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Imperfect Bose Gas with Hard-Sphere Interaction

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The method developed in the previous paper for the treatment of the quantum-mechanical N-body hard-sphere problem is applied to a calculation of the grand partition function of an imperfect Bose gas with hard-sphere interactions. The grand partition function is calculated to second order in an expansion in powers of a/λ, where a is the hard-sphere diameter and λ the thermal wavelength. The approximate equation of state for the gas phase is thereby obtained by calculating all the virial coefficients to order $(a/\lambda)^2$.

The first-order energy levels obtained in the previous paper embody some interesting physical properties. A fictitious system with exactly such energy levels is considered. The partition function for such a system can be calculated exactly and the exact equation of state obtained. It is shown that there is a phase transition, which more closely resembles an ordinary gas-liquid transition than the Bose-Einstein condensation.

1. INTRODUCTION

IN this paper, we shall calculate the virial coefficients for an imperfect Bose gas with hard-sphere interactions, using the method of the pseudopotential developed in the preceding paper.[1] *The calculation of the virial coefficients requires only a knowledge of the behavior of the system in the neighborhood of zero density*, since they are the coefficients appearing in the expansion of the equation of state in a Taylor series about zero density. There is therefore no question that a perturbation treatment with the diameter a of the hard spheres as expansion parameter is valid. Accordingly, we adopt for the Hamiltonian of the system, in the same notations as I,

$$\begin{aligned} H &= H_0 + H', \\ H_0 &= -(\hbar^2/2m)(\nabla_1^2+\cdots+\nabla_N^2), \\ H' &= (4\pi a\hbar^2/m)\sum_{i<j}\delta(\mathbf{r}_i-\mathbf{r}_j)\frac{\partial}{\partial r_{ij}}r_{ij}, \end{aligned} \tag{1}$$

where $r_{ij}\equiv|\mathbf{r}_i-\mathbf{r}_j|$. The interaction Hamiltonian H' will be treated as a small perturbation, and will correctly account for effects up to order a^2.

We shall see that this program will enable us to calculate *all* the virial coefficients; but each virial coefficient is calculated only approximately to order a^2. Actually, the dimensionless perturbation parameter will turn out to be a/λ, where

$$\lambda=(2\pi\hbar^2/mkT)^{\frac{1}{2}} \tag{2}$$

is the "thermal wavelength," of the order of the de Broglie wavelength of a particle with energy kT. What we have then will be a low-temperature expansion of the virial coefficients.

To make such a calculation is not entirely a trivial matter. We recall that the calculation of virial coefficients in quantum-statistical mechanics is vastly more difficult than in classical statistical mechanics. In the latter case, with the help of the well-known Ursell-Mayer expansion of the partition function into cluster integrals, *all* virial coefficients are formulated in a volume-independent manner in terms of well-defined integrals involving the interaction potential. We may say that the problem there has been "reduced to quadruture." In quantum-statistical mechanics, on the other hand, no such volume-independent formulation so far exists for virial coefficients higher than the second. The quantum-mechanical lth cluster integral involves either the wave functions or energy levels of l interacting particles, so that to evaluate it explicitly we would have to solve the general quantum-mechanical l-body problem in a box. It is therefore not surprising that only for the second virial coefficient do we have a volume-independent formula involving the scattering phase shifts of the two-body system.[2]

An interesting question that arises in any theory of imperfect Bose gases is the effect of the imperfection on the Bose condensation. A mere knowledge of the virial coefficients, however, is not sufficient for the discussion of this question. Accordingly, no attempt has been made here to discuss the Bose condensation on the basis of the perturbation calculation; but purely for heuristic purposes we have included in Sec. 6 a certain example of an imperfect Bose gas for which the condensation can be rigorously discussed, and which a hard-sphere Bose gas may in some sense resemble.

2. FORMULATION OF THE PROBLEM

We collect here first a few definitions and formulas well known in statistical mechanics.[3] The partition function of a Bose gas of N interacting particles enclosed in a volume V is

$$Q_N=\mathrm{Sp}\,e^{-\beta H}, \tag{3}$$

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[1] K. Huang and C. N. Yang, preceding paper [Phys. Rev. **105**, 767 (1956)] hereafter referred to as I.

[2] E. Beth and G. E. Uhlenbeck, Physica 4, 915 (1937).

[3] See, for example, D. ter Haar, *Elements of Statistical Mechanics* (Rinehart Publishing Corporation, New York, 1954).

where $\beta=1/kT$, and the spur is taken over symmetrical states only. The grand partition function $\mathfrak{Q}$ is defined by

$$\mathfrak{Q}=\sum_{N=0}^{\infty} z^N Q_N, \tag{4}$$

where z is the fugacity, related to the chemical potential ν by

$$z=e^{\nu}. \tag{5}$$

The equation of state is then obtained by the usual prescription of eliminating z between the following equations:

$$\begin{aligned} PV/kT&=\log\mathfrak{Q},\\ N&=z\frac{\partial}{\partial z}\log\mathfrak{Q}. \end{aligned} \tag{6}$$

It is customary to expand $\log\mathfrak{Q}$ in a power series in z, so that

$$\begin{aligned} \frac{P}{kT}&=\frac{1}{V}\log\mathfrak{Q}=\sum_{l=1}^{\infty} b_l z^l,\\ \frac{N}{V}&=z\frac{\partial}{\partial z}\left(\frac{P}{kT}\right)=\sum_{l=1}^{\infty} l b_l z^l. \end{aligned} \tag{7}$$

The coefficients b_l are the coefficients which correspond to the classical cluster integrals. They are actually functions of the volume V, but we shall be interested only in their values at $V\rightarrow\infty$. (In doing so we forsake all possible knowledge concerning the system except in the gaseous state.[4])

Our program consists in putting the Hamiltonian in (3) equal to that of N hard spheres of diameter a with periodic boundary conditions, and computing the coefficients b_l:

$$b_l=b_l^{(0)}+b_l^{(1)}+b_l^{(2)}+\cdots, \tag{8}$$

in ascending powers of a.

The coefficients $b_l^{(0)}$, i.e., the value of b_l for free particles, is well known:

$$b_l^{(0)}=\lambda^{-3}l^{-5/2}. \tag{9}$$

Since the Hamiltonian in (1) gives the same result as the hard-sphere Hamiltonian up to order a^2, we shall use it in (3) for the calculation of $b_l^{(1)}$ and $b_l^{(2)}$.

The calculation proceeds by expanding the partition function and the grand partition function in ascending powers of a:

$$Q_N=Q_N^{(0)}+Q_N^{(1)}+Q_N^{(2)}+\cdots, \tag{10}$$

where

$$\begin{aligned} Q_N^{(0)}&=\mathrm{Sp}e^{-\beta H_0},\\ Q_N^{(1)}&=-\beta\,\mathrm{Sp}(e^{-\beta H_0}H'),\\ Q_N^{(2)}&=\mathrm{Sp}\left[\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\frac{(k+1)(-\beta)^{j+k+2}}{(j+k+2)!}H_0^kH'H_0^jH'\right], \end{aligned} \tag{11}$$

where H_0^k means H_0 to the power k. Correspondingly, $\mathfrak{Q}$ will have the expansion

$$\begin{aligned} \mathfrak{Q}&=\mathfrak{Q}^{(0)}+\mathfrak{Q}^{(1)}+\mathfrak{Q}^{(2)}+\cdots,\\ \mathfrak{Q}^{(n)}&=\sum_{N=0}^{\infty} z^N Q_N^{(n)}. \end{aligned} \tag{12}$$

We have, therefore,

$$\begin{aligned} \log\mathfrak{Q}&=\log\left[\mathfrak{Q}^{(0)}\left(1+\frac{\mathfrak{Q}^{(1)}}{\mathfrak{Q}^{(0)}}+\frac{\mathfrak{Q}^{(2)}}{\mathfrak{Q}^{(0)}}+\cdots\right)\right]\\ &=\log\mathfrak{Q}^{(0)}+\frac{\mathfrak{Q}^{(1)}}{\mathfrak{Q}^{(0)}}+\left[\frac{\mathfrak{Q}^{(2)}}{\mathfrak{Q}^{(0)}}-\frac{1}{2}\left(\frac{\mathfrak{Q}^{(1)}}{\mathfrak{Q}^{(0)}}\right)^2\right]+\cdots. \end{aligned}$$

Thus

$$\sum_1^{\infty} b_l^{(0)}z^l=\frac{1}{V}\log\mathfrak{Q}^{(0)}, \tag{13}$$

$$\sum_1^{\infty} b_l^{(1)}z^l=\frac{1}{V}\frac{\mathfrak{Q}^{(1)}}{\mathfrak{Q}^{(0)}}, \tag{13a}$$

and

$$\sum_1^{\infty} b_l^{(2)}z^l=\frac{1}{V}\left[\frac{\mathfrak{Q}^{(2)}}{\mathfrak{Q}^{(0)}}-\frac{1}{2}\left(\frac{\mathfrak{Q}^{(1)}}{\mathfrak{Q}^{(0)}}\right)^2\right]. \tag{13b}$$

It should be emphasized that by confining ourselves to the calculation of b_l *we do not have to investigate or to make assumptions concerning the infinitely many body problem at finite density N/V.* This is so because for any fixed l, the calculation of b_l involves first the calculations of $Q_1, Q_2, \cdots Q_l$, and then the limiting process $V\rightarrow\infty$. The calculation therefore requires knowledge only of the l body problem at zero density. In this process we lose information, of course, concerning the condensed state. It is our feeling that to treat with rigor the problem of the condensed state (which requires a knowledge of the infinitely many body problem at finite density) is a mathematical task of a different order of magnitude in its difficulty.

In the calculation of the series expansion of Q_N and $\mathfrak{Q}$, it is important that all orders of V be kept. The limiting process $V\rightarrow\infty$ should only be taken after the expression for b_l has been obtained from (13).

3. FIRST-ORDER CALCULATION

The first-order partition function can be calculated as follows:

$$\begin{aligned} Q_N^{(1)}&=-\beta\sum_n\exp(-\beta E_n^{(0)})(\Psi_n^{(0)},H'\Psi_n^{(0)})\\ &=-\left(\frac{4\pi a\hbar^2\beta}{mV}\right)\sum_{n_\alpha,\Sigma n_\alpha=N}\exp(-\beta\textstyle\sum_\alpha n_\alpha\epsilon_\alpha)\\ &\qquad\times(N^2-\tfrac{1}{2}N-\tfrac{1}{2}\textstyle\sum_\alpha n_\alpha^2), \end{aligned} \tag{14}$$

where the notations are the same as those in I, and use has been made of (41) of I. The first-order grand parti-

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[4] Compare, e.g., C. N. Yang and T. D. Lee, Phys. Rev. 87, 404 (1952).

tion function is therefore

$$\mathcal{Q}^{(1)} = -\left(\frac{4\pi a\hbar^2\beta}{mV}\right)\sum_{n_\alpha=0}^{\infty}\prod_{\alpha}[z\exp(-\beta\epsilon_\alpha)]^{n_\alpha}]$$
$$\times[\sum_{\alpha\neq\beta} n_\alpha n_\beta + \tfrac{1}{2}\sum_{\alpha}(n_\alpha{}^2 - n_\alpha)].$$

Hence

$$\frac{\mathcal{Q}^{(1)}}{\mathcal{Q}^{(0)}} = -\left(\frac{4\pi a\hbar^2\beta}{mV}\right)$$
$$\times[\sum_{\alpha\neq\beta}\langle n_\alpha\rangle\langle n_\beta\rangle + \tfrac{1}{2}\sum_{\alpha}(\langle n_\alpha{}^2\rangle - \tfrac{1}{2}\langle n_\alpha\rangle)], \quad (15)$$

where $\langle\ \rangle$ denotes ensemble average. For example,

$$\langle n_\alpha\rangle \equiv \sum_{n=0}^{\infty} n[z\exp(-\beta\epsilon_\alpha)]^n / \sum_{n=0}^{\infty}[z\exp(-\beta\epsilon_\alpha)]^n$$
$$= \frac{z\exp(-\beta\epsilon_\alpha)}{1 - z\exp(-\beta\epsilon_\alpha)}. \quad (16)$$

One can perform the summations in (15) by converting them into integrals. Upon substituting into (13a) and taking the limit $V\rightarrow\infty$, one obtains

$$\sum_{1}^{\infty} b_l{}^{(1)} z^l = -\frac{2a}{\lambda}\frac{1}{\lambda^3}\left(\sum_{1}^{\infty} l^{-\frac{3}{2}} z^l\right)^2, \quad (17)$$

where λ is defined by (2).

4. SECOND-ORDER CALCULATION[5]

The direct second-order perturbation calculation is complicated owing to the existence of degeneracies in the unperturbed system. We shall show now, however, that in the calculation of the partition function, and subsequently the equations of state, this difficulty can be easily circumvented. A similar situation exists for the first-order calculation. We recall that in (14), it is the diagonal matrix elements of H' that enter into the calculations. These matrix elements, which are known, give the first-order energy shifts only in an average sense, because of the degeneracies of the unperturbed system. The detailed first-order level splitting is more difficult to obtain, but is unnecessary for the calculation of the partition function.

The second-order partition function, defined in (11), can be reduced as follows:

$$Q_N{}^{(2)} = \sum_n\left(\Psi_n, \sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\frac{(k+1)(-\beta)^{j+k+2}}{(j+k+2)!}\right.$$
$$\left.\times(E_n)^k H' \sum_m (E_m)^j H'_{mn}\Psi_m\right),$$

where $H'_{mn} = (\Psi_m, H'\Psi_n)$. It is important that the summation over m be carried out first, *before* the operator H' is applied. Let

$$S(x,y) \equiv \sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\frac{k+1}{(j+k+2)!}x^k y^j = \frac{e^y - e^x - (y-x)e^x}{(y-x)^2}.$$

Then

$$Q_N{}^{(2)} = \beta^2\sum_n(\Psi_n, H'\sum_m[S(-\beta E_n, -\beta E_m)H'_{mn}\Psi_m]).$$

Therefore[6]

$$Q_N{}^{(2)} = \beta\sum_n e^{-\beta E_n}\left(\Psi_n, H'\sum_{\substack{n\\E_m\neq E_n}}\frac{H'_{mn}}{E_m - E_n}\Psi_m\right)$$
$$+\tfrac{1}{2}\beta^2\sum_{\substack{m,n\\E_m=E_n}} e^{-\beta E_n}|H'_{mn}|^2. \quad (18)$$

In the matrix element in the first term of (18), we must not interchange H' with the summation $\sum_m$, since H' involves a differentiation—a precaution we learned from I. The second term of (18) isolates the degenerate states, which now present no difficulty. [If there were no degeneracy in the unperturbed system, and if H' were Hermitian, then (18) would reduce to the usual formula of second-order perturbation theory.]

From (18), the second-order grand partition can be written down. However, we are actually interested in the combination $(\mathcal{Q}^{(2)}/\mathcal{Q}^{(0)}) - \frac{1}{2}(\mathcal{Q}^{(1)}/\mathcal{Q}^{(0)})^2$ which appears in (13b). In fact, each term of the bracket above would have a leading volume dependence of V^2, giving a divergent contribution to $b_l{}^{(2)}$, in the limit of infinite volume. In the combination above, these divergent terms cancel. The explicit calculation for this quantity is given in the Appendix. We shall merely give the result here:

$$\sum_{1}^{\infty} b_l{}^{(2)} z^l = 8\left(\frac{a}{\lambda}\right)^2\frac{1}{\lambda^3}\left\{[\sum_{1}^{\infty} l^{-\frac{1}{2}} z^l][\sum_{1}^{\infty} l^{-\frac{3}{2}} z^l]^2\right.$$
$$\left.+\sum_{1}^{\infty}\sum_{1}^{\infty}\sum_{1}^{\infty}\frac{z^{j+k+l}}{(j+l)(k+l)(jkl)^{\frac{1}{2}}}\right\}. \quad (19)$$

5. EQUATION OF STATE AND THE VIRIAL COEFFICIENTS

Collecting the formulas (7), (9), (17), and (19), one obtains the equations:

$$\lambda^3\left(\frac{P}{kT}\right) = g_{\frac{5}{2}}(z) - \frac{2a}{\lambda}[g_{\frac{3}{2}}(z)]^2$$
$$+8\left(\frac{a}{\lambda}\right)^2\left\{[g_{\frac{3}{2}}(z)]^2[g_{\frac{1}{2}}(z)]\right.$$
$$\left.+\sum_{1}^{\infty}\sum_{1}^{\infty}\sum_{1}^{\infty}\frac{z^{j+k+l}}{(j+l)(k+l)(jkl)^{\frac{1}{2}}}\right\}$$
$$+\text{higher orders of } (a/\lambda), \quad (20)$$

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[5] From now on, we shall omit the superscript (0) on the wave functions $\Psi_n{}^{(0)}$ and eigenvalues $E_n{}^{(0)}$.

[6] The term $\sum_n\left[\Psi_n, H'\left\{\sum_{m,E_m\neq E_n}\frac{e^{-\beta E_m} - e^{-\beta E_n}}{(E_m - E_n)^2}H'_{mn}\Psi_m\right\}\right]$ vanishes because the expression in the curly brackets is a wave function that is regular everywhere. Consequently H' can be replaced by its Hermitian part: $(4\pi a\hbar^2/m)\Sigma_{i<j}\delta(\mathbf{r}_i - \mathbf{r}_j)$, which can be put under the Σ_m sign. The expression then obviously reduces to zero.

$$\lambda^3\frac{N}{V}=z\frac{\partial}{\partial z}\left(\frac{\lambda^3 P}{kT}\right), \tag{21}$$

where

$$g_n(z)=\sum_1^{\infty} l^{-n}z^l. \tag{22}$$

The equation of state is obtained by eliminating z from (20) and (21). The virial coefficients α_l are defined by

$$\frac{PV}{NkT}=1+\sum_{l=2}^{\infty}\alpha_l\left(\frac{\lambda^3 N}{V}\right)^{l-1}, \tag{23}$$

and may be worked out from (20)–(23). It is convenient to decompose α_l into two parts.

$$\alpha_l=\alpha_l^{(0)}+\alpha_l',$$

where $\alpha_l^{(0)}$ are independent of a and are the well-known virial coefficients for the ideal Bose gas.[3] The contributions from the imperfection is contained in α_l', a few of which are (to order a^2/λ^2):

$$\alpha_2'=2(a/\lambda), \tag{24}$$

$$\alpha_3'=-4(a/\lambda)^2, \tag{25}$$

$$\alpha_4'=\frac{67\sqrt{2}}{6}\left(\frac{a}{\lambda}\right)^2. \tag{26}$$

As we have mentioned before, for the second virial coefficient α_2' (and only for this coefficient), there exists a volume-independent formulation in terms of the scattering phase shifts. The result for the hard-sphere potential may be quoted here for comparison[7]:

$$\alpha_2'=2(a/\lambda)-(44\pi^2/3)(a/\lambda)^5+O(a/\lambda)^9. \tag{27}$$

The convergence of the expansion in powers of a/λ is therefore very good.

It is important to note that the expansion here is a low-temperature one, where quantum effects are predominant. The hard-sphere diameter a enters into the calculations as a scattering length rather than as the radius of an excluded volume. The excluded-volume effect of the hard-sphere interaction—the only effect in the high-temperature classical region—does not enter into the present calculation, because it is at least of order a^3.

The virial coefficients given in (24)–(26) contain the parameter a as the scattering length of the interaction considered. We can be sure, therefore, that any interaction which possesses the same scattering length a will give rise to virial coefficients whose lowest order terms are given by these expressions. Shape-dependent terms occur only in the higher approximations. The importance of the higher terms relative to the scattering length term depends, of course, on the particular interaction.

6. BOSE CONDENSATION

The virial coefficients calculated previously give the equation of state only in the gas phase, but furnish no information whatsoever about the condensed phase, nor the nature of the condensation. Nevertheless, we would like to have a hint of the existence and the nature of the Bose condensation of this imperfect gas, even though we cannot hope to obtain a rigorous treatment at the moment.

In this section, we shall discuss the condensation of a *fictitious* imperfect Bose gas whose energy levels are rigorously given by the first order results for the hard-sphere gas derived in (41) of I:

$$E_n=\textstyle\sum_\alpha n_\alpha\epsilon_\alpha+(4\pi a\hbar^2/mV)(N^2-\frac{1}{2}n_0^2), \tag{28}$$

where the term $\frac{1}{2}n_0^2$ is all that we retain in the original sum $\frac{1}{2}\sum_\alpha n_\alpha^2$. This is justifiable, because near the condensation region, the average occupation number n_0 of the single-particle "ground" state[8] is much greater than those for the "excited" states.

Such a fictitious system, as we have pointed out in I, embodies some interesting physical properties. For example, it clearly exhibits the phenomenon, arising from the uncertainty principle and from the symmetry of the wave function under exchange of particles, that a spatial repulsion gives rise to a momentum-space attraction. The energy levels which correspond to states of the system differing in n_0 become separated by energy gaps—leading to a behavior of the system not dissimilar to that of a superfluid. It is felt, intuitively, that these are the properties which a hard-sphere Bose gas might really have, and that, although they have so far been demonstrated only to the first order, they might survive more rigorous calculations. It might therefore be interesting to look at the equation of state of a system whose energy levels are rigorously given by (28).

It is important to stress that while any similarity between this fictitious system and an actual hard-sphere gas can only be advanced on a heuristic basis, the calculation of the equation of state arising from (28) will be rigorous.

Briefly, then, we consider the partition function Q_N of this fictitious system:

$$Q_N=e^{-\beta F_N}=\sum_{n_\alpha,\,\Sigma n_\alpha=N}\times\exp\{-\beta[\textstyle\sum n_\alpha\epsilon_\alpha+(4\pi a\hbar^2/mV)(N^2-\frac{1}{2}n_0^2)]\}, \tag{29}$$

where F_N, defined by the above equation, is the Helmholtz free energy. The partition sum over n_α in (29),

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[7] J. de Boer and R. B. Bird, article in Hirschfelder, Curtis, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954).

[8] Single-particle states no longer exist, of course, in the presence of interaction. The terminology "single-particle ground states," etc., are used only for convenience. The quantum number n_0 is a label identifying the state which (28) reduces to when the interaction is switched off.

subject to $\sum n_\alpha = N$, may be decomposed in the following manner:

$$\sum_{n_\alpha, \Sigma n_\alpha = N} = \sum_{n_0=0}^{N} \sum_{n_\alpha, \Sigma n_\alpha = N-n_0} . \tag{30}$$

We note that, by definition,

$$\sum_{n_\alpha, \Sigma n_\alpha = N-n_0} \exp(-\beta \sum n_\alpha \epsilon_\alpha) = Q_{N-n_0}{}^{(0)} = \exp(-\beta F_{N-n_0}{}^{(0)}), \tag{31}$$

where $F_{N-n_0}{}^{(0)}$ is the Helmholtz for energy of an *ideal* Bose gas of $N-n_0$ particles. We can write

$$\log Q_N = -\beta F_N = -(2a\lambda^2 N^2/V) + \log[\sum_{n_0} \exp(a\lambda^2 n_0^2/V) \exp(-\beta F_{N-n_0}{}^{(0)})]. \tag{32}$$

In the second term above, the argument of the logarithm is a sum of positive terms. We can therefore apply the usual theorem that this logarithm may be replaced by the logarithm of the largest term of the summand and obtain

$$-\beta F_N = -\beta F_{N-n_0}{}^{(0)} - (2a\lambda^2 N^2/V) + (a\lambda^2 n_0^2/V), \tag{33}$$

where n_0 assumes that value which maximizes the summand in (32).

If $n_0 = 0$, then (33) gives

$$-\beta F_N = -\beta F_N{}^{(0)} - (2a\lambda^2 N^2/V), \quad (n_0 = 0). \tag{34}$$

The equation of state for this case is then not essentially different from that of an ideal Bose gas in the uncondensed state.

If $n_0 \neq 0$, the value for n_0 is determined by

$$\beta\left(\frac{\partial F_{N'}{}^{(0)}}{\partial N'}\right)_{N'=N-n_0} = -\frac{2a\lambda^2 n_0}{V}, \quad (n_0 \neq 0). \tag{35}$$

We note that the left-hand side is just the chemical potential ν for an ideal Bose gas of $N-n_0$ particles, whose behavior is well known.[3] Thus, n_0 will be obtained by eliminating the parameter $z = e^\nu$ from the following coupled equations:

$$(2a\lambda^2 n_0/V) = -\log z, \tag{36}$$

$$N - n_0 = (V/\lambda^3) g_{\frac{3}{2}}(z), \tag{37}$$

where

$$g_n(z) \equiv \sum_1^\infty l^{-n} z^l. \tag{38}$$

The equation of state, for $n_0 \neq 0$, is then obtained by standard procedures resulting in the parametric equations:

$$\frac{P}{kT} = \frac{1}{\lambda^3} g_{\frac{5}{2}}(z) + \frac{2a\lambda^2 N^2}{V^2} - \frac{1}{4a\lambda^2}(\log z)^2,$$
$$\frac{N}{V} = \frac{1}{\lambda^3} g_{\frac{3}{2}}(z) - \frac{1}{2a\lambda^2} \log z. \tag{39}$$

To sketch the isotherms, we may first plot z as a function of V, at fixed N and T, as shown in Fig. 1. There are two branches of the curve. Branch I, which corresponds to $n_0 = 0$, is essentially that for an ideal gas; but whereas the ideal gas curve would remain constant with $z = 1$ below the critical volume

$$V_2 = N\lambda^3/2\cdot 61, \tag{40}$$

the actual curve now goes over to branch II. Between V_1 and V_2, z becomes triple-valued, with

$$V_1 = 2\cdot 61 V_2[g_{\frac{3}{2}}(z_0) - (\lambda/2a)\log z_0]^{-1}, \tag{41}$$

where z_0 is the root of the equation

$$g_{\frac{1}{2}}(z_0) = \lambda/2a. \tag{42}$$

Only one value of z will be realized, of course. It is determined by requiring the Helmholtz free energy F_N to be minimum—a condition which mathematically follows from the procedure we used: that of taking the largest term in the summand in (32).

Taking the behavior of z from Fig. 1, an isotherm is obtained as shown in the full curve of Fig. 2(a). This is not the equilibrium curve, because P is triple-valued between V_1 and V_2. The equilibrium curve is that with the vertical dotted line, *a b c d e f g*, which results from minimizing

$$F_N = -\int P dV, \quad \text{at constant } T, \tag{43}$$

such that the shaded areas are equal. The minimizing procedure is obvious from Fig. 2(b).

Thus in the canonical ensemble, the isotherm obtained is a very unphysical one, in which the pressure drops discontinuously at a particular volume. However, we may go over to the grand canonical ensemble. It can be easily shown that this is achieved by applying the usual double-tangent construction shown in Fig. 2(b). The resulting isotherm in the grand canonical ensemble, *a b d f g*, is in fact equivalent to that obtained by a Maxwell's construction on the original curve, as indicated by the heavy horizontal line in Fig. 2(a). This new isotherm now exhibits a phase transition similar to that of an ordinary gas-liquid transition.

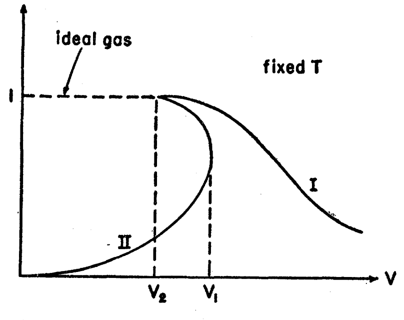

FIG. 1. The fugacity of the imperfect Bose gas as a function of V at fixed T. Branch I—$n_0 = 0$. Branch II—$n_0 \neq 0$.

It thus appears that for our fictitious system, the canonical ensemble and grand canonical ensemble yield different thermodynamic properties. In particular, the canonical ensemble predicts a nonphysical behavior that is not in accordance with van Hove's theorem[9] which states that the isotherm must be a monotonic function of V. This is not surprising, because the energy levels, as given by (28), describe a system which favors such strong density fluctuations that it does not satisfy the assumptions one usually makes about a physical system. In particular, if we cut the system into two volumes by inserting into it an impenetrable wall, the energy does not necessarily increase, as it must for van Hove's theorem to be valid. [The first term of the expression (28), proportional to N^2, satisfies that requirement. However, the second term, $-\frac{1}{2}n_0^2$ works exactly in the opposite direction. That is, if ever it becomes favorable to have particles go into the single-particle ground level in one side of the wall, this will happen in an avalanche until the entire system is transformed.]

The grand canonical ensemble, on the other hand, has implicitly given the system the possibility of a two-phase equilibrium. For physical systems, in which such a possibility is inherent in the system anyway, the grand canonical ensemble yields the same results as the canonical ensemble. For the present case, the grand canonical ensemble disagrees with the canonical ensemble in that the former does not take the energy level formula as literally as the latter. If we adopt the grand canonical ensemble, then the energy formula (28) is to be understood in the sense that it only gives the energy levels of the system in one single phase, and we have to assume in addition that a two-phase separation of the system is possible. Therefore, in the partition sum we would not only sum over possible states of the system in a single phase, but also states in which the system is broken up into two phases in equilibrium with each other. This in practice is achieved by using the grand canonical ensemble.[10]

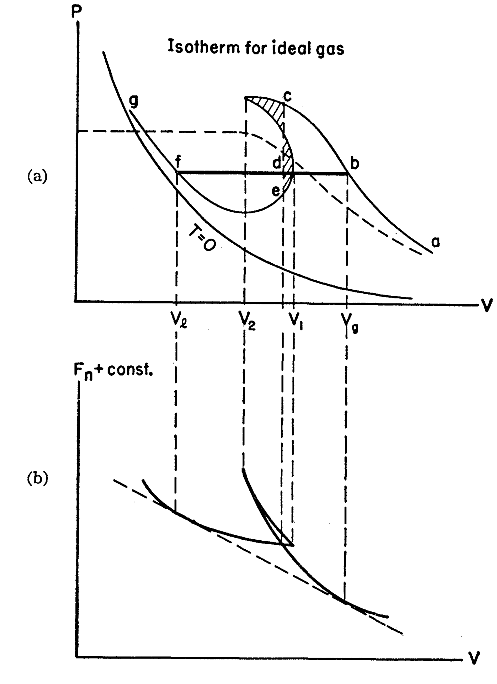

FIG. 2. (a) Isotherm for the imperfect Bose gas. Calculated with canonical ensemble: *a b c d e f g*. Calculated with grand canonical ensemble: *a b d f g*. (b) Free energy of the imperfect Bose gas. Minimization of free energy leads to the isotherm *a b c d e f g* of Fig. 2(a) (canonical ensemble), while the double tangent construction, equivalent to a Maxwell's construction on the isotherm, leads to the isotherm *a b d f g* of Fig. 2(a) (grand canonical ensemble).

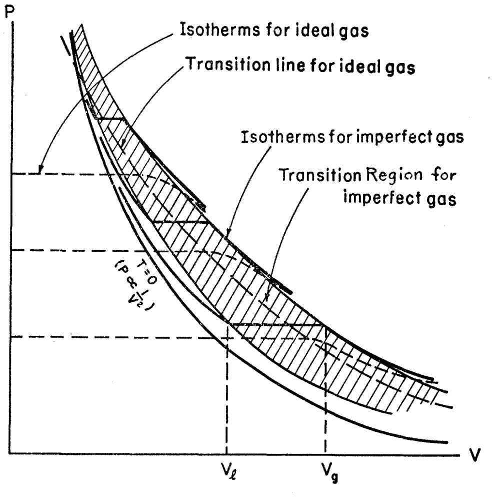

FIG. 3. Qualitative sketch of the isotherms of the imperfect Bose gas, calculated in the grand canonical ensemble.

Taking the point of view of the grand canonical ensemble, then, we arrive at the isotherms for the system qualitatively summarized in Fig. 3, which is self-explanatory. For large volumes, the isotherm closely approximates that for the ideal Bose gas. At a volume V_g, which is greater than the transition volume of the ideal Bose gas, the system breaks up into two phases. Then, at some smaller volume V_l, the system is in a single phase again, and the pressure goes up with decreasing volume, because the energy of the system, as shown by (28), increases rapidly at high density. The condensed phase in this case has a finite density equal to N/V_l, unlike the ideal Bose case where the condensed phase has infinite density. Note that at the transition point V_g, the isotherm is discontinuous in slope, in contradistinction to the case of the ideal Bose gas. This is a reflection of the fact that the spatial repulsion of the interaction enhances the momentum-space attraction.

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[9] L. van Hove, Physica 15, 951 (1949).

[10] It is this difference between the predictions of the canonical and grand canonical ensembles which suggested the speculation mentioned in I, that a better treatment of the quantum-mechanical hard-sphere many-body problem may be obtained by applying the methods in I only to smaller subsystems, while employing hydrodynamic methods for the treatment of long-ranged correlations.

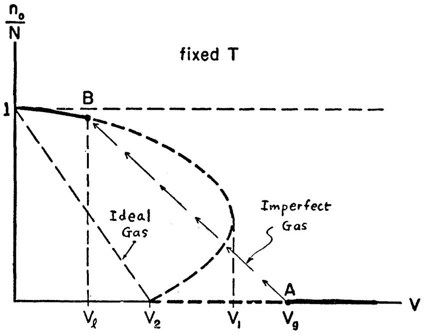

FIG. 4. Number of particles n_0 in the single-particle "ground" state, as a function of V at fixed T. For an ideal Bose gas, n_0/N is zero for $V>V_2$, and increases linearly to unity between $V=V_2$ and $V=0$. For the imperfect gas the system breaks up into two phases at $V=V_g$ (point A). For one phase, n_0/N remains zero, while for the other phase assumes the value at $V=V_l$ (point B).

The transition region, shown shaded in Fig. 3, does not terminate at a critical point.

The nature of the two phases for this imperfect gas can best be described in terms of n_0, the number of particles in the single-particle ground level. A plot of n_0 is shown in Fig. 4, making use of (36) and the behavior of z from Fig. 1. At very large volumes, $n_0=0$. This region corresponds to the "gas phase" of the system. When the volume is reduced to V_g, indicated by point A in Fig. 4, a part of the system goes into a different phase in which the ratio n_0/N (where N is the number of particles in this second phase) assumes some finite value less than unity, as indicated by point B in Fig. 4. When the volume is decreased further, the pressure remains constant. Only the relative amount of these two phases is changed, while the compositions of the phases remain at their respective states A and B. Finally, when $V=V_l$, there is only a single phase, and the entire system is at point B of Fig. 4. Upon further compression, the ratio n_0/N approaches unity. The transition process may be pictured by the series of schematic diagrams shown in Fig. 5. At the instant of its formation, the "liquid phase" possesses a finite ratio of n_0/N, so that the number of particles in the ground state increases discontinuously in going from the "gas" to the "liquid" phase. This again reflects the enhancement of the momentum-space attraction due to the repulsive interaction.

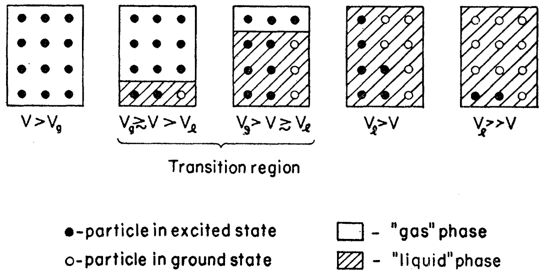

FIG. 5. Schematic pictures of the imperfect Bose gas when the volume is varied at constant temperature.

APPENDIX

In this appendix we shall derive (19). The second-order grand partition function will be written

$$\mathcal{Q}^{(2)}=\mathcal{Q}'+\mathcal{Q}'', \tag{A1}$$

where, from (18)

$$\mathcal{Q}'=\beta\sum_n e^{-\beta E_n}\left(\Psi_n, H' \sum_{\substack{m\\E_m\neq E_n}} \frac{H'_{mn}}{E_m-E_n}\Psi_m\right), \tag{A2}$$

$$\mathcal{Q}''=\tfrac{1}{2}\beta^2 \sum_{\substack{m,n\\E_m=E_n}} e^{-\beta E_n}|H'_{mn}|^2. \tag{A3}$$

To evaluate $\mathcal{Q}'$, let us first examine the matrix elements H'_{mn} in (A2). Let the initial and final states be characterized by their respective occupation numbers:

$$\begin{aligned}|n\rangle&=|n_0,n_1,n_2,\cdots\rangle,\\|m\rangle&=|m_0,m_1,m_2,\cdots\rangle.\end{aligned} \tag{A4}$$

Then, for a given initial state $|n\rangle$, H'_{mn} connects only three types of final states $|m\rangle$, all subject to conservation of total momentum, and all off the energy shell. It is best to list these types by displaying their occupation numbers that are *different* from those of $|n\rangle$:

Type 1,

$$\begin{aligned}&|n\rangle=|\cdots n_\gamma\cdots n_\lambda\cdots n_\alpha\cdots n_\beta\cdots\rangle,\\&|m\rangle=|\cdots n_\gamma-1\cdots n_\lambda-1\cdots n_\alpha+1\cdots n_\beta+1\cdots\rangle,\\&\gamma,\lambda,\alpha,\beta\text{ all unequal,}\\&\mathbf{K}_{\gamma\lambda}=\mathbf{K}_{\alpha\beta},\qquad \mathbf{K}_{\gamma\lambda}\equiv\mathbf{k}_\gamma+\mathbf{k}_\lambda,\\&\mathbf{k}_{\gamma\lambda}\neq\pm\mathbf{k}_{\alpha\beta},\quad \mathbf{k}_{\gamma\lambda}\equiv\tfrac{1}{2}(\mathbf{k}_\gamma-\mathbf{k}_\lambda),\\&H'_{mn}=(8\pi a\hbar^2/mV)[n_\gamma n_\lambda(n_\alpha+1)(n_\beta+1)]^{\frac{1}{2}}.\end{aligned} \tag{A5}$$

Type 2,

$$\begin{aligned}&|n\rangle=|\cdots n_\gamma\cdots n_\lambda\cdots n_\alpha\cdots\rangle,\\&|m\rangle=|\cdots n_\gamma-1\cdots n_\lambda-1\cdots n_\alpha+2\cdots\rangle,\\&\gamma,\lambda,\alpha\text{ all unequal,}\\&\mathbf{K}_{\gamma\lambda}=2\mathbf{k}_\alpha,\\&\mathbf{k}_{\gamma\lambda}\neq 0,\\&H'_{mn}=(8\pi a\hbar^2/mV)[n_\gamma n_\lambda(n_\alpha+1)(n_\alpha+2)]^{\frac{1}{2}}.\end{aligned} \tag{A6}$$

Type 3,

$$\begin{aligned}&|n\rangle=|\cdots n_\gamma\cdots n_\lambda\cdots n_\alpha\cdots\rangle,\\&|m\rangle=|\cdots n_\gamma+1\cdots n_\lambda+1\cdots n_\alpha-2\cdots\rangle\end{aligned} \tag{A7}$$

(reversed transition of type 2).

Restrictions same as type 2,

$$H'_{mn}=(8\pi a\hbar^2/mV)[(n_\gamma+1)(n_\lambda+1)(n_\alpha-1)n_\alpha]^{\frac{1}{2}}.$$

The sum over m in (A2), for given n, is then the sum over these three types (i.e., over the indexes $\alpha, \beta, \gamma, \lambda$), subject to conditions given for each type. Hence we have

$$\mathrm{X}_n \equiv \sum_{\substack{m\\ E_m\neq E_n}} \frac{H'_{mn}}{E_m-E_n}\Psi_m = \left(\frac{8\pi a\hbar^2}{mV}\right)\left\{\sum{}^{(1)}\frac{[n_\gamma n_\lambda(n_\alpha+1)(n_\beta+1)]^{\frac{1}{2}}}{(\hbar^2/m)(k_{\alpha\beta}{}^2-k_{\gamma\lambda}{}^2)}|n_\gamma-1,\,n_\lambda-1,\,n_\alpha+1,\,n_\beta+1\rangle \right.$$
$$-\sum{}^{(2)}\frac{[n_\gamma n_\lambda(n_\alpha+1)(n_\alpha+2)]^{\frac{1}{2}}}{(\hbar^2/m)k_{\gamma\lambda}{}^2}|n_\gamma-1,\,n_\lambda-1,\,n_\alpha+2\rangle$$
$$\left.+\sum{}^{(3)}\frac{[(n_\gamma+1)(n_\lambda+1)(n_\alpha-1)n_\alpha]^{\frac{1}{2}}}{(\hbar^2/m)k_{\gamma\lambda}{}^2}|n_\gamma+1,\,n_\lambda+1,\,n_\alpha-2\rangle\right\}, \quad \text{(A8)}$$

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where $\sum^{(1)}$ denotes a sum over states of type 1, etc.

Now the expression X_n is to be operated on by H'. This is best done by representing H' in the second quantized form given by (38) of I, and note that although the differential operator $(\partial/\partial r)r$ in H' may not be taken to the right across any summation, the creation and annihilation operators may. Performing then the required operations, we obtain, after some straightforward reduction:

$$(\Psi_n, H'\mathrm{X}_n) = \left(\frac{8\pi^2a^2\hbar^2}{mV^2}\right)\left\{8\sum{}^{(1)}\frac{n_\gamma n_\lambda(n_\alpha n_\beta+n_\alpha+n_\beta)}{k_{\alpha\beta}{}^2-k_{\gamma\lambda}{}^2}\right.$$
$$+2\sum_{\gamma\neq\lambda} n_\gamma n_\lambda \frac{\partial}{\partial r}[rG(k_{\gamma\lambda},\mathbf{r})]_{\mathbf{r}=0} - \sum_{\gamma\neq\lambda}\frac{n_\gamma n_\lambda(n_\alpha+1)(n_\alpha+2)}{k_{\gamma\lambda}{}^2}$$
$$+4\sum{}^{(3)}\frac{n_\alpha(n_\alpha-1)(n_\gamma n_\lambda+n_\gamma+n_\lambda)}{k_{\gamma\lambda}{}^2}$$
$$\left.+\sum_\alpha n_\alpha(n_\alpha-1)\frac{\partial}{\partial r}[rF(\mathbf{r})]_{\mathbf{r}=0}\right\}, \quad \text{(A9)}$$

where $F(\mathbf{r})=\sum_{\mathbf{k}\neq0}(e^{i\mathbf{k}\cdot\mathbf{r}}/k^2)$ and has been calculated in (53) of I, and

$$G(k_0,\mathbf{r}) \equiv \sum_{\mathbf{k}\neq0,\,k\neq k_0}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2-k_0{}^2}, \quad (k_0\neq0), \quad \text{(A10)}$$

where all $\mathbf{k}$ vectors are single-particle momenta defined in a box of volume $V=L^3$ with periodic boundary conditions. We note that the quantity $G(k_0,\mathbf{r})-F(\mathbf{r})$ is not singular at $\mathbf{r}=0$. It is thus convenient to consider

$$G(k_0,\mathbf{r})-F(\mathbf{r})$$
$$=k_0{}^2\sum_{\mathbf{k}\neq0,\,k\neq k_0}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2(k^2-k_0{}^2)}-\frac{1}{k_0{}^2}\sum_{k=k_0}e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \text{(A11)}$$

from which we conclude

$$\frac{\partial}{\partial r}[rG(k_0,\mathbf{r})]_{\mathbf{r}=0}=\frac{\partial}{\partial r}[rF(\mathbf{r})]_{\mathbf{r}=0}$$
$$+k_0{}^2\sum_{\mathbf{k}\neq0,\,k\neq k_0}\frac{1}{k^2(k^2-k_0{}^2)}-\frac{1}{k_0{}^2}\sum_{k=k_0}1, \quad \text{(A12)}$$

where we already know, from (53) of I, that

$$\frac{\partial}{\partial r}[rF(\mathbf{r})]_{\mathbf{r}=0}=-\frac{V}{4\pi}\left(\frac{2\cdot37}{L}\right). \quad \text{(A13)}$$

Substituting these into (A9), we see that all terms in (A9) other than the first sum (the one involving the summation $\sum^{(1)}$) may be neglected, since they are all smaller than the first sum by at least one power of the volume V. Furthermore, in the first sum itself, the terms involving four occupation numbers sum to zero. Substituting (A9), thus calculated, into (A2), we obtain in the limit $V\to\infty$,

$$\frac{\mathcal{Q}'}{\mathcal{Q}^{(0)}}=\frac{64\pi a^2\lambda^2}{V^2}\sum{}^{(1)}\frac{\langle n_\alpha\rangle\langle n_\gamma\rangle\langle n_\lambda\rangle}{k_{\alpha\beta}{}^2-k_{\gamma\lambda}{}^2}, \quad \text{(A14)}$$

where $\langle n_\alpha\rangle$ has been defined in (16). The states $|m\rangle$ of type (1) are characterized by the momenta of the single particles levels α, β, γ, and λ: $\mathbf{k}_\alpha, \mathbf{k}_\beta, \mathbf{k}_\gamma, \mathbf{k}_\lambda$. Interchanges of $\mathbf{k}_\alpha$ and $\mathbf{k}_\beta$, or $\mathbf{k}_\gamma$ and $\mathbf{k}_\lambda$ produce the same state. We shall explicitly display (A14) as a sum over the independent momenta $\mathbf{k}_\alpha, \mathbf{k}_\beta, \mathbf{k}_\gamma, \mathbf{k}_\lambda$ as follows:

$$\frac{\mathcal{Q}'}{\mathcal{Q}^{(0)}}=\frac{16\pi a^2\lambda^2}{V^2}\sum{}'\frac{\langle n_\alpha\rangle\langle n_\gamma\rangle\langle n_\lambda\rangle}{\frac{1}{2}(k_\alpha{}^2+k_\beta{}^2-k_\gamma{}^2-k_\lambda{}^2)}$$
$$\times\delta(\mathbf{k}_\alpha+\mathbf{k}_\beta-\mathbf{k}_\gamma-\mathbf{k}_\lambda), \quad \text{(A15)}$$

where the $\sum'$ is taken over all $\mathbf{k}_\alpha$, $\mathbf{k}_\beta$, $\mathbf{k}_\gamma$, and $\mathbf{k}_\lambda$ with the restrictions that $\mathbf{k}_\alpha\neq\mathbf{k}_\beta$, $\mathbf{k}_\gamma\neq\mathbf{k}_\lambda$, and that terms with a vanishing denominator $k_\alpha{}^2+k_\beta{}^2-k_\gamma{}^2-k_\lambda{}^2$ are omitted.

To calculate (A15) explicitly, we convert the sum $\sum'$ into an integral. To take into account the restriction $k_\alpha{}^2+k_\beta{}^2-k_\gamma{}^2-k_\beta{}^2\neq0$, the singularity in the denominator in (A14) is avoided by taking the Cauchy principal value of the integral. We then have

$$\frac{\mathcal{Q}'}{\mathcal{Q}^{(0)}}=\frac{16\pi a^2\lambda^2}{V^2}\left(\frac{4V^3}{\pi^3\lambda^5}\right)\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}$$
$$\times\frac{z^{j+k+l}}{(j+k+l)^{\frac{1}{2}}(j-k)l}\frac{\partial}{\partial u}J(u,v,w), \quad \text{(A16)}$$

where

$$J(u,v,w)=P\int_0^\infty dp\int_0^\infty dq\frac{\cosh(uqp)}{q^2-p^2}\times\exp(-vq^2-wp^2), \tag{A17}$$

$$u=\frac{\hbar^2\beta}{2m}\left(\frac{2(j-k)l}{j+k+l}\right),$$

$$v=\frac{\hbar^2\beta}{2m}\left(\frac{(j+k)l}{j+k+l}\right), \tag{A18}$$

$$w=\frac{\hbar^2\beta}{2m}\left(\frac{(j+k)l+4jk}{j+k+l}\right).$$

Calculation yields

$$\frac{\partial J}{\partial u}=\frac{\pi}{4}\frac{u(w-v)}{[(w+v)^2-u^2][4wv-u^2]^{\frac{1}{2}}}$$

$$=\frac{\pi^2}{8\lambda^2}\frac{(j+k+l)^{\frac{1}{2}}(j-k)l}{(j+l)(k+l)(jkl)^{\frac{1}{2}}}. \tag{A19}$$

Substituting this into (A16), and (A16) into (A14), we finally obtain

$$\frac{\mathcal{Q}'}{\mathcal{Q}^{(0)}}=\frac{8a^2V}{\lambda^5}\sum_{j=1}^\infty\sum_{k=1}^\infty\sum_{l=1}^\infty\frac{z^{j+k+l}}{(j+l)(k+l)(jkl)^{\frac{1}{2}}}. \tag{A20}$$

The calculation of $\mathcal{Q}''$ is easier. It can be readily proved that in (A3) we need only retain the terms for which $m=n$. The other terms do not contribute to $b_l^{(2)}$ in the limit $V\rightarrow\infty$. One therefore obtains, after some algebra,

$$\frac{\mathcal{Q}''}{\mathcal{Q}^{(0)}}=\frac{a^2\lambda^4}{2V^2}\langle(2\sum_{\alpha\neq\beta}n_\alpha n_\beta+\sum_\alpha n_\alpha{}^2-\sum_\alpha n_\alpha)^2\rangle.$$

But we have, from (15),

$$\frac{\mathcal{Q}^{(1)}}{\mathcal{Q}^{(0)}}=-\frac{a\lambda^2}{V}[2\sum_{\alpha\neq\beta}\langle n_\alpha\rangle\langle n_\beta\rangle+\sum_\alpha\langle n_\alpha{}^2\rangle-\sum_\alpha\langle n_\alpha\rangle].$$

We obtain, therefore, as $V\rightarrow\infty$,

$$\frac{\mathcal{Q}''}{\mathcal{Q}^{(0)}}-\frac{1}{2}\left(\frac{\mathcal{Q}^{(1)}}{\mathcal{Q}^{(0)}}\right)^2=\frac{8a^2\lambda^4}{V^2}(\sum_\alpha\langle n_\alpha\rangle)^2\sum_\beta(\langle n_\beta{}^2\rangle-\langle n_\beta\rangle^2)$$

$$=\frac{8a^2V}{\lambda^5}[\sum_1^\infty l^{-\frac{3}{2}}z^l]^2[\sum_1^\infty l^{-\frac{1}{2}}z^l]. \tag{A21}$$

Adding (A20) and (A21), and using (13b), one obtains (19).

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