J. K. Percus and G. J. Yevick, Phys. Rev. **101**, 1192 (1956), Paper II; Nuovo cimento **5**, 65 (1957), Paper III; **5**, 1057 (1957), Paper IV.

as constituting somewhat of a shift in the philosophy of our approach. By this we mean that cognizance must be taken of the fact that whereas one would ideally want to utilize all of the Fourier components of the density, only $3N$ (N = number of particles) coordinates are available. Rather than increase the allowed number of coordinates by imposition of a small[2] or large[3] number of supplementary conditions, with numerous attendant difficulties, we prefer to use precisely $3N$ collective coordinates. There is then a choice of either selecting one coordinate set as optimal for the system, and this is what we have previously done, or having the set used depend upon the particular quantity under consideration. The latter sampling technique is the one which we use in the following analysis; clearly, however, there is not a sharp dividing line between the two approaches, and indeed, the present approximation is formulated so as to be independent of the sample chosen.

Finally, it should be observed that the purpose of the emphasis laid upon the low-density region in the latter part of the ensuing analysis is twofold. First, it enables us to compare our approximate theory with known exact results. Second, and of greater importance, since it is in this region that the assumption of the separability of the collective coordinates is of most questionable validity, a severe test is thereby made of the adequacy of the approximate formulation, which is implicitly based upon such an assumption.

I. COLLECTIVE COORDINATE PICTURE

We now extend (to 3 dimensions) and modify the formulation developed in Papers III and IV. The classical N-body problem to be considered is represented by the Hamiltonian

$$H=\sum_i \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{2m}+\tfrac{1}{2}\sum_i\sum_{j\neq i} V(\mathbf{x}_i-\mathbf{x}_j), \tag{1}$$

where $\mathbf{x}_i$ and $\mathbf{p}_i$ are coordinate and momentum of the ith particle ($i=1,\cdots,N$), located in a periodic cube of side L; V is the periodic potential obtained by allowing a given particle to interact with all periodic images of any other particle.

The Hamiltonian (1) is to undergo an extended point transformation in which the new coordinates are those of the center of mass

$$\mathbf{X}=\textstyle\sum_i \mathbf{x}_i/N, \tag{2}$$

and $3N-3$ collective coordinates

$$q_{\mathbf{k}}=\textstyle\sum_i \exp(i\mathbf{k}\cdot\mathbf{x}_i), \tag{3}$$

the latter being, to within a volume factor, Fourier components of the particle density $\sum_i \delta(\mathbf{x}-\mathbf{x}_i)$. The vector $\mathbf{k}$ is a vector integer multiple of the basic wave number k_0 for the periodic cube,

$$k_0=2\pi/L, \tag{4}$$

and the set[4] $\{\mathbf{k}\}$ is restricted only by the conditions that it shall not contain the zero vector but shall contain the pair $\mathbf{k}$, $-\mathbf{k}$ whenever $\mathbf{k}$ is a member.

According to the properties of an extended point transformation,[5] new canonical momenta p_s' resulting from a transformation from x_s to x_s' may be specified by $p_s=\sum_t p_t'\partial x_t'/\partial x_s$, so that, $\mathbf{P}$ and $\pi_{\mathbf{k}}$ being conjugate to $\mathbf{X}$ and $q_{\mathbf{k}}$, we obtain the implicit definition

$$\mathbf{p}_j=i\sum_{\{\mathbf{k}\}} \mathbf{k}\pi_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{x}_j)+\mathbf{P}/N. \tag{5}$$

We shall separately transform the potential and kinetic energy terms in (1). From (5), we have at once

$$2m\,\text{K.E.}=\sum_{\{\mathbf{k},\mathbf{l}\}} \mathbf{k}\cdot\mathbf{l}\,q_{\mathbf{k}-\mathbf{l}}\pi_{\mathbf{k}}\pi_{\mathbf{l}} +2i\sum_{\{\mathbf{k}\}} q_{\mathbf{k}}\pi_{\mathbf{k}}\mathbf{k}\cdot\mathbf{P}/N+\mathbf{P}\cdot\mathbf{P}/N. \tag{6}$$

Now our attention is to be restricted to uniform or translation invariant states of the system; hence all average values must be unaltered under the substitution $\mathbf{x}_j\rightarrow\mathbf{x}_j+\boldsymbol{\varphi}$ for all j, with $\boldsymbol{\varphi}$ arbitrary. But it then follows that the average $\langle q_{\mathbf{k}}(\mathbf{x}_j)\rangle=\langle q_{\mathbf{k}}(\mathbf{x}_j+\boldsymbol{\varphi})\rangle=\langle q_{\mathbf{k}}(\mathbf{x}_j)\rangle \times\exp(i\mathbf{k}\cdot\boldsymbol{\varphi})$, from which we conclude that

$$\langle q_{\mathbf{k}}\rangle=N\delta_{\mathbf{k},0}. \tag{7}$$

If the coefficients of the momenta in (6) are replaced by their mean values, we then obtain as an approximation to (6)

$$2m\,\text{K.E.}=N\sum_{\{\mathbf{k}\}} k^2\pi_{\mathbf{k}}\pi_{-\mathbf{k}}+P^2/N. \tag{8}$$

The potential energy remains to be written in terms of the $q_{\mathbf{k}}$. Observing that

$$\sum_{i\neq j}\exp[i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)]=q_{\mathbf{k}}q_{-\mathbf{k}}-N, \tag{9}$$

it follows that

$$2\,\text{P.E.}=\textstyle\sum_{\mathbf{k}} V_{\mathbf{k}}(q_{\mathbf{k}}q_{-\mathbf{k}}-N), \tag{10}$$

where the Fourier coefficient $V_{\mathbf{k}}$ is defined as

$$V_{\mathbf{k}}=\frac{1}{L^3}\int V(\mathbf{x})\exp(i\mathbf{k}\cdot\mathbf{x})d^3x. \tag{11}$$

But all $\mathbf{k}$ are used in (10) and we have only $(3N-3)$ $q_{\mathbf{k}}$ available; thus we replace (10) by the approximation

$$2\,\text{P.E.}=\sum_{\{\mathbf{k},0\}} \nu_{\mathbf{k}}(q_{\mathbf{k}}q_{-\mathbf{k}}-N), \tag{12}$$

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[2] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[3] N. Bogoliubov and D. N. Zubarev, J. Exptl. Theoret. Phys. U.S.S.R. **28**, 129 (1955) [translation: Soviet Physics JETP **1**, 71 (1955)].

[4] The $(3N-3)$ k's at our disposal will hereafter be denoted explicitly by the symbol $\{\mathbf{k}\}$.

[5] H. C. Corben and P. Stehle, *Classical Mechanics* (John Wiley and Sons, Inc., New York, 1950), p. 229.

where the $\nu_\mathbf{k}$ are determined so as to optimize the approximation.

The term optimization is a nebulous one. A simple criterion which has been used is that the squared difference between exact and approximate potentials be small, or to be more definite, that the $\nu_\mathbf{k}$ minimize the expression

$$\langle\{V(\mathbf{x}_i-\mathbf{x}_j)-\sum_{\{\mathbf{k},0\}}\nu_\mathbf{k}\exp[-i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)]\}^2\rangle. \quad (13)$$

If $\sigma(\mathbf{x})$ is the two-body distribution function,[6] defined by

$$\langle g(\mathbf{x}_i-\mathbf{x}_j)\rangle=\frac{1}{L^3}\int g(\mathbf{x})\sigma(\mathbf{x})d^3x \quad (14)$$

for arbitrary g, the minimization of (13) readily leads to the relations

$$\sum_{\{\mathbf{l},0\}}\sigma_{\mathbf{k}-\mathbf{l}}\nu_\mathbf{l}=[V(\mathbf{x})\sigma(\mathbf{x})]_\mathbf{k} \quad (15)$$

to be solved for the $\nu_\mathbf{k}$. In the event that the density of wave vectors in $\{\mathbf{k}\}$ is small, only the $\sigma_0=1$ term contributes to (15) (since $\sigma_\mathbf{k}\sim 1/N$ for $k\neq 0$) and we have

$$\nu_\mathbf{k}=[V(\mathbf{x})\sigma(\mathbf{x})]_\mathbf{k}: \quad (16)$$

the potential $V(\mathbf{x}_i-\mathbf{x}_j)$ is replaced by an effective potential which is weighted according to the probability of occurrence of the pair of positions $\mathbf{x}_i$, $\mathbf{x}_j$. For potentials small enough to avoid severe nonlinear effects, one expects (16) to be quite generally valid.

Inserting (8) and (12), we have now replaced the Hamiltonian (1) by the approximate collective coordinate Hamiltonian,

$$H=\sum_{\{\mathbf{k}\}}\left[\frac{Nk^2}{2m}\pi_\mathbf{k}\pi_{-\mathbf{k}}+\frac{\nu_\mathbf{k}}{2}(q_\mathbf{k}q_{-\mathbf{k}}-N)\right]+\frac{P^2}{2mN}+\frac{N(N-1)}{2}\nu_0. \quad (17)$$

Thus we appear to have complete separation of the system into harmonic oscillator pairs $(q_\mathbf{k},q_{-\mathbf{k}})$, in addition to the center-of-mass motion. However, as has been seen in Paper IV, the loss of memory of the transformation engendered by approximation (8) must be compensated for by attributing a nonuniform domain of action to the $q_\mathbf{k}$. This warping of q-space results, e.g., in modified oscillation frequencies[7] as well as modified expressions for phase space integrals which have been discussed in Paper IV. Fortunately, in the succeeding analysis, all computations will be done in x space, with (17) and the implied separability of q space as required background, but with approximation (12) alone employed. Interpretation in terms of the domain of action of q space will be made when appropriate, but further detailed consideration of this aspect will not be necessary.

II. TWO-BODY CORRELATIONS IN A STATISTICAL STATE

It has been observed that the solution to our N-body problem will ultimately be made to depend upon the two-body correlation or distribution function $\sigma(\mathbf{x})$. Since $\sigma(\mathbf{x})$ is certainly determined by the solution, a self-consistent method is then available. We now inquire as to the manner in which $\sigma(\mathbf{x})$ is obtained from the solution. As a first step, we note that, from the defining relation (14),

$$\sigma_\mathbf{k}=\frac{1}{L^3}\int\sigma(\mathbf{x})\exp(i\mathbf{k}\cdot\mathbf{x})d^3x=\langle\exp i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)\rangle$$

$$=\frac{1}{N(N-1)}\langle\sum_{i\neq j}\exp i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)\rangle,$$

or

$$\sigma_\mathbf{k}=\frac{1}{N(N-1)}\langle q_\mathbf{k}q_{-\mathbf{k}}-N\rangle. \quad (18)$$

This fundamental relation was similarly employed to advantage by Feynman[8] in his work on He II.

To make use of (18), we must know the state of the system, and this will be taken as a Gibbsian canonical state: one in which the unnormalized probability density in phase space is given by

$$\rho(\cdots\mathbf{x}_j,\mathbf{p}_j\cdots)=\exp(-\theta H),\quad \theta\equiv 1/KT, \quad (19)$$

K being the Boltzmann constant, H the system Hamiltonian, and T the system temperature. Of course in principle the problem is now solved, but in practice, this is no help. What does help is the knowledge that the potential energy replacement (12) is indicated and that the approximate separability of q space should thereupon introduce important simplifications.

Let us then insert (12) into the probability function (19) and compute the expectation (18); the momentum integrations drop out and there remains (to within $1/N$)

$$\sigma_\mathbf{k}=\frac{1}{N^2}\frac{\int\exp(-\theta\sum_{\{\mathbf{l}>0\}}\nu_\mathbf{l}q_\mathbf{l}q_{-\mathbf{l}})(q_\mathbf{k}q_{-\mathbf{k}}-N)dx^{3N}}{\int\exp(-\theta\sum_{\{\mathbf{l}>0\}}\nu_\mathbf{l}q_\mathbf{l}q_{-\mathbf{l}})dx^{3N}}. \quad (20)$$

The notation $\{\mathbf{l}>0\}$ refers to any half of the set $\{\mathbf{l}\}$ which contains just one member of each pair $\mathbf{l}$, $-\mathbf{l}$; to employ this notation in (20), we have used the assumption $\nu_\mathbf{l}=\nu_{-\mathbf{l}}$, a clear consequence of the fact that $V(\mathbf{x})=V(-\mathbf{x})$. We shall suppose that $\mathbf{k}$ is one of the

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[6] For a translation-invariant system, the one-body distribution is uniform or constant and the two-body distribution a function of relative coordinates alone.

[7] These particular difficulties may be overcome, others arising, by a redefinition of the $q_\mathbf{k}$. See D. Pines and D. Bohm, Phys. Rev. **85**, 338 (1952).

[8] R. P. Feynman, Phys. Rev. **94**, 262 (1954).

set $\{\mathbf{l}>0\}$; since $\sigma_{\mathbf{k}}$ is a slowly varying function of $\mathbf{k}$, even a set $\{\mathbf{l}\}$ of very low density will completely determine the functional form of $\sigma_{\mathbf{k}}$.

To apply q-space decomposability, we first prove a simple theorem. Let $\mathfrak{L}$ be a linear functional (linear transformation onto the complex numbers), normalized so that $\mathfrak{L}(1)=1$; then we have

$$\begin{aligned}\mathfrak{L}\left(\prod_{i=1}^{n}A_i\right)\\ &=\mathfrak{L}\prod_{i=1}^{n}\{\mathfrak{L}(A_i)+[A_i-\mathfrak{L}(A_i)]\}\\ &=\mathfrak{L}\Bigg\{\prod_{i=1}^{n}[\mathfrak{L}(A_i)]+\sum_{j}([A_j-\mathfrak{L}(A_j)]\prod_{i\neq j}\mathfrak{L}(A_i))\\ &\quad+\sum_{j,k<j}([A_j-\mathfrak{L}(A_j)][A_k-\mathfrak{L}(A_k)]\prod_{i\neq j,k}\mathfrak{L}(A_i))\\ &\qquad+\cdots\Bigg\},\end{aligned}$$

from which we see that

$$\mathfrak{L}(\prod_i A_i)=\left\{1+\sum_{j,k<j}\left[\frac{\mathfrak{L}(A_jA_k)}{\mathfrak{L}(A_j)\mathfrak{L}(A_k)}-1\right]+\cdots\right\}\prod_i\mathfrak{L}(A_i),\quad\text{if}\quad\mathfrak{L}(1)=1.\tag{21}$$

The correspondence between (20) and (21) is achieved by taking $\mathfrak{L}(\ \ )$ as $L^{-3N}\int(\ \ )dx^{3N}$, with $A_{\mathbf{l}}=\exp(-\theta\nu_{\mathbf{l}}q_{\mathbf{l}}q_{-\mathbf{l}})$ for $\mathbf{l}\neq\mathbf{k}$, $A_{\mathbf{k}}=\exp(-\theta\nu_{\mathbf{k}}q_{\mathbf{k}}q_{-\mathbf{k}})$ for the denominator, and $A_{\mathbf{k}}=(q_{\mathbf{k}}q_{-\mathbf{k}}-N)\exp(-\theta\nu_{\mathbf{k}}q_{\mathbf{k}}q_{-\mathbf{k}})$ for the numerator. We are then led to inspect quantities of the form

$$\frac{\int f(q_{\mathbf{l}}q_{-\mathbf{l}})g(q_{\mathbf{m}}q_{-\mathbf{m}})dx^{3N}L^{3N}}{\int f(q_{\mathbf{l}}q_{-\mathbf{l}})dx^{3N}\int g(q_{\mathbf{m}}q_{-\mathbf{m}})dx^{3N}}-1.\tag{22}$$

The discussion of Paper IV, extended to three dimensions, informs us that the nonzero contributions to (22) arise from terms of the form $(q_{\mathbf{l}}q_{-\mathbf{l}})^a(q_{\mathbf{m}}q_{-\mathbf{m}})^b$ where $a\,\mathbf{l}=\pm\mathbf{m}b$; these contributions can be arbitrarily diminished by making the density of wave vectors in $\{\mathbf{l}\}$ sufficiently low (so that any two $\mathbf{k}$'s are "nearly" incommensurable) in which case the leading term of (21) suffices. Substituting into (20), we conclude that for low enough density of wave vectors,

$$\sigma_{\mathbf{k}}=\frac{1}{N^2}\frac{\int\exp(-\theta\nu_{\mathbf{k}}q_{\mathbf{k}}q_{-\mathbf{k}})(q_{\mathbf{k}}q_{-\mathbf{k}}-N)dx^{3N}}{\int\exp(-\theta\nu_{\mathbf{k}}q_{\mathbf{k}}q_{-\mathbf{k}})dx^{3N}}.\tag{23}$$

Several obvious extensions of (21) permit finer computation of $\sigma_{\mathbf{k}}$ but will not be considered at this time.

Finally, for the evaluation of (23), or indeed more generally of $\int f(q_{\mathbf{k}}q_{-\mathbf{k}})dx^{3N}$, it suffices to compute

$$J_{\mathbf{k}}(Q,\varphi)\equiv\int\delta(Q_{\mathbf{k}}\cos\varphi_{\mathbf{k}}-Q\cos\varphi)\delta(Q_{\mathbf{k}}\sin\varphi_{\mathbf{k}}-Q\sin\varphi)dx^{3N},\tag{24}$$

where

$$Q_{\mathbf{k}}=(q_{\mathbf{k}}q_{-\mathbf{k}})^{\frac{1}{2}},\quad\varphi_{\mathbf{k}}=\tfrac{1}{2}i\ln(q_{-\mathbf{k}}/q_{\mathbf{k}})\tag{25}$$

are the oftentimes more convenient polar components of $q_{\mathbf{k}}$, for then we have

$$\int f(Q_{\mathbf{k}},\varphi_{\mathbf{k}})dx^{3N}=\int f(Q,\varphi)J_{\mathbf{k}}(Q,\varphi)Q^2dQd\varphi.\tag{26}$$

It may be remarked that $J_{\mathbf{k}}(Q,\varphi)$, being the additional factor required to perform a q-space integration if one regards the $q_{\mathbf{k}}$'s as an independent Cartesian system, is precisely the "domain of action" correction previously alluded to.

To evaluate (24), we have, on Fourier-representing the δ functions and noting that $Q_{\mathbf{k}}\cos\varphi_{\mathbf{k}}=\frac{1}{2}(q_{\mathbf{k}}+q_{-\mathbf{k}})$, $Q_{\mathbf{k}}\sin\varphi_{\mathbf{k}}=-\frac{1}{2}i(q_{\mathbf{k}}-q_{-\mathbf{k}})$,

$$\begin{aligned}J_{\mathbf{k}}(Q,\varphi)=(2\pi)^{-2}\int\cdots\int\exp[-i(tQ\cos\varphi\\ +uQ\sin\varphi)]\exp[i(t\textstyle\sum_j\cos\mathbf{k}\cdot\mathbf{x}_j\\ +u\textstyle\sum_j\sin\mathbf{k}\cdot\mathbf{x}_j)]dx^{3N}dtdu,\end{aligned}\tag{27}$$

or, shifting to polar coordinates, this becomes

$$(2\pi)^{-2}\int\int\exp[-izQ\sin(\varphi+\theta)]\times\left[\int\exp iz\sin(\mathbf{k}\cdot\mathbf{x}+\theta)d^3x\right]^N zdzd\theta.\tag{28}$$

But[9]

$$\exp[iz\sin(\mathbf{k}\cdot\mathbf{x}+\theta)]=\sum_{n=-\infty}^{\infty}J_n(z)\exp[i(\mathbf{k}\cdot\mathbf{x}+\theta)n],\tag{29}$$

whence

$$\begin{aligned}J_{\mathbf{k}}(Q,\varphi)&=(2\pi)^{-2}L^{3N}\int\int\exp[-izQ\sin(\varphi+\theta)]\times[J_0(z)]^N zdzd\theta\\ &=\frac{L^{3N}}{2\pi}\int J_0(Qz)J_0(z)^N zdz,\end{aligned}\tag{30}$$

or expanding[10] $J_0(z)$ and performing the indicated Laplace transform,[11]

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[9] Grey, Matthews, and Macrobert, *Bessel Functions* (MacMillan and Company, Ltd., London, 1952), p. 32.

[10] W. Magnus and F. Oberhettinger, *Special Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), p. 16.

[11] Erdelyi, Magnus, Oberhettinger, and Tricomi, *Table of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), p. 185.

$$J_{\mathbf{k}}(Q,\varphi)=\frac{L^{3N}}{2\pi}\int J_0(Qz)(1-Nz^4/32+\cdots)\times\exp(-Nz^2/4)zdz$$

$$=\frac{L^{3N}}{\pi}\int J_0(2Qy^{\frac{1}{2}})(1-\tfrac{1}{2}Ny^2+\cdots)\exp(-Ny)dy$$

$$=(L^{3N}/\pi)\{N^{-1}\exp(-Q^2/N)-N^{-2}[1-2Q^2/N+\tfrac{1}{2}(Q^2/N)^2]\exp(-Q^2/N)+\cdots\}. \quad (31)$$

Thus, neglecting terms of relative order $1/N$,

$$J_{\mathbf{k}}(Q,\varphi)=(L^{3N}/\pi N)\exp(-Q^2/N). \quad (32)$$

We can now evaluate (23) by the use of (26) and (32). This readily yields, for $\mathbf{k}\neq 0$,

$$\sigma_{\mathbf{k}}=-\theta\nu_{\mathbf{k}}/(1+N\theta\nu_{\mathbf{k}}), \quad (33)$$

which is the key result of this section.

III. INTERPRETATION OF THE CORRELATION-FREQUENCY RELATION

The function $\nu_{\mathbf{k}}$ which represents the force constant for phonon oscillations has occurred in the work of Ornstein and Zernike in a different aspect. If $h(\mathbf{x})$ is the Fourier transform of $-N\theta\nu_{\mathbf{k}}$ (properly normalized, since (33) does not hold for $\mathbf{k}=0$), we may write, as a consequence of $N\sigma_{\mathbf{k}}+N\sigma_{\mathbf{k}}N\theta\nu_{\mathbf{k}}+N\theta\nu_{\mathbf{k}}=0$, which follows from (33),

$$N\sigma(\mathbf{x}-\mathbf{x}_1)=h(\mathbf{x}-\mathbf{x}_1)+\int h(\mathbf{x}-\mathbf{x}_2)h(\mathbf{x}_2-\mathbf{x}_1)d^3x_2+\int\int h(\mathbf{x}-\mathbf{x}_3)h(\mathbf{x}_3-\mathbf{x}_2)h(\mathbf{x}_2-\mathbf{x}_1)d^3x_2d^3x_3+\cdots. \quad (34)$$

Thus $h(\mathbf{x})$ may be regarded as the "intrinsic" 2-body correlation: $N\sigma(\mathbf{x})$ is composed of direct correlation, correlation with intercession of one body, with two bodies, etc. For further discussion of this intrinsic correlation, see Goldstein.[12]

On the other hand, the interpretation of $\nu_{\mathbf{k}}$ as a force constant yields an important verifiable result, first obtained in a different form again by Ornstein and Zernike.[13] First we must consider the oscillation frequency of the $\mathbf{k}$th collective harmonic oscillator, which, since the q space appropriate to (17) is warped, is not given simply by $\omega_{\mathbf{k}}^2=Nk^2\nu_{\mathbf{k}}/m$. Observing from (32) that the spacial distortion may be accounted for by insertion of the factor $\exp(-q_{\mathbf{k}}q_{-\mathbf{k}}/N)$ for each pair $q_{\mathbf{k}}$, $q_{-\mathbf{k}}$, we see that since the result is to replace $\nu_{\mathbf{k}}$ in the phase space density (19) by $\nu_{\mathbf{k}}+(1/N\theta)$, then

$$\omega_{\mathbf{k}}=(Nk^2/m)^{\frac{1}{2}}(\nu_{\mathbf{k}}+1/N\theta)^{\frac{1}{2}}. \quad (35)$$

Thus the sound velocity in the long wave limit, c, is given by $c=\partial\omega_{\mathbf{k}}/\partial k|_{k\to 0}$ or

$$c=(N/m)^{\frac{1}{2}}(\nu_{0+}+1/N\theta)^{\frac{1}{2}}, \quad (36)$$

where it is now convenient to restrict ourselves to a spherically symmetric potential and thus to an isotropic medium. It must be recalled that since the system is fixed in temperature, c is an unusual quantity, the isothermal sound velocity; however, we may at once obtain the isothermal compressibility K_T: $K_T^{-1}=n(\partial p/\partial n)_T=nc^2$, or

$$K_T^{-1}=nN(\nu_{0+}+1/N\theta), \quad (37)$$

where $n=N/L^3$ is the particle density. Our relation (33), in the form $(1+N\theta\nu_{\mathbf{k}})(1+N\sigma_{\mathbf{k}})=1$, will then be verified for $k\to 0$ if we can show by standard equilibrium arguments (since $k\to 0$ implies equilibrium) that

$$K_T^{-1}=\frac{n}{\theta}\left(\frac{1}{1+N\sigma_{0+}}\right) \quad \text{(Ornstein-Zernike)} \quad (38)$$

is valid.

The standard arguments[14] for relation (38) take place outside the constant-N body system we are examining; we shall therefore present an alternative scheme which seems more suitable.

To obtain the isothermal compressibility of a uniform system, we apply an infinitesimal external potential $\sum U(\mathbf{x}_i)$, where U is very slowly varying (compared, e.g., to intermolecular spacing) and, for convenience, averages to zero: $\int U(\mathbf{x})d^3x=0$. The trick is then to compute the work done on the system in two different fashions. For this purpose, we first find the new partition function (subscript 0 denoting quantities as $U\to 0$):

$$Z=\int e^{-\theta H}\exp[-\theta\sum U(x_i)]d\tau^{6N}$$

$$=\int\{e^{-\theta H}-\theta\textstyle\sum_i U(\mathbf{x}_i)e^{-\theta H}+\tfrac{1}{2}\theta^2\sum_i[U(\mathbf{x}_i)]^2e^{-\theta H}+\tfrac{1}{2}\theta^2\sum_{i\neq j}U(\mathbf{x}_i)U(\mathbf{x}_j)e^{-\theta H}\cdots\}d\tau^{6N}$$

$$=Z_0+\tfrac{1}{2}\theta^2\frac{N}{L^3}\int[U(\mathbf{x})]^2d^3xZ_0+\tfrac{1}{2}\theta^2\frac{N(N-1)}{L^6}\times\int U(\mathbf{x})\sigma(\mathbf{x}-\mathbf{y})U(\mathbf{y})d^3xd^3yZ_0+\cdots. \quad (39)$$

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[12] L. Goldstein, Phys. Rev. **100**, 981 (1955).

[13] L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914).

[14] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 236.

Next we find the altered density:

$$n(\mathbf{x})=\langle\sum\delta(\mathbf{x}-\mathbf{x}_i)\rangle$$

$$=(1/Z)\int\sum\delta(\mathbf{x}-\mathbf{x}_i)e^{-\theta H}\exp[-\theta\sum U(\mathbf{x}_i)]d\tau^{6N}$$

$$=(1/Z)\int(\textstyle\sum_i\delta(\mathbf{x}-\mathbf{x}_i)e^{-\theta H}$$

$$-\theta\textstyle\sum_i\delta(\mathbf{x}-\mathbf{x}_i)U(\mathbf{x}_i)e^{-\theta H}$$

$$-\theta\textstyle\sum_{i\neq j}\delta(\mathbf{x}-\mathbf{x}_i)U(\mathbf{x}_j)e^{-\theta H}\cdots)d\tau^{6H},$$

or

$$n(\mathbf{x})=\frac{1}{Z}\left[\frac{N}{L^3}Z_0-\theta U(\mathbf{x})\frac{N}{L^3}Z_0\right. \tag{40}$$

$$\left.-N(N-1)\frac{\theta Z_0}{L^6}\int\sigma(\mathbf{x}-\mathbf{y})U(\mathbf{y})d^3y\cdots\right].$$

Now if σ_{As} is the asymptotic part of $\sigma(\mathbf{x})$, then $\sigma(\mathbf{x})-\sigma_{As}$ is of short range, with area determined by

$$L^{-3}\int[\sigma(\mathbf{x})-\sigma_{As}]d^3x$$

$$=\lim_{k\to 0}\int[\sigma(\mathbf{x})-\sigma_{As}]\exp i\mathbf{k}\cdot\mathbf{x}d^3x=\sigma_{0+}$$

(with the additional consequence that $\sigma_{As}=1-\sigma_{0+}$). Thus

$$L^{-3}\int\sigma(\mathbf{x}-\mathbf{y})U(\mathbf{y})d^3y$$

$$=\sigma_{0+}U(\mathbf{x})+(1-\sigma_{0+})L^{-3}\int U(\mathbf{y})d^3y$$

$$=\sigma_{0+}U(\mathbf{x}) \tag{41}$$

in our case. The previous expressions then become simply

$$Z=Z_0\left[1+\tfrac{1}{2}n_0\theta^2(1+N\sigma_{0+})\int[U(\mathbf{x})]^2d^3x+\cdots\right], \tag{42}$$

$$n(\mathbf{x})=n_0[1-\theta(1+N\sigma_{0+})U(\mathbf{x})+\cdots].$$

The work done in an isothermal process is given[15] by the change of free energy, so that here

$$W=\theta\ln(Z/Z_0)$$

$$=\tfrac{1}{2}n_0\theta^3(1+N\sigma_{0+})\int U(\mathbf{x})^2d^3x+\cdots. \tag{43}$$

On the other hand, the work done in isothermally compressing an amount of matter n_0v from volume v to volume $v-\delta v$ and so to density $n_0(1+\delta v/v)$ is clearly

$$\int_0^{\delta v}[p_0+n_0(\Delta/v)(\partial p/\partial n)_T+\cdots]d\Delta$$

$$=p_0\delta v+\tfrac{1}{2}(n_0/v)(\partial p/\partial n)_T(\delta v)^2+\cdots$$

$$=p_0\delta v+[\tfrac{1}{2}(\delta n)^2(n_0)^{-1}(\partial p/\partial n)_T+\cdots]v. \tag{44}$$

Hence the total work done in application of the external $U(\mathbf{x})$ to a constant volume is

$$W=\tfrac{1}{2}(\partial p/\partial n)_T(n_0)^{-1}\int[\delta n(\mathbf{x})]^2d^3x+\cdots$$

$$=\tfrac{1}{2}K_T^{-1}\int[\delta n(\mathbf{x})/n_0]^2d^3x+\cdots, \tag{45}$$

or according to the preceding Eq. (42),

$$W=\tfrac{1}{2}K_T^{-1}\theta^2(1+N\sigma_{0+})^2\int[U(\mathbf{x})]^2d^3x+\cdots. \tag{46}$$

Comparing (43) and (46), we conclude that (dropping subscript on n)

$$K_T^{-1}=\frac{n}{\theta}\left(\frac{1}{1+N\sigma_{0+}}\right), \tag{38}$$

as desired.

It is interesting to remark that if we assume simply that low amplitude low-frequency sound propagation is the result of harmonic oscillation of the single corresponding pair $q_{\mathbf{k}}$ and $q_{-\mathbf{k}}$, then relation (38) is very quickly implied. For if $q_{\mathbf{k}}$ and $q_{-\mathbf{k}}$ oscillate harmonically at angular frequency $\omega_{\mathbf{k}}$, then we must have

$$\omega_{\mathbf{k}}^2=\langle\dot{q}_{\mathbf{k}}\dot{q}_{-\mathbf{k}}\rangle/\langle q_{\mathbf{k}}q_{-\mathbf{k}}\rangle, \tag{47}$$

where $\dot{q}_{\mathbf{k}}\equiv dq_{\mathbf{k}}/dt$. But

$$\langle\dot{q}_{\mathbf{k}}\dot{q}_{-\mathbf{k}}\rangle=\langle\textstyle\sum_{i,j}\mathbf{k}\cdot\mathbf{v}_i\,\mathbf{k}\cdot\mathbf{v}_j\exp[i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)]\rangle$$

$$=\langle\textstyle\sum_{i,j}k^2\delta_{ij}\mathbf{v}_i\cdot\mathbf{v}_j\exp[i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)]\rangle$$

$$=Nk^2\langle v^2\rangle=Nk^2/m\theta;$$

inserting (18) as well, (47) then yields precisely (38).

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[15] P. S. Epstein, *Textbook of Thermodynamics* (John Wiley and Sons, Inc., New York, 1937), p. 87.

IV. EFFECTIVE POTENTIAL FOR A STATISTICAL STATE

In Sec. II, Eq. (20), we effectively replaced the two-body potential $V(\mathbf{x})$ in the phase space distribution function by

$$V^*(\mathbf{x}) \equiv \sum_{\{\mathbf{k},0\}} \nu_{\mathbf{k}} \exp(-i\mathbf{k}\cdot\mathbf{x}), \tag{48}$$

and computed the correlation coefficients $\sigma_{\mathbf{k}}$ on this basis. The computational method employed increased in accuracy as the density of wave numbers in $\{\mathbf{k}\}$ decreased. Our problem now is to obtain the optimal coefficients $\nu_{\mathbf{k}}$ to be inserted into the effective potential V^*; the $\nu_{\mathbf{k}}$ are expected to occur in a form not radically different from (16).

The basic fact which we shall utilize is that the $\nu_{\mathbf{k}}$ may be determined not merely as optimal but indeed as exact. A brief explanation is in order. Suppose that the "sample" of $(3N-3)$ $\{\mathbf{k}\}$ has been chosen; using the continuity of $\sigma_{\mathbf{k}}$, it suffices to evaluate $\sigma_{\mathbf{k}}$ at each of the $3N-3$ wave numbers. Now the $\nu_{\mathbf{k}}$ are introduced so that the expression (20) when evaluated yields the correct $\sigma_{\mathbf{k}}$, i.e., that which would be obtained by using the true $V(\mathbf{x})$ in (20) rather than $V^*(\mathbf{x})$. But $3N-3$ relations thereby result:

$$\frac{\int \exp[-\theta \sum_{i>j} V^*(\mathbf{x}_i-\mathbf{x}_j)](q_{\mathbf{k}}q_{-\mathbf{k}}-N)dx^{3N}}{\int \exp[-\theta \sum_{i>j} V^*(\mathbf{x}_i-\mathbf{x}_j)]dx^{3N}} = \frac{\int \exp[-\theta \sum_{i>j} V(\mathbf{x}_i-\mathbf{x}_j)](q_{\mathbf{k}}q_{-\mathbf{k}}-N)dx^{3N}}{\int \exp[-\theta \sum_{i>j} V(\mathbf{x}_i-\mathbf{x}_j)]dx^{3N}}, \tag{49}$$

just enough to determine the $\nu_{\mathbf{k}}$ uniquely (since ν_0 does not appear in the ratio).

If we now define ν_0 by the condition

$$\int \exp[-\theta \textstyle\sum_{i>j} V^*(\mathbf{x}_i-\mathbf{x}_j)]dx^{3N} = \int \exp[-\theta \textstyle\sum_{i>j} V(\mathbf{x}_i-\mathbf{x}_j)]dx^{3N}, \tag{50}$$

then (49) and (50) may be combined into $3N-2$ relations:

$$\int \{\exp[-\theta \textstyle\sum_{i>j} V^*(\mathbf{x}_i-\mathbf{x}_j)]-\exp[-\theta \textstyle\sum_{i>j} V(\mathbf{x}_i-\mathbf{x}_j)]\}(q_{\mathbf{k}}q_{-\mathbf{k}}-N)dx^{3N}=0, \tag{51}$$

for the full set $\{\mathbf{k},0\}$. Since the integrand is symmetric, $q_{\mathbf{k}}q_{-\mathbf{k}}-N$ may be replaced by $N(N-1)\exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1)]$; we may thus rewrite (51) as

$$\int \exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1)]\{\prod_{i>j} \exp[\theta(V(\mathbf{x}_i-\mathbf{x}_j)-V^*(\mathbf{x}_i-\mathbf{x}_j))]-1\} \exp[-\theta \sum_{i>j} V(\mathbf{x}_i-\mathbf{x}_j)]dx^{3N}=0, \tag{52}$$

or simply as

$$\left\langle \exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1)+\theta V(\mathbf{x}_2-\mathbf{x}_1)-\theta V^*(\mathbf{x}_2-\mathbf{x}_1)]\prod_{i>j}^{i>2} \exp\{\theta[V(\mathbf{x}_i-\mathbf{x}_j)-V^*(\mathbf{x}_i-\mathbf{x}_j)]\}-\exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1)]\right\rangle=0. \tag{53}$$

To solve (53) for the $\nu_{\mathbf{k}}$, some approximation must be made, and it would be too much to expect this to be similar to the approximation used in (33), i.e., that the density of $\{\mathbf{k}\}$ be sufficiently low. In fact, we shall suppose that the wave number density be high enough that the deviations, for different pairs i, j, of the $\exp[\theta(V(\mathbf{x}_i-\mathbf{x}_j)-V^*(\mathbf{x}_i-\mathbf{x}_j))]$ from their means be sufficiently small and random to be deemed independent. It then follows from the theorem of (21), with $\mathfrak{L}=\langle\ \ \rangle$, that (53) may be written as

$$\langle\exp[i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1)+\theta(V(\mathbf{x}_2-\mathbf{x}_1)-V^*(\mathbf{x}_2-\mathbf{x}_1))]\rangle\prod_{i>j}^{i>2}\langle\exp[\theta(V(\mathbf{x}_i-\mathbf{x}_j)-V^*(\mathbf{x}_i-\mathbf{x}_j))]\rangle-\langle\exp i\mathbf{k}\cdot(\mathbf{x}_2-\mathbf{x}_1)\rangle=0, \tag{54}$$

or dividing by the $k=0$ case, and using the definition (14) of σ,

$$[\sigma(\mathbf{x})e^{\theta V(\mathbf{x})}e^{-\theta V^*(\mathbf{x})}]_{\mathbf{k}}=\sigma_{\mathbf{k}}. \tag{55}$$

A computation similar to that of (54) has been used by Butler and Friedman[16] in their work on He II.

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[16] S. Butler and M. Friedman, Phys. Rev. **98**, 287 (1955).

Let us examine (55) in two limiting situations: those of long-range and of short-range forces. If $V(\mathbf{x})$ is of long range compared to interparticle spacing and is not singular at short distances, then $V(\mathbf{x})$ may be represented by a finite Fourier series of type (10); thus $V(\mathbf{x})=V^*(\mathbf{x})$ and (55) is satisfied identically. Deviations of V^* from V can then be treated iteratively. A first approximation is available at once if $\theta V(\mathbf{x})\gg 1$ for most of its range; in such a case, $\sigma(\mathbf{x})$ will consist of $(N-1)$ δ-like functions corresponding to the equilibrium positions (if stable) of all particles with respect to one. Thus, we require $V(\mathbf{x})=V^*(\mathbf{x})$ at the equilibrium positions, which determines the constants $\nu_{\mathbf{k}}$. Of course, our collective method is almost guaranteed to be valid in such high-density systems. More crucial is the short-range potential or low- to moderate-density region in which a collective description might be inappropriate for the individual encounters which predominate. Such a region offers a severe test for our approximate formulation, and so we henceforth restrict our attention to systems in which short-range potentials are effective.

In order to reduce (55) to tractable form, we now revert to the assumption that $\{\mathbf{k}\}$ be sufficiently diffuse that any two members are virtually incommensurable.[17] It readily follows that the Fourier component $[\exp(-\theta V^*(\mathbf{x})]_{\mathbf{l}}$ exists only if $\mathbf{l}$ is a member of $\{\mathbf{k}\}$, and further that for $\mathbf{l}\neq 0$,

$$[e^{-\theta V^*(\mathbf{x})}]_{\mathbf{l}}=\{\exp[-\theta\nu_{\mathbf{l}}(\exp(i\mathbf{l}\cdot\mathbf{x})+\exp(-i\mathbf{l}\cdot\mathbf{x}))]\}_{\mathbf{l}} \times\{\exp[\theta\nu_{\mathbf{l}}(\exp(i\mathbf{l}\cdot\mathbf{x})+\exp(-i\mathbf{l}\cdot\mathbf{x}))e^{-\theta V^*(\mathbf{x})}]\}_0. \tag{56}$$

Since $\theta\nu_{\mathbf{k}}$ is of order $1/N$ for all $\mathbf{k}$ (i.e., ratio of molecular volume to total volume), (56) may be reduced, to within terms of order $1/N^2$, to

$$[e^{-\theta V^*(\mathbf{x})}]_{\mathbf{l}}=-\theta\nu_{\mathbf{l}}[e^{-\theta V^*(\mathbf{x})}]_0, \tag{57}$$

so that (55) becomes

$$[\sigma(\mathbf{x})e^{\theta V(\mathbf{x})}]_{\mathbf{k}}-\sum_{\{\mathbf{l}\}}[\sigma(\mathbf{x})e^{\theta V(\mathbf{x})}]_{\mathbf{k}-\mathbf{l}}\theta\nu_{\mathbf{l}}=\sigma_{\mathbf{k}}/[e^{-\theta V^*(\mathbf{x})}]_0. \tag{58}$$

Finally, we make direct use of the low density of $\{\mathbf{k}\}$, so that, as in (16), only the $\mathbf{l}=\mathbf{k}$ term in (58) contributes. Further, then, $[\exp-\theta V^*(\mathbf{x})]_0\to 1$ and we know that in general $[\sigma(\mathbf{x})\exp\theta V(\mathbf{x})]_0=1$ to order $1/N$. Thus for $\mathbf{k}\neq 0$, (58) contracts to

$$\theta\nu_{\mathbf{k}}=[(e^{\theta V(\mathbf{x})}-1)\sigma(\mathbf{x})]_{\mathbf{k}}, \tag{59}$$

which is our desired relation. We may say that the effective potential is now given by

$$\nu(\mathbf{x})=\frac{1}{\theta}(e^{\theta V(\mathbf{x})}-1)\sigma(\mathbf{x}); \tag{60}$$

if $\theta V(\mathbf{x})$ is small, this coincides as expected with $V(\mathbf{x})\sigma(\mathbf{x})$ of (16).

V. INTEGRAL EQUATION FOR $\sigma(\mathbf{x})$

We now construct a coordinate-space integral equation from which the correlation function, and consequently the thermodynamic quantities, may be determined. It has been shown that in our "zeroth order" approximation to (20) and (53), $\sigma(\mathbf{x})$ is specified (except perhaps for $\sigma_{As}-1$, which alone may be in error due to neglect of terms of order $1/N$) by the relations

$$\begin{aligned}&\theta\nu_{\mathbf{k}}=[(e^{\theta V(\mathbf{x})}-1)\sigma(\mathbf{x})]_{\mathbf{k}},\\&\sigma_{\mathbf{k}}=-\theta\nu_{\mathbf{k}}/(1+N\theta\nu_{\mathbf{k}}),\quad \mathbf{k}\neq 0,\\&\sigma_0=1,\end{aligned} \tag{61}$$

representing (59), (33) and normalization of σ.

Eliminating $\theta\nu_{\mathbf{k}}$ and reversing the Fourier transform in (61), we then have

$$\begin{aligned}&\sigma(\mathbf{x})+(e^{\theta V(\mathbf{x})}-1)\sigma(\mathbf{x})\\&\qquad+(N/L^3)\int(e^{\theta V(\mathbf{y})}-1)\sigma(\mathbf{y})\sigma(\mathbf{x}-\mathbf{y})d^3y=c,\\&\qquad\qquad(1/L^3)\int\sigma(\mathbf{x})d^3x=1\end{aligned} \tag{62}$$

for some constant c.

Integrating the first equation of (62) and using the second, the constant is then determined by

$$1+(N+1)L^{-3}\int(e^{\theta V(\mathbf{x})}-1)\sigma(\mathbf{x})d^3x=c. \tag{63}$$

Again dropping the 1 in $N+1$, we obtain the integral equation for $\sigma(\mathbf{x})$:

$$e^{\theta V(\mathbf{x})}\sigma(\mathbf{x})=1-n\int(e^{\theta V(\mathbf{y})}-1)\sigma(\mathbf{y})[\sigma(\mathbf{x}-\mathbf{y})-1]d^3y. \tag{64}$$

The family resemblance of (64) to the Born-Green-Yvon[18] and Kirkwood[19] integral equations is pronounced, with the very welcome distinction that (64) is quadratic in $\sigma(\mathbf{x})$ and not transcendental. It will develop that other than merely computational advantages thereby result.

For the sake of convenience in general and of necessity when dealing with singular potentials, it is preferable to regard

$$\tau(\mathbf{x})\equiv e^{\theta V(\mathbf{x})}\sigma(\mathbf{x}) \tag{65}$$

as the basic unknown quantity; the corresponding

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[17] The prescription of Paper II appears a likely candidate to best satisfy our apparently incompatible restrictions on $\{\mathbf{k}\}$. An explicit density of $\mathbf{k}$'s may be determined to annihilate the second order corrections in theorem (21), but we shall defer such considerations.

[18] H. S. Green, *Molecular Theory of Fluids* (Interscience Publishers, Inc., New York, 1952), p. 77.

[19] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), p. 330.

integral equation is then

$$\tau(\mathbf{x})=1+n\int(e^{-\theta V(\mathbf{y})}-1)\times\tau(\mathbf{y})[e^{-\theta V(\mathbf{x}-\mathbf{y})}\tau(\mathbf{x}-\mathbf{y})-1]d^3y. \quad (66)$$

A crude picture of the new function $\tau(\mathbf{x})$ is obtained if we note that $\tau(\mathbf{x})$ reduces to $\sigma(\mathbf{x})$ for small $V(\mathbf{x})$ and to the effective potential $\theta\nu(\mathbf{x})$ for large $V(\mathbf{x})$; actually of course, (65) and (60) tell us that

$$\tau(\mathbf{x})=\sigma(\mathbf{x})+\theta\nu(\mathbf{x}). \quad (67)$$

VI. THERMODYNAMIC QUANTITIES

Having in principle solved for the two-body distribution function, we are now prepared to obtain the various thermodynamic properties of the system. One can imagine a number of methods, all equivalent, of utilizing exact knowledge of $\sigma(\mathbf{x})$ to construct these quantities. However, if $\sigma(\mathbf{x})$ is known only approximately, these methods yield different results, and one must choose the one which is most suitable for the particular approximation employed. Since the characteristic relation for the isothermal compressibility is demanded by our theory, it seems clear that it will be particularly appropriate to obtain the thermodynamic properties from K_T^{-1}. To offer some measure of comparison, we shall carry along in parallel a more usual method, elegant in form, based upon the variation of the (Helmholtz) free energy.

First, then, we recall from our expression (38) for isothermal compressibility that

$$\left(\frac{\partial p}{\partial n}\right)_\theta=\frac{1}{\theta}(1+N\theta\nu_{0+}). \quad (68)$$

Further, from (59) and (65), we have for $\mathbf{k}\neq 0$

$$\theta\nu_{\mathbf{k}}=-[(e^{-\theta V(\mathbf{x})}-1)\tau(\mathbf{x})]_{\mathbf{k}}; \quad (69)$$

but if $V(\mathbf{x})$ vanishes for large x, so does $e^{-\theta V(\mathbf{x})}-1$, whence

$$\theta\nu_{0+}=-[(e^{-\theta V(\mathbf{x})}-1)\tau(\mathbf{x})]_0=-L^{-3}\int(e^{-\theta V(\mathbf{x})}-1)\tau(\mathbf{x})d^3x.$$

Thus, (68) yields

$$\left(\frac{\partial p}{\partial n}\right)_\theta=\frac{1}{\theta}\left[1-n\int(e^{-\theta V(\mathbf{x})}-1)\tau(\mathbf{x})d^3x\right]. \quad (70)$$

It is now an easy matter to generate all pertinent thermodynamic quantities from relation (70). Integrating over n, observing that $p=0$ when $n=0$ [and from (60) that τ is a function of x, n, and θ alone] we have

$$p=\frac{1}{\theta}\left(n-\int(e^{-\theta V(\mathbf{x})}-1)\left[\int_0^n n'\tau(\mathbf{x},n')dn'\right]d^3x\right). \quad (71)$$

The Helmholtz free energy A may then be determined by

$$p=-\left(\frac{\partial A}{\partial L^3}\right)_\theta=\frac{n^2}{N}\left(\frac{\partial A}{\partial n}\right)_\theta; \quad (72)$$

we reduce the double integral obtained from the integration of (72) by the general observation that

$$-\left(\int_0^z(\quad)dz\right)g'(z)\left(\int_0^z(\quad)dz\right)=\left[\int_0^z(\quad)dz,g(z)\right] \quad (73)$$

for any integrand vanishing strongly enough at $z=0$. If we take $g(z)=1/z$ in (73), then (72) integrates at once to

$$A=\frac{N}{\theta}\left[a_0+\tfrac{3}{2}\ln\theta+\ln n-\int(e^{-\theta V(\mathbf{x})}-1)\int_0^n\left(1-\frac{n'}{n}\right)\tau(\mathbf{x},n')dn'd^3x\right], \quad (74)$$

where a_0 is a normalization constant and the θ dependence results from the known zero-interaction limit. The internal energy and specific heat are of course now computed from

$$E=\frac{\partial}{\partial\theta}(\theta A),\quad C_V=-K\theta^2\frac{\partial^2}{\partial\theta^2}(\theta A). \quad (75)$$

The second method of determining the thermodynamic quantities hinges on computing the variation of A, which may rigorously be divided into kinetic and potential portions[20]:

$$A=A_{\mathrm{K.E.}}+A_{\mathrm{P.E.}},$$

$$A_{\mathrm{K.E.}}=(N/\theta)(a_0+\tfrac{3}{2}\ln\theta+\ln n),$$

$$A_{\mathrm{P.E.}}=-(1/\theta)\ln\left\{\int\exp[-\theta\textstyle\sum_{i>j}V(\mathbf{x}_i-\mathbf{x}_j)]\times dx^{3N}\Big/L^{3N}\right\}. \quad (76)$$

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[20] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), p. 235.

For a change not involving volume, clearly

$$\delta(\theta A_{\mathrm{P.E.}})=\int\left[\sum_{i>j}\delta\theta V(\mathbf{x}_i-\mathbf{x}_j)\right]\times\exp\left[-\theta\sum_{i>j}V(\mathbf{x}_i-\mathbf{x}_j)\right]dx^{3N}\Big/\int\exp\left[-\theta\sum_{i>j}V(\mathbf{x}_i-\mathbf{x}_j)\right]dx^{3N},$$

or

$$\delta(\theta A_{\mathrm{P.E.}})=\tfrac{1}{2}N(N-1)L^{-3}\int\delta(\theta V(\mathbf{x}))\sigma(\mathbf{x})dx^3. \quad (77)$$

On the other hand, for a change in the length L,

$$\int\exp\left[-\theta\sum_{i>j}V(\mathbf{x}_i-\mathbf{x}_j)\right]dx^{3N}/L^{3N}\rightarrow\int\exp\left[-\theta\sum_{i>j}V(\mathbf{x}_i'-\mathbf{x}_j')\right](dx')^{3N}/(L+dL)^{3N},$$

which, under the substitution $\mathbf{x}'=(1+dL/L)\mathbf{x}$, becomes

$$\int\exp\left\{-\theta\sum_{i>j}V[(\mathbf{x}_i-\mathbf{x}_j)(1+dL/L)]\right\}dx^{3N}/L^{3N},$$

as if the potential had changed:

$$\begin{aligned}\delta(\theta V(\mathbf{x}))&=\theta V[(1+dL/L)\mathbf{x}]-\theta V(\mathbf{x})\\&=(dL/L)\mathbf{x}\cdot\nabla\theta V(\mathbf{x}).\end{aligned} \quad (78)$$

Hence under a change of θ, V, or L, we have

$$\delta(\theta A_{\mathrm{P.E.}})=\frac{N}{2}n\int\sigma(\mathbf{x})\left[\delta\theta V(\mathbf{x})+\frac{\delta L}{L}\mathbf{x}\cdot\nabla\theta V(\mathbf{x})\right]dx^3. \quad (79)$$

Applying (79) to the special cases (75) and (72), we obtain

$$E=N\left(\frac{3}{2}\frac{1}{\theta}+\frac{1}{2}n\int V(\mathbf{x})\sigma(\mathbf{x})dx^3\right), \quad (80)$$

$$p=\frac{n}{\theta}\left(1+\frac{n}{6}\int\tau(\mathbf{x})\mathbf{x}\cdot\nabla e^{-\theta V(\mathbf{x})}dx^3\right). \quad (81)$$

The fact that the equation of state in virial form (81) involves differentiation, whereas that in compressibility form (71) requires integration, suggests that the latter may rather generally be a superior approach when approximations are involved, aside from the specific indications for the suitability of (71) in our particular approach.

VII. VIRIAL COEFFICIENTS

A useful form in which to solve our fundamental integral equation (66), which provides as well a check against precisely known results, is in a virial (power series in density) expansion. For the leading terms, this is most readily done by iteration, for which purpose we write Eq. (66) as

$$\tau_{12}=1+n\int f_{23}\tau_{23}(\tau_{13}-1)d^3x_3+n\int f_{23}f_{13}\tau_{23}\tau_{13}d^3x_3, \quad (82)$$

where

$$f_{ij}\equiv\exp[-\theta V(\mathbf{x}_i-\mathbf{x}_j)]-1, \quad \tau_{ij}\equiv\tau(\mathbf{x}_i-\mathbf{x}_j).$$

Commencing at $\tau_{12}=1$, we readily iterate out a power series, obtaining

$$\tau_{12}=1+n\int f_{23}f_{13}d^3x_3+n^2\int\int[f_{23}f_{34}f_{14}+2f_{23}f_{34}f_{14}f_{24}]d^3x_3d^3x_4+\cdots. \quad (83)$$

In order to compare (83) with standard virial expansions, it is convenient to have numbers, rather than functions. In particular, defining the virial coefficients B_s by the series for the equation of state,

$$p\theta=\sum_{s=1}^{\infty}B_s n^s, \quad (84)$$

let us compute the B_s from (83), using both (71) and (81). Substituting in (71), we have at once the "compressibility-derived" coefficients:

$$\begin{aligned}B_1^{(C)}&=1,\\B_2^{(C)}&=-\tfrac{1}{2}\int f_{12}d^3x_2,\\B_3^{(C)}&=-\tfrac{1}{3}\int f_{12}f_{23}f_{13}d^3x_2d^3x_3,\\B_4^{(C)}&=-\tfrac{1}{4}\int[f_{12}f_{23}f_{34}f_{14}+2f_{12}f_{23}f_{34}f_{14}f_{24}]d^3x_2d^3x_3d^3x_4,\\&\cdots.\end{aligned} \quad (85)$$

Correspondingly, the virial form (81) yields on substitution

$$\begin{aligned}6B_1^{(V)}&=6,\\6B_2^{(V)}&=\int(\mathbf{x}_{12}\cdot\nabla_{12})f_{12}d^3x_2,\\6B_3^{(V)}&=\int f_{23}f_{13}(\mathbf{x}_{12}\cdot\nabla_{12})f_{12}d^3x_2d^3x_3,\\6B_4^{(V)}&=\int[f_{23}f_{34}f_{14}+2f_{23}f_{34}f_{14}f_{24}]\times(\mathbf{x}_{12}\cdot\nabla_{12})f_{12}d^3x_2d^3x_3d^3x_4, \quad\cdots\end{aligned} \quad (86)$$

which requires further elucidation. We first write (86) as

$$6B_2^{(V)}=\int(\mathbf{x}_1\cdot\nabla_1+\mathbf{x}_2\cdot\nabla_2)f_{12}d^3x_1d^3x_2/L^3,$$

$$6B_3^{(V)}=\int(\mathbf{x}_1\cdot\nabla_1+\mathbf{x}_2\cdot\nabla_2+\mathbf{x}_3\cdot\nabla_3)\times(f_{12}f_{23}f_{13})d^3x_1d^3x_2d^3x_3/3L^3, \quad (87)$$

$$6B_4^{(V)}=\int[(\mathbf{x}_1\cdot\nabla_1+\mathbf{x}_2\cdot\nabla_2+\mathbf{x}_3\cdot\nabla_3+\mathbf{x}_4\cdot\nabla_4)\times(f_{12}f_{23}f_{34}f_{14}+2f_{12}f_{23}f_{34}f_{14}f_{24})-2f_{12}f_{23}f_{34}f_{14}\mathbf{x}_{24}\cdot\nabla_{24}f_{24}]d^3x_1d^3x_2d^3x_3d^4x_4/4L^3.$$

But, in general,

$$\int(\mathbf{x}_1\cdot\nabla_1+\cdots\mathbf{x}_s\cdot\nabla_s)F(f_{12},f_{13},\cdots)d^3x_1\cdots d^3x_s$$
$$=\sum_j\left[\int F(f_{12},f_{13},\cdots)d^3x_1\cdots\mathbf{x}_j\cdot d\mathbf{S}_j\cdots d^3x_s\right]-\int F(f_{12},f_{13},\cdots)\sum_j\nabla_j\cdot\mathbf{x}_jd^3x_1\cdots d^3x_s.$$

Since $\int\mathbf{x}_j\cdot d\mathbf{S}_j=3L^3$, and the remaining integrand is independent of x_j, we then have

$$\int(\mathbf{x}_1\cdot\nabla_1+\cdots+\mathbf{x}_s\cdot\nabla_s)F(f_{12},f_{13},\cdots)d^3x_1\cdots d^3x_s=-3(s-1)\int F(f_{12},f_{13},\cdots)d^3x_1\cdots d^3x_s. \quad (88)$$

Substituting into (87), we conclude that

$$B_1^{(V)}=1,$$
$$B_2^{(V)}=-\tfrac{1}{2}\int f_{12}d^3x_2,$$
$$B_3^{(V)}=-\tfrac{1}{3}\int f_{12}f_{23}f_{13}d^3x_2d^3x_3, \quad (89)$$
$$B_4^{(V)}=-\tfrac{1}{8}\int(3f_{12}f_{23}f_{34}f_{14}+6f_{12}f_{23}f_{34}f_{14}f_{24}+\tfrac{2}{3}f_{12}f_{23}f_{34}f_{14}\mathbf{x}_{24}\cdot\nabla_{24}f_{24})d^3x_2d^3x_3d^3x_4,\quad\cdots.$$

Now by the exact cluster expansion of Ursell,[21] one finds

$$B_1=1,$$
$$B_2=-\tfrac{1}{2}\int f_{12}d^3x_2,$$
$$B_3=-\tfrac{1}{3}\int f_{12}f_{23}f_{13}d^3x_2d^3x_3, \quad (90)$$
$$B_4=-\tfrac{1}{8}\int(3f_{12}f_{23}f_{34}f_{14}+6f_{12}f_{23}f_{34}f_{14}f_{24}+f_{12}f_{23}f_{34}f_{14}f_{24}f_{13})d^3x_2d^3x_3d^3x_4,\quad\cdots.$$

Thus, comparing (85), (89), and (90), we find that B_1, B_2, B_3 are reproduced exactly by either compressional or virial form of our approximation. Further, the difference between $B_4^{(V)}$ and B_4 occurs in a term of small coefficient, indicating that the deviation may not be large. On the other hand, we see that

$$B_4^{(C)}-B_4=\tfrac{1}{8}\int f_{12}f_{23}f_{34}f_{41}(1+f_{24})\times(1+f_{13})d^3x_2d^3x_3d^3x_4; \quad (91)$$

since the integrand is small unless, crudely, the pairs of positions 12, 13, 34, and 14 are close, but the pairs 13 and 24 distant, the difference $B_4^{(C)}-B_4$ is expected to be very small indeed. Although we shall show that the higher $B_s^{(C)}$ are characterized as containing only plane convex irreducible clusters, accurate estimate of the validity of further $B_s^{(C)}$ is fraught with difficulty.

VIII. GAS OF HARD SPHERES

To further investigate our approximate virial coefficients, let us consider a gas of hard spheres of diameter a:

$$V(x)=\infty \quad \text{for} \quad |x|<a,$$
$$V(x)=0 \quad \text{for} \quad |x|>a. \quad (92)$$

The leading virial coefficients have been computed[22]:

$$B_1=1,\quad B_3=\tfrac{5}{8}(\tfrac{2}{3}\pi a^3)^2,$$
$$B_2=\tfrac{2}{3}\pi a^3,\quad B_4=0.2869(\tfrac{2}{3}\pi a^3)^3, \quad (93)$$

and the approximate values of B_4 as well[23]:

$$B_4^{(C)}=0.2969(\tfrac{2}{3}\pi a^3)^3,$$
$$B_4^{(V)}=0.2500(\tfrac{2}{3}\pi a^3)^3. \quad (94)$$

Thus the fourth virial coefficient $B_4^{(C)}$ is in error by only 3%, while $B_4^{(V)}$ is off by 13%, even this being an improvement over the results of current approximate theories.

It is of interest to observe that our expressions for

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[21] J. E. Mayer and M. G. Mayer, reference 20, p. 287.

[22] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1952), p. 289.

[23] B. R. A. Nijboer and L. Van Hove, Phys. Rev. **85**, 777 (1952).

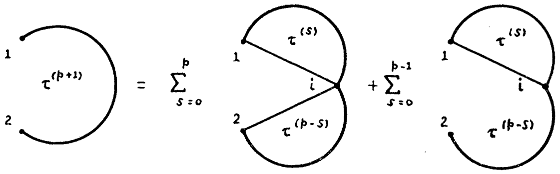

FIG. 1. Recurrence relation for $\tau^{(p)}$.

B_4, and for its sire in $\tau(\mathbf{x})$, were postulated by Nijboer and Van Hove[23] solely on the basis of their numerical computations on hard spheres, as being a simple approximation which would give results far superior (for virial expansions) to those obtained by application of the Kirkwood superposition principle.[24] We have now found that the relevant principle which appears to replace superposition, for the gaseous state, is that of independence of collective oscillations. Since the collective approach was set up with a dense rather than a rare medium in mind, we may then have derived a fairly broad spectrum approximation.

IX. COMPLETE CLUSTER EXPANSION

It is not difficult to obtain, in form, the full set of coefficients in the expansion of our approximation to

$$\tau(\mathbf{x}) = \sum_{s=0}^{\infty} n^s \tau^{(s)}(\mathbf{x}). \qquad (95)$$

One simply substitutes (95) into the defining relation (82) and equates coefficients of n^{p+1}. For $p \geqslant 0$, the result is that

$$\tau_{12}^{(p+1)} = \sum_{s=0}^{p} \int f_{23} f_{13} \tau_{23}^{(s)} \tau_{13}^{(p-s)} d^3x_3 + \sum_{s=1}^{p} \int f_{23} \tau_{23}^{(s)} \tau_{13}^{(p-s)} d^3x_3. \qquad (96)$$

We represent the recurrence relation (96) symbolically in the accompanying Fig. 1, the straight lines denoting f factors, the curved lines τ factors, and particle i being integrated over each case.

The claim is now made that $\tau^{(p)}$ consists of all geometrically distinct (unaltered by a cyclic rotation) $(p+2)$-particle plane convex irreducible diagrams with a single peripheral link missing. That is, set up a polygon of $p+2$ ordered vertices, connect all adjacent positions but 1–2, and make any set of internal connections such that no two intersect inside the polygon. Since the statement is true for $p=1$ [see (83)], we may proceed inductively, assuming that all $\tau^{(r)}$ are as described for $r \leqslant p$. Consider then $\tau^{(p+1)}$; if 1 and 2 are connected to the same vertex i, then they will be represented by the center graph of Fig. 1, but since i must be unique, the graph is not duplicated. If 1 and 2 are not connected to a common vertex, let i be the vertex nearest 2 to which 1 is connected; the preceding argument applies verbatim.

Upon inserting (95) into (70), which we write as

$$\theta \frac{\partial p}{\partial n} = 1 - n \int f_{12} \tau_{12} d^3x_2, \qquad (97)$$

this yields at once the prescription that in our approximation,

$$\theta \frac{\partial p}{\partial n} = 1 - \sum_{s=1}^{\infty} n^s \times [\text{sum of pictorially distinct plane convex irreducible } (s+1)\text{-particle clusters}]. \qquad (98)$$

Here, pictorially distinct refers to the fact that since the distinguished pair 1–2 has disappeared, then with the vertices undesignated, rotation may produce a distinct diagram. Expression (98) is to be compared with the "exact" (with the usual stipulations) Mayer-Ursell[25]

$$\theta \frac{\partial p}{\partial n} = 1 - \sum_{s=1}^{\infty} \frac{n^s}{s-1!} \times [\text{sum of irreducible } (s+1)\text{-particle clusters}]. \qquad (99)$$

The first five virial coefficients, defined by (84), and

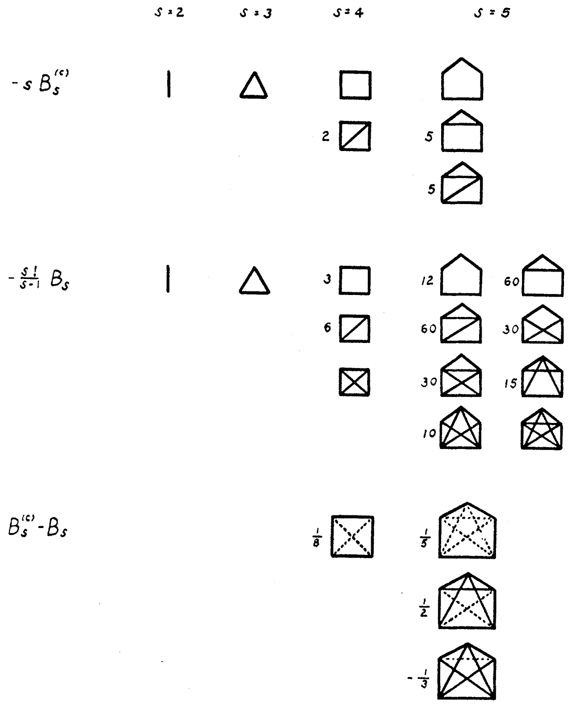

FIG. 2. Exact virial coefficients compared to those in collective coordinate approximation.

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[24] J. G. Kirkwood and E. M. Boggs, J. Chem. Phys. 10, 394 (1942).

[25] J. E. Mayer and M. G. Mayer, reference 20, p. 293.

their differences are shown pictorially in Fig. 2. The dotted line in the third row of Fig. 2 denotes the factor $1+f$. It is observed that the difference $B_5^{(C)}-B_5$ is small in the same sense as $B_4^{(C)}-B_4$, which was discussed following (91).

It is not hard to see that the deviation $B_s^{(C)}-B_s$ can always be pictured so as to contain at least one factor of $1+f$, for this requires only that $B_s^{(C)}-B_s$ vanish formally when $f\equiv -1$. Now when $f\equiv -1$, (82) may be solved trivially and yields

$$\tau(\mathbf{x})=(1-nL^3)^{-1}, \tag{100}$$

from which, employing (97),

$$\begin{aligned} \theta(\partial p/\partial n)&=(1-nL^3)^{-1},\\ \theta p&=-L^{-3}\ln(1-nL^3), \\ B_s^{(C)}&=(L^3)^{s-1}/s. \end{aligned} \tag{101}$$

On the other hand, the cluster expansion virial coefficients are precisely those obtained[26] from the grand canonical partition function:

$$\theta p=L^{-3}\ln[\textstyle\sum_0^\infty (Z_N/N!)z^N], \tag{102}$$

where

$$Z_N=\int\cdots\int \exp[-\tfrac{1}{2}\theta \textstyle\sum_{i>j} V(\mathbf{x}_i-\mathbf{x}_j)]dx^{3N},$$

$$n=\theta z(\partial p/\partial z).$$

For the special case $f\equiv -1$, (102) reduces easily to

$$\theta p=L^{-3}\ln(1+L^3z),\quad n=z/(1+L^3z), \tag{103}$$

so that again

$$\theta p=-L^{-3}\ln(1-nL^3), \tag{104}$$

showing, as desired, that $B_s^{(C)}=B_s$ for all s, and establishing that in general $B_s^{(C)}-B_s$ has the factor $1+f$. However, the $1+f$ factors will certainly not in general reduce the difference of $B_s^{(C)}$ and B_s as severely as in the case $s=4$.

X. CONCLUDING REMARKS

We have shown that a careful self-consistent formulation of the classical statistical mechanics of the many-body problem, based upon the approximation of independent dynamical behavior of the Fourier components of the matter density, yields exceptionally accurate results not only in the high-density region[27] for which it appears most appropriate, but for low density as well. The approximation thus appears to have a wide range of validity.

It is worth noting that the combination $\sigma(e^{\theta V}-1)/\theta$, which does not arise in our previous work[1] on the subject and which characterizes the form of the statistical state, is necessary for quantitative accuracy, but very often not for qualitative accuracy. This follows from the fact that the replacement of $\sigma(e^{\theta V}-1)/\theta$ by σV itself results in the replacement of $f\equiv e^{-\theta V}-1$ by $f'\equiv -\theta V/(1+\theta V)$; f and f' differ by at most 30% for $V>0$ and coincide for $V=0$ or ∞ (as in the hard-sphere case, for which our approximation is nearly optimal). Of course, the equality between f and f' fails dismally for large negative θV, a region in which the metastable two-particle "bound states" become important. We see, however, that the crude and tentative approach to the determination of the oscillation frequency, reviewed in Sec. I, is justified over a considerable domain.

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[26] D. ter Haar, *Statistical Mechanics* (Rinehart and Company, New York, 1954), p. 175.

[27] A more detailed analysis of this region will appear in a succeeding paper.