Application of Faddeev Techniques to the Quantum Theory of the Third Virial Coefficient

A. S. REINER
Weizmann Institute of Science, Rehovoth, Israel
(Received 27 June 1966)

Cluster coefficients for a quantum gas can be related by means of a Laplace transform to the resolvent of an interacting system. Techniques developed by Faddeev are applied in order to express resolvents in terms of quantities which satisfy coupled integral equations. The resulting theory for the cluster coefficients is free of convergence difficulties encountered in series expansions of those coefficients in terms of a binary-collision kernel or two-body scattering matrix. Present computational difficulties necessitate an approximate solution of the Faddeev equations. The assumption of a separable two-body scattering matrix makes possible such a solution and a subsequent calculation of cluster coefficients.

I. INTRODUCTION

THE equation of state of an imperfect gas of low density ρ,

$$p\beta=\sum_{n=1}^{\infty}B_n(\beta)\rho^n,\quad B_1\equiv 1. \tag{1.1}$$

expresses the pressure p in terms of virial coefficients B_n, which are functions only of the temperature T [$\beta=(kT)^{-1}$]. Those coefficients derive their importance from being a measure of correlations, both dynamical and statistical, of no more than n particles. Their calculation consequently requires the solution of the n-body problem.

An expression for the second virial coefficient valid for all temperatures was given by Beth and Uhlenbeck[1] more than 30 years ago. But even a formulation of the quantum theory of the nth virial coefficients for $n\geqslant 3$ had to wait for many years, in contrast to its classical counterpart.

Lee and Yang, in dealing with imperfect gases, made, among others, the following crucial observations[2]:

(1) It is possible to isolate the effects of statistics from dynamics in a unique way. If, in other words, one has found a technique for treating the problem in Boltzmann statistics, no difficulties in principle are encountered in Bose-Einstein (BE) or Fermi-Dirac (FD) statistics.

(2) So-called cluster operators, describing the correlation between precisely n particles and not fewer, can be expanded in a binary-collision operator provided only pair interactions are present in the n-body Hamiltonian H_n. The binary-collision operator serves then as a tool to calculate cluster and virial coefficients.

Pais and Uhlenbeck[3] and later Larsen[4] subsequently applied the Lee-Yang theory to a calculation of the third virial coefficient. Even for temperatures as low as 1°K, convergence is annoyingly slow. The presence of two- and/or three-body bound states is likely even to invalidate entirely the series expansion in the binary-collision kernel.

It has been noted in the meantime[5,6] that the Laplace-transform relation between the statistical operator $\exp(-\beta H_n)$ on the one hand and the resolvent $(Z-H_n)^{-1}$ on the other enables a concise formulation of the Lee-Yang theory. The binary-collision operator corresponds to the two-body scattering operator continued off the energy shell, and the Lee-Yang series has its parallel in Watson's[7] multiple-scattering expansion of the resolvent. Statistics there may be handled with the help of a diagrammatical representation of the partition function $\mathrm{Tr}\exp(-\beta H)$ as given by Bloch and de Dominicis.[8] The result of all manipulations is a theory which runs parallel to the binary-collision expansion of Lee and Yang. Though far easier to handle, it leaves all inherent convergence difficulties unsolved.

Recent years have witnessed striking developments in many-particle scattering theory. A formalism first proposed by Faddeev[9] has been further developed and generalized by Weinberg,[10] Lovelace,[11] and Rosenberg[12] and may be said to replace the multiple-scattering expansion of a resolvent with a set of coupled integral equations. It is of interest to remark that one incentive has been the wish to formulate integral equations with Schmidt-Hilbert kernels which allow Fredholm-type solutions. Formulated in diagrammatical language, one aims at the removal of unlinked parts from the resolvent or equivalently from the scattering matrix. It has been observed by Weinberg[10] that a formally similar procedure is required to obtain cluster coefficients from the partition function.[13]

The following is an account of a closed theory of the third virial coefficient based on Faddeev-type tech-

[1] E. Beth and G. H. Uhlenbeck, Physica **3**, 729 (1936); **4**, 915 (1937).
[2] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959).
[3] A. Pais and G. H. Uhlenbeck, Phys. Rev. **116**, 250 (1959).
[4] S. Y. Larsen, Phys. Rev. **130**, 1426 (1963).
[5] A. J. F. Siegert and E. Teramoto, Phys. Rev. **110**, 1232 (1958).
[6] A. S. Reiner, Physica **26**, 700 (1960).
[7] K. M. Watson, Phys. Rev. **89**, 575 (1953).
[8] C. Bloch and C. de Dominicis, Nucl. Phys. **7**, 459 (1958); **10**, 181 (1959).
[9] L. D. Faddeev, Zh. Eksperim. i Teor. Fiz. **39**, 1459 (1960) [English transl.: Soviet Phys.—JETP **12**, 1014 (1961)].
[10] S. Weinberg, Phys. Rev. **133**, B232 (1964).
[11] C. Lovelace, Phys. Rev. **135**, B1225 (1964).
[12] L. Rosenberg, Phys. Rev. **140**, B217 (1965).
[13] The idea of applying Faddeev techniques to statistical physics has already occurred to Faddeev (Ref. 9) and has also been suggested by J. M. Blatt (private communication).

niques with application to a boson gas. We recapitulate in Sec. II the elements of the Lee-Yang theory bearing on the statistical aspect. It is then shown in Sec. III how one may obtain the third cluster coefficient (the only nonelementary coefficient present in B_3) by means of quantities which satisfy coupled integral equations. The technique is by far superior to series expansions, since no convergence difficulties are ever encountered, nor do bound states pose problems.

Present-day computers still lack the capacity to solve coupled integral equations in three variables, as the exact Faddeev equations happen to be. One has therefore from a practical point of view to resort to an approximation. All approximations of this kind have to our knowledge assumed a factorizable two-body off-energy-shell t matrix which forms the basic elements of the kernel of the integral equations. Those approximations turn the Faddeev equations into a set with a simpler kernel. Elsewhere[14] we have discussed separable t matrices which provide an accurate approximation in the neighborhood of all bound states and resonances of the two-particle subsystems. Approximately correct behavior over as wide an energy range as possible is necessary, since the quantity of interest is not the resolvent but the partition function. The operation that links the two is a weighted energy integration. Unless, therefore, the intermolecular potential is assumed to be separable (leading to a separable t matrix for all energies), such an approximation will yield trustworthy results only for low temperatures. Those may, however, be far higher than the temperature below which expansion methods converge.

Section IV contains the version of the theory of the third cluster coefficient in the approximation of a separable t matrix. Although we have a particular expression in mind for actual calculations, the formulation can be applied for any other choice. The approximation in a way answers the question posed by Pais and Uhlenbeck[3]: whether higher virial coefficients are expressible in terms of scattering data, as is the case with B_2. The input data are, among others, energies of bound states and resonances as well as form factors at those singularities.

In the last section, we compare the Faddeev approach with the Pais-Uhlenbeck calculations.

II. CLUSTER COEFFCIENTS FOR A QUANTUM GAS

We recall the two Mayer equations[15]

$$\begin{aligned} p\beta &= \lim_{V\to\infty} \sum_{n=1} b_n(V,\beta) z^n, \\ \rho &= \lim_{V\to\infty} \sum_{n=1} n b_n(V,\beta) z^n, \end{aligned} \tag{2.1}$$

from which the virial series (1.1) results after elimination of the fugacity z. The coefficients $b_n(V,\beta)$ tend to the so-called cluster coefficients $b_n(\beta)$ which are independent of the volume V if $V\to\infty$. By comparison one finds, for instance,

$$B_2=-(b_2/b_1^2);\quad B_3=-b_1^{-4}(4b_2^2-2b_2b_3);\quad \text{etc.} \tag{2.2}$$

A theory of the measurable virial coefficients B_n therefore addresses itself to the cluster coefficients b_m $(1\leqslant m\leqslant n)$ in which all m-body correlations reside.

Cluster coefficients are related to dynamics, i.e., to the n-body Hamiltonian H_n, through the density operator

$$W_n=\exp(-\beta H_n). \tag{2.3}$$

By recursion one defines cluster operators U_n which carry particle labels $1, 2, \cdots$:

$$U_1(1)=W_1(1), \tag{2.4a}$$

$$U_2(12)=W_2(12)-W_1(1)W_1(2), \tag{2.4b}$$

$$\begin{aligned} U_3(123)=W_3(123)&-[W_2(12)W_1(3) \\ &+\text{cyclic permutations of the arguments}], \\ &+2W_1(1)W_1(2)W_1(3), \text{ etc.} \end{aligned} \tag{2.4c}$$

It can be shown[15] that the following relations hold between b_n and U_n:

$$b_n(\beta)=\lim_{V\to\infty} \frac{1}{n!V} \mathrm{Tr} U_n. \tag{2.5}$$

It is through the symmetry of the states used in the trace calculation that the specific statistics enter. Lee and Yang[2] have shown that it us useful (although devoid of any realistic meaning) to calculate the matrix elements of the cluster operator U_n in Boltzman statistics. These elements for BE or FD statistics may then be expressed in terms of matrix elements of U_m, $m\leqslant n$, for Boltzman statistics.

Their reasoning goes as follows. Consider an element

$$\begin{aligned} &\langle 1'\cdots N'|W_N|1\cdots N\rangle \\ &\quad=\sum_i \psi_i(1'\cdots N')\psi_i^*(1\cdots N)\exp(-\beta\epsilon_i^{(N)}), \end{aligned} \tag{2.6}$$

where ψ_i denotes an eigenstate of H_N belonging to the eigenvalue $\epsilon_i^{(N)}$, and where $1\cdots N$ represent a set of, say, single-particle momenta. For the corresponding matrix element in BE statistics one has

$$\begin{aligned} &\langle 1'\cdots N'|W_N{}^{\mathrm{BE}}|1\cdots N\rangle \\ &\quad=N!\sum_{i,\mathrm{symm}} \psi_i(1'\cdots N')\psi_i^*(1\cdots N) \\ &\qquad\qquad\times\exp(-\beta\epsilon_i^{(N)}) \\ &\quad=\sum_{i,P} \psi_i\{P(1'\cdots N')\}\psi_i^*(1\cdots N) \\ &\qquad\qquad\times\exp(-\beta\epsilon_i^{(N)}). \end{aligned} \tag{2.7}$$

[14] A. S. Reiner, Nuovo Cimento (to be published). See also H. P. Noyes, Phys. Rev. Letters **15**, 538 (1965).

[15] See, for instance, K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963).

The first sum is over symmetric states only; the second runs over all permutations of $1\cdots N$.

Defining

$$\langle 1'\cdots N'|U_N{}^S|1\cdots N\rangle\equiv\sum_P\langle P(1'\cdots N')|U_N|1\cdots N\rangle, \tag{2.8}$$

one establishes the following relations for matrix elements of the first three cluster operators:

$$\langle 1'|U_1{}^{BE}|1\rangle=\langle 1'|U_1|1\rangle, \tag{2.9a}$$

$$\langle 1'2'|U_2{}^{BE}|12\rangle=\langle 1'2'|U_2{}^S|12\rangle+\langle 2'|U_1|1\rangle\langle 1'|U_1|2\rangle, \tag{2.9b}$$

$$\begin{aligned}\langle 1'2'3'|U_3{}^{BE}|123\rangle=&\langle 1'2'3'|U_3{}^S|123\rangle\\&+\langle 1'3'|U_2{}^S|12\rangle\langle 2'|U_1|3\rangle\\&+\langle 2'3'|U_2{}^S|12\rangle\langle 1'|U_1|3\rangle\\&+\langle 2'3'|U_2{}^S|13\rangle\langle 1|U_1|2\rangle\\&+\langle 1'2'|U_2{}^S|13\rangle\langle 3'|U_1|2\rangle\\&+\langle 1'3'|U_2{}^S|23\rangle\langle 2'|U_1|1\rangle\\&+\langle 1'2'|U_2{}^S|23\rangle\langle 3'|U_1|1\rangle\\&+\langle 2'|U_1|1\rangle\langle 3'|U_1|2\rangle\langle 1'|U_1|3\rangle\\&+\langle 3'|U_1|1\rangle\langle 1'|U_1|2\rangle\langle 2'|U_1|3\rangle.\end{aligned} \tag{2.9c}$$

Equations (2.5), (2.8), and (2.9) then define the cluster coefficients for a boson gas in terms of matrix elements of cluster operators in Boltzmann statistics.

At this point we mention the relation[7] between the statistical operators W_n, (2.3), and the resolvents $G_n=(z-H_n)^{-1}$;

$$W_n(\beta)=\frac{1}{2\pi i}\oint_C e^{-\beta z}G_n(z)dz. \tag{2.10}$$

The integration path C is counterclockwise along a deformed contour of the inverse Laplace transform and passes from $\infty+i\epsilon$ in a loop around the left-most singularity of the integrand to $\infty-i\epsilon$.

The difference between perturbed and unperturbed resolvents may be related in a standard fashion to the scattering operator T_n:

$$G_n(z)=G_n{}^0(z)[1+T_n(z)G_n{}^0(z)]. \tag{2.11}$$

T_n satisfies a Lippmann-Schwinger equation

$$T_n=V+VG_n{}^0T_n=V+VG_nV, \tag{2.12}$$

with $V=\sum_\alpha v_\alpha$, where α denotes a pair index.

We consider in particular $T_2=\hat{t}$ and use a partial-wave expansion in the relative momenta:

$$\begin{aligned}&\langle\mathbf{k}_1\mathbf{k}_2|\hat{t}(z)|\mathbf{k}_1'\mathbf{k}_2'\rangle\\&=\delta(\mathbf{K}-\mathbf{K}')(1/2\pi^2)\textstyle\sum_l(2l+1)\hat{t}_l(kk',z-\frac{1}{4}K^2)\\&\qquad\times P_l(\hat{k}\cdot\hat{k}'),\end{aligned} \tag{2.13}$$

where $2\mathbf{k}=\mathbf{k}_1-\mathbf{k}_2$, $\mathbf{K}=\mathbf{k}_1+\mathbf{k}_2$. Units $\hbar=m=1$ are used throughout.

Defining $v_l(kk')$ in a similar way we observe from the second identity (2.12) the following spectral decomposition of $\hat{t}_l$ (see, for instance, Ref. 14):

$$\begin{aligned}\hat{t}_l(kk',z)=&v_l(kk')+\sum_n\frac{g_{nl}(k)g_{nl}(k')}{z+\epsilon_{nl}{}^{(2)}}\\&+\frac{2}{\pi}\int_0^\infty\frac{\hat{t}_l(kq,q^2+i\epsilon)\hat{t}_l{}^*(k'q,q^2+i\epsilon)}{z-q^2}q^2\,dq.\end{aligned} \tag{2.14}$$

$g_{nl}(k)$ above is the bound-state form factor

$$g_{nl}(k)=-(k^2+\epsilon_{nl})\int_0^\infty j_l(kr)\psi_{nl}(r)r^2dr, \tag{2.15}$$

$j_l(kr)$ and ψ_{ln} being the unperturbed and perturbed radial wave functions. After noticing that (2.14) displays the analytic behavior of t_l in z, we turn to a calculation of the first cluster coefficients.

III. THE FIRST THREE CLUSTER COEFFICIENTS FOR A BOSON GAS

All matrix elements of $U_n{}^{\mathrm{BE}}$, Eq. (2.9), contain parts exclusively made up of operators U_1. Since U_1 does not contain the interaction, their contribution gives the cluster coefficients of an ideal boson gas. These read, in terms of the thermal de Broglie wavelength $\lambda=(2\pi\beta)^{1/2}$,

$$\begin{aligned}b_{n,0}&=\lambda^{-3}n^{-5/2},\\b_1&\equiv b_{1,0}{}^{\mathrm{BE}}.\end{aligned} \tag{3.1}$$

The second cluster coefficient depends only on two-particle dynamics. The well-known exact Beth-Uhlenbeck result[1]

$$b_2=b_{2,0}+2^{3/2}\lambda^{-3}\sum_{l,\mathrm{even}}(2l+1)\left\{\sum_n e^{\beta\epsilon_{nl}{}^{(2)}}+\frac{1}{\pi}\int_0^\infty\frac{d\delta_l(k)}{dk}e^{-\beta k^2}dk\right\}, \tag{3.2}$$

expresses b_2 in terms of $\epsilon_{nl}{}^{(2)}$, the binding energy of the nth bound state of the relative motion of a pair, and $\delta_l(k)$, the scattering phase shift—both of the partial wave l.

We now turn to the third cluster coefficient b_3, which by Eqs. (2.5) and (2.9c) invites the following decomposition[3]:

$$b_3=b_{3,0}+b_{3,1}+b_{3,2}, \tag{3.3}$$

with $b_{3,0}$ given by (3.1).

$b_{3,1}$ in (3.3) comprises all 3-particle correlations due to a single pair interaction with a third particle being only statistically correlated to the pair. One may

readily verify that

$$b_{3,1}=\tfrac{1}{2}\lim_{V\to\infty} V^{-1}\int\int\int d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3\langle \mathbf{k}_2|\,U_1|\,\mathbf{k}_3\rangle \times\{\langle \mathbf{k}_1\mathbf{k}_3|\,U_2{}^S|\,\mathbf{k}_1\mathbf{k}_2\rangle+\langle \mathbf{k}_3\mathbf{k}_1|\,U_2{}^S|\,\mathbf{k}_1\mathbf{k}_2\rangle\}. \quad (3.4)$$

The cluster operators U_2 appearing in (3.4) can now be reduced by means of Eqs. (2.3), (2.4), (2.11), and (2.13) to partial-wave $\hat{t}$ matrices. Performing all but one k integrations, one is left with

$$b_{3,1}=2^4\lambda^{-3}3^{-3/2}\pi^{-1}\sum_{l,\text{even}}(2l+1)\int_0^\infty k^2dke^{-(1/3)\beta k^2}\frac{1}{2\pi i}\times\oint_C e^{-\beta z}\frac{\hat{t}_l(kk,z)}{(z-k^2)^2}dz. \quad (3.5)$$

Equation (3.5) is a first example where one intermediate bound state may occur. The part of the contour to the left of the branch point $z=0$ of both $\hat{t}_l$ and the denominator may be considered separately, and leads by way of Eq. (2.14) to

$$b_{3,1}{}^{\mathrm{BS}}{}_2=2^4\lambda^{-3}3^{-3/2}\pi^{-1}\sum_{l,\text{even}}(2l+1)e^{+\beta\epsilon_{nl}(2)}\times\int_0^\infty dk\,k^2e^{-(1/3)\beta k^2}\left[\int_0^\infty j_l(kr)\psi_{ln}(r)r^2dr\right]^2. \quad (3.6)$$

The continuum part of $b_{3,1}$ can be rewritten in a non-singular form which is convenient for an actual calculation[16]:

$$b_{3,1}{}^c=2^4\lambda^{-3}3^{-3/2}\pi^{-1}\sum_{l,\text{even}}(2l+1)\times\left[\int_0^\infty e^{-(4/3)\beta k^2}k^2dk\left\{\begin{matrix}\beta\\ -e^{i\delta_l(k)}\sin\delta_l(k)\\ k\end{matrix}\right.\right.$$
$$\left.\left.+\frac{1}{\pi}\int_\beta^\infty d\beta'\int_0^\infty\frac{\mathrm{Im}[\hat{t}_l(kk,\,k^2+i\epsilon)-\hat{t}_l(kk,\,x+i\epsilon)]}{x-k^2}\times e^{-\beta' x}dx\right\}\right], \quad (3.7)$$

where we have used

$$\hat{t}_l(kk,\,k^2+i\epsilon)=-k^{-1}e^{i\delta_l(k)}\sin\delta_l(k). \quad (3.8)$$

The most interesting part of b_3, Eq. (3.3), is $b_{3,2}$ in which dynamical three-particle correlations are contained. Again one finds from Eqs. (2.5), (2.9c), (2.4c), (2.3), (2.10), and (2.11)

$$b_{3,2}=\lim_{V\to\infty}\frac{1}{6V}\int\int\int d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3\frac{1}{2\pi i}\times\int_C e^{-\beta z}\sum_P\langle P(\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3)|\,G_3{}^c|\,\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\rangle. \quad (3.9)$$

Here we have introduced[10]

$$G_3{}^c=G_3-\textstyle\sum_\alpha G_{3,\alpha}+2G_3{}^0, \quad (3.10)$$

the connected part of the three-particle resolvent, in terms of G_3, $G_3{}^0$, and

$$G_{3,\alpha}=(z-H_3{}^0-v_\alpha)^{-1}. \quad (3.11)$$

The latter is the resolvent of a three-particle system interacting only through a single pair interaction v_α.

It is just the connected operator $G_3{}^c$ which has extensively been studied by Faddeev,[9] Weinberg,[10] Lovelace,[11] and Rosenberg.[12] Defining a particular 3-body scattering operator t_α by

$$G_{3,\alpha}=G_3{}^0[1+t_\alpha G_3{}^0], \quad (3.12)$$

one finds for $G_3{}^c$ [Eq. (3.10) by means of (2.11)]

$$G_3{}^c=G_3{}^0(T_3-\textstyle\sum_\alpha t_\alpha)G_3{}^0. \quad (3.13)$$

With Faddeev we write

$$T_3=\textstyle\sum_\alpha T_\alpha, \quad (3.14)$$

with each component T_α satisfying

$$T_\alpha=v_\alpha+v_\alpha G_3{}^0T_3=t_\alpha+t_\alpha G_3{}^0\sum_{\beta\neq\alpha}T_\beta. \quad (3.15)$$

Then $b_{3,2}$ can, by means of (3.13) and (3.15), be cast in a form containing only t_α and the solutions of the Faddeev equations (3.15), viz.,

$$b_{3,2}=\lim_{V\to\infty}\frac{1}{6V}\int\int\int d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{k}_3\frac{1}{2\pi i}\oint_C dz\,e^{-\beta z}\times\frac{\sum_P\langle P(\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3)|\,\sum_\alpha t_\alpha G_3{}^0\sum_{\beta\neq\alpha}T_\beta|\,\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\rangle}{(z-\frac{1}{2}k_1{}^2-\frac{1}{2}k_2{}^2-\frac{1}{2}k_3{}^2)^2}. \quad (3.16)$$

Regarding the kinematics we shall, here and in the ensuing developments, keep as close as possible to the notation of Lovelace.[11] Define a center-of-mass momentum

$$\mathbf{P}=\frac{1}{\sqrt{6}}(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3), \quad (3.17)$$

and, further, three pairs of additional momenta, which are, for each pair ij, its relative momentum

$$p_{ij}=\tfrac{1}{2}(\mathbf{k}_i-\mathbf{k}_j), \quad (3.18)$$

[16] Expressions similar to (3.6) and (3.7) result in a treatment of the second cluster coefficient along these lines. Whereas the bound-state part is readily reproduced, no *direct* evaluation of the continuum part of (3.2) has succeeded (Ref. 6). At any rate, $b_{3,1}$ can in principle be exactly calculated for any temperature.

and $\mathbf{q}_{ij}$, the momentum of the remaining particle with respect to the center of mass of the pair:

$$\mathbf{q}_{ij}=(1/2\sqrt{3})(\mathbf{k}_i+\mathbf{k}_j-2\mathbf{k}_l). \tag{3.19}$$

The index ij will again be replaced by α, and the set $\mathbf{P}$, $\mathbf{p}_\alpha$, $\mathbf{q}_\alpha$ can be used interchangeably for any α. For instance, if $\alpha=1$ and $\beta=2$,

$$\begin{aligned}\mathbf{p}_\beta&=-\tfrac{1}{2}\mathbf{p}_\alpha+\tfrac{1}{2}\sqrt{3}\mathbf{q}_\alpha,\\ \mathbf{q}_\beta&=-\tfrac{1}{2}\sqrt{3}\mathbf{p}_\alpha-\tfrac{1}{2}\mathbf{q}_\alpha.\end{aligned} \tag{3.20a}$$

In fact, any two momenta out of the set $\mathbf{p}_\alpha,\mathbf{q}_\alpha(\alpha=1,2,3)$ can be chosen to be independent, and we have for the case chosen above

$$\begin{aligned}\mathbf{p}_\alpha&=-(1/\sqrt{3})\mathbf{q}_\alpha-(2/\sqrt{3})\mathbf{q}_\beta,\\ \mathbf{p}_\beta&=(2/\sqrt{3})\mathbf{q}_\alpha-(1/\sqrt{3})\mathbf{q}_\beta.\end{aligned} \tag{3.20b}$$

It is sometimes convenient to use dependent momenta instead of lengthy expressions like (3.20a) and (3.20b). We shall adhere to Lovelace's convention: Sets of more than two momenta carrying the same number of primes are linearly dependent. The kinetic energy H_3^0, for example, can be expressed as

$$H_3^0=\mathbf{P}^2+\mathbf{p}_\alpha^2+\mathbf{q}_\alpha^2=\mathbf{P}^2+\mathbf{p}_\beta^2+\mathbf{q}_\beta^2. \tag{3.21}$$

We now return to the specific matrix elements appearing in (3.16). It is permissible to redefine for each element of the sum α the most convenient set $\mathbf{P},\mathbf{p},\mathbf{q}$. It is then readily seen that the six states $P(\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3)$ may, for fixed $\mathbf{P}$, be specified by the sets $\pm\mathbf{p}_\alpha\mathbf{q}_\alpha$, $\pm\mathbf{p}_\beta\mathbf{q}_\beta$, $\pm\mathbf{p}_\gamma\mathbf{q}_\gamma$. Integrating out the center-of-mass momentum one finds for (3.16)

$$b_{3,2}=2^2\lambda^{-3}\int d\mathbf{p}_\alpha d\mathbf{q}_\alpha\frac{1}{2\pi i}\oint_C\frac{e^{-\beta z}}{(z-p_\alpha^2-q_\alpha^2)^2}\times\langle\Xi|t_\alpha G_3^0\sum_{\beta\neq\alpha}T_\beta|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle. \tag{3.22}$$

We denote by $|\Xi\rangle$ the state vector

$$|\Xi\rangle=\sum_\gamma\{|\mathbf{p}_\gamma\mathbf{q}_\gamma\rangle+|-\mathbf{p}_\gamma\mathbf{q}_\gamma\rangle\} \tag{3.23}$$

again with $\mathbf{p}_\gamma$, $\mathbf{q}_\gamma$ combinations of $\mathbf{p}$, $\mathbf{q}_\alpha$.

As above with $b_{3,1}$, we first discuss the contribution of bound states. Three-body bound states will appear whenever the determinant of the matrix resolvent of the Faddeev equations vanishes, i.e., when

$$\Delta(z)\equiv\begin{vmatrix}1 & -t_{23}G_3^0 & -t_{23}G_3^0\\ -t_{31}G_3^0 & 1 & -t_{31}G_3^0\\ -t_{23}G_3^0 & -t_{23}G_3^0 & 1\end{vmatrix}=0. \tag{3.24}$$

Any method which leads to a solution of the Faddeev equations (3.15) will also make possible a solution of the eigenvalue equation (3.24). Having thus in principle determined the spectrum $-\epsilon_\nu^{(3)}$, we may assess their contribution to $b_{3,2}$. Again we consider the part of the contour C which consists of small circles around $z=-\epsilon_\nu^{(3)}$. The contributions of those poles are of course the same as those from T_3 directly. Just as in the two-body bound-state contribution of $b_{3,1}$, (3.6), one concludes that the 3-body counterparts read, in terms of the bound-state vectors $|\psi_\nu^3\rangle$,

$$b_{3,2}^{\mathrm{BS}_3}=2^2\lambda^{-3}\sum_\nu e^{\beta\epsilon_\nu^{(3)}}\int\int d\mathbf{p}_\alpha d\mathbf{q}_\alpha\times\langle\Xi|\psi_\nu^3\rangle\langle\psi_\nu^3|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle. \tag{3.25}$$

A further evaluation of (3.25) requires a detailed analysis of the symmetries of the wave function $\psi_\nu^{(3)}$, for instance, its reflection properties.

Far more complicated is the remaining part. One may note that from its definition (3.12), t_α is seen to be related to the two-particle scattering matrix t (2.13) as follows:

$$\begin{aligned}&\langle\mathbf{p}_\alpha\mathbf{q}_\alpha|t_\alpha(z)|\mathbf{p}_\alpha'\mathbf{q}_\alpha'\rangle\\ &=\delta(\mathbf{q}_\alpha-\mathbf{q}_\alpha')\sum_{l_\alpha}\frac{(2l_\alpha+1)}{2\pi^2}\hat{t}_{l_\alpha}(p_\alpha p_\alpha';z-q_\alpha^2)P_{l_\alpha}(\hat{p}_\alpha\cdot\hat{p}_\alpha').\end{aligned} \tag{3.26}$$

When substituted into (3.22) this gives

$$b'_{3,2}=8\pi^{-1}\lambda^{-3}\sum_{l_\alpha m_\alpha}\int d\mathbf{p}_\alpha d\mathbf{q}_\alpha d\mathbf{p}_\alpha' d\mathbf{q}_\alpha' d\mathbf{p}_\alpha''\frac{1}{2\pi i}\oint_C e^{-\beta z}\times\frac{\langle\Xi|\mathbf{p}_\alpha''\mathbf{q}_\alpha'\rangle Y_{l_\alpha m_\alpha}(\hat{p}'')\hat{t}_l(p_\alpha''p_\alpha',z-q_\alpha^2)Y_{l_\alpha m_\alpha}^*(\hat{p}_\alpha')}{(z-p_\alpha^2-q_\alpha^2)^2(z-p_\alpha'^2-q_\alpha'^2)}\times\langle\mathbf{p}_\alpha'\mathbf{q}_\alpha'|\sum_{\beta\neq\alpha}T_\beta(z)|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle. \tag{3.27}$$

After using conservation of total angular momentum one has exhausted all possibilities for further reduction. Then one will have to solve for the matrix elements of T_β which satisfy integral equations in three variables. Even when known, (3.27) is still extremely complicated. But in principle one has in the results of this section all the ingredients of the third virial coefficient for all temperatures expressed in terms of the off-energy-shell t matrix and the solution of the Faddeev equations.

IV. SEPARABLE-t-MATRIX APPROXIMATIONS

The task of solving coupled integral equations in three variables is too formidable for present-day computers. One has therefore to invoke approximations, which to the best of our knowledge have so far all consisted of the retention of some separable part of t. A t matrix separable for all z is exact only if the interaction itself is separable. However, one notices from (2.14), the spectral decomposition of t, that the residue of t factorizes at bound-state poles, which is in fact also true for resonances.[11,14] In particular, Lovelace justified

the use of a separable t matrix provided the bound-state or scattering energy of the three-particle system is in the neighborhood of a dominant singularity. The satisfactory description of n-d scattering and the H^3 binding energy using nucleon-nucleon scattering data and the energy of the bound and virtual states in d shows the expediency of such a simple choice for certain static three-body problems.[17]

An application of the Faddeev techniques to statistical physics puts more stringent requirements on an approximation. It should be borne in mind that it is not G_3 but connected parts of the partition function one needs to calculate. The operation that links the two is a weighted integration over the energy variable. Whatever the approximation, therefore, one should try to obtain a t matrix close to the exact one over as broad an energy interval as possible.

We have discussed elsewhere[14] the merits of a number of separable t matrices which include all poles and resonances for a given partial wave and which can be applied in the Faddeev equations without undue increase of the number of channels. Those $\hat{t}$ matrices should therefore give a correct description for relatively low values of the energy parameter. The weighting function $e^{-\beta z}$ will favor those values provided T is low enough. As a result, the validity of calculations of B_3 based on separable t matrices will be limited to a low-temperature region, which can, however, be far wider than in expansion approximations (see below).

Our starting point will now be a t matrix assumed to be of the form

$$\langle \mathbf{pq}|\hat{t}(z)|\mathbf{p}'\mathbf{q}'\rangle=\delta(\mathbf{q}-\mathbf{q}')\sum_{lm}\sigma_{lm}(\mathbf{p},z-q^2)\sigma_{lm}(\mathbf{p}',z-q^2)$$
$$\equiv\delta(\mathbf{q}-\mathbf{q}')(2/\pi)\sum_{lm}Y_{lm}(\hat{p})\hat{t}_l(p,z-q^2)\quad(4.1)$$
$$\times Y_{lm}^*(\hat{p}')\hat{t}_l(p',z-q^2).$$

All approximations for t we have in mind will have poles and resonances, as well as residues at these singularities, like the exact t matrix. We now show that the approximation (4.1) leads to more tractable expressions and start with the three-body bound-state contribution (3.22). The following is a generalization of the single-pole procedure used by Phillips.[17] The bound-state wave function $|\psi^3\rangle$ is a solution of the homogeneous integral equation

$$|\psi^3\rangle=G_3^0T_3|\psi^3\rangle.\quad(4.2)$$

With Faddeev we expand $|\psi^3\rangle$:

$$|\psi^3\rangle=\sum_\alpha|\psi_\alpha\rangle,\quad(4.3)$$

each of the components $|\psi_\alpha\rangle$ satisfying[9]

$$|\psi_\alpha\rangle=G_3^0t_\alpha\sum_{\beta\neq\alpha}|\psi_\beta\rangle.\quad(4.4)$$

[17] A. C. Phillips, Phys. Rev. **142**, 984 (1966); and to be published.

Consider the amplitude $\langle\mathbf{p}_\alpha\mathbf{q}_\alpha|\psi_\alpha\rangle$, which by means of (4.1) may be written as

$$\langle\mathbf{p}_\alpha\mathbf{q}_\alpha|\psi\rangle=-(\epsilon^{(3)}+p_\alpha^2+q_\alpha^2)^{-1}$$
$$\times\sum_{l_\alpha m_\alpha}\sigma_{l_\alpha m_\alpha}(\mathbf{p}_\alpha,-\epsilon^{(3)}-q_\alpha^2)$$
$$\times\int d\mathbf{p}_\alpha'\sigma_{l_\alpha m_\alpha}(\mathbf{p}_\alpha',-\epsilon^{(3)}-q_\alpha^2)\langle\mathbf{p}_\alpha'\mathbf{q}_\alpha|\sum_{\beta\neq\alpha}\psi_\beta\rangle$$
$$\equiv-(\epsilon^{(3)}+p_\alpha^2+q_\alpha^2)^{-1}$$
$$\times\sum_{l_\alpha m_\alpha}\sigma_{l_\alpha m_\alpha}(p_\alpha,-\epsilon^{(3)}-q_\alpha^2)$$
$$\times\langle\mathbf{q}_\alpha|Q_{l_\alpha m_\alpha}\rangle.\quad(4.5)$$

Next consider the amplitude $\langle\mathbf{p}_\alpha\mathbf{q}_\alpha|\psi_\beta\rangle$, which by means of (4.4) is seen to satisfy ($\beta\neq\alpha$)

$$\langle\mathbf{p}_\alpha\mathbf{q}_\alpha|\psi_\beta\rangle=-\tfrac{1}{2}\sqrt{3}(\epsilon^{(3)}+p_\alpha^2+q_\alpha^2)^{-1}$$
$$\times\sum_{l_\beta m_\beta}\sigma_{l_\beta m_\beta}(\mathbf{p}_\beta,-\epsilon^{(3)}-q_\beta^2)\langle\mathbf{q}_\beta|Q_{l_\beta m_\beta}\rangle,\quad(4.6)$$

where $\mathbf{p}_\beta$, $\mathbf{q}_\beta$ are the combinations (3.20a) in terms of the independent momenta $\mathbf{p}_\alpha$, $\mathbf{q}_\alpha$. From (4.5) and (4.6) one establishes the homogeneous coupled integral equations

$$\langle\mathbf{q}_\alpha|Q_{l_\alpha m_\alpha}\rangle=2\sum_{l_\beta m_\beta}\int\langle\mathbf{q}_\alpha|\mathfrak{d}_{l_\alpha m_\alpha,l_\beta m_\beta}|\mathbf{q}_\beta'\rangle$$
$$\times\langle\mathbf{q}_\beta'|Q_{l_\beta m_\beta}\rangle d\mathbf{q}_\beta'.\quad(4.7)$$

The quantities $\mathfrak{d}$ are the following functions of the independent momenta $\mathbf{q}_\alpha$, $\mathbf{q}_\beta$:

$$\langle\mathbf{q}_\alpha|\mathfrak{d}_{l_\alpha m_\alpha,l_\beta m_\beta}(z)|\mathbf{q}_\beta\rangle$$
$$=(1-\delta_{\alpha\beta})\frac{\sqrt{3}}{2}\frac{\sigma_{l_\alpha m_\alpha}(\mathbf{p}_\alpha,z-q_\alpha^2)\sigma_{l_\beta m_\beta}(\mathbf{p}_\beta,z-q_\beta^2)}{z-p_\alpha^2-q_\alpha^2}.\quad(4.8)$$

$\mathfrak{d}$ is a generalization of the potentials Z introduced by Lovelace[10] which describe the interaction between the bound or resonating systems in channels α and β. The set (4.7) serves as an eigenvalue equation, and the determinant of its matrix resolvent replaces (3.24) in the separable approximation. Once solved, (4.5) and (4.6) yield the amplitudes which by (3.23), (3.25), and (4.3) are seen to enter the three-body bound-state contribution. For its evaluation one needs integrals of the type

$$I_{\alpha\alpha}=\int d\mathbf{p}_\alpha d\mathbf{q}_\alpha\langle\mathbf{p}_\alpha\mathbf{q}_\alpha|\psi_\alpha\rangle\{\langle\psi_\alpha|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle+\langle\psi_\alpha|-\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle\}$$
$$=\frac{2}{\pi}\sum_{\substack{\text{even}\\ m_\alpha,\lambda}}\int\int p_\alpha^2dp_\alpha q_\alpha^2dq_\alpha|t_{l_\alpha}(p_\alpha,-\epsilon^{(3)}-q_\alpha^2|^2|$$
$$\times\langle q_\alpha\lambda|Q_{l_\alpha m_\alpha}\rangle|^2,\quad(4.9)$$

as well as

$$I_{\alpha\beta}=\int\int d\mathbf{p}_\alpha d\mathbf{q}_\alpha\langle\mathbf{p}_\alpha\mathbf{q}_\alpha|\psi_\beta\rangle \times\{\langle\psi_\beta|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle+\langle\psi_\beta|-\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle\}, \quad (4.10)$$

and

$$I_{\beta\alpha}=\int d\mathbf{p}_\alpha d\mathbf{q}_\alpha\langle\mathbf{p}_\beta\mathbf{q}_\beta|\psi_\alpha\rangle \times\{\langle\psi_\beta|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle+\langle\psi_\beta|-\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle\}. \quad (4.11)$$

Unlike the result (4.9), one cannot give $I_{\alpha\beta}$, $I_{\beta\alpha}$ in closed form without first expressing $\mathbf{p}_\beta$, $\mathbf{q}_\beta$ in terms of $\mathbf{p}_\alpha$, $\mathbf{q}_\alpha$ in (4.6). But clearly, whatever the form for t used, only a double integral will result. Substitution into (3.25) leads to

$$b_{3,2}{}^{\mathrm{BS}_2}=2^2\lambda^{-3}\sum_\nu e^{\beta\epsilon_\nu{}^{(2)}}\int\int p_\alpha{}^2dp_\alpha q_\alpha{}^2dq_\alpha\sum_{\beta,\gamma}I_{\beta\gamma}. \quad (4.12)$$

Next we will be concerned with the reduction of $b_{3,2}{}'$, Eq. (3.27), which will require a solution of the Faddeev equation (3.15), but now under the assumption (4.1) for t. Consider

$$\langle\mathbf{p}_\alpha{}'\mathbf{q}_\alpha{}'|T_\alpha|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle = \sum_{l_\alpha m_\alpha}\delta_{l_\alpha m_\alpha}(\mathbf{p}_\alpha{}', z-q_\alpha{}^2)[\delta(\mathbf{q}_\alpha-\mathbf{q}_\alpha{}')\sigma_{l_\alpha m_\alpha}(\mathbf{p}_\alpha, z-q_\alpha{}^2) \times\int d\mathbf{p}_\alpha{}''\frac{\sigma_{l_\alpha m_\alpha}(\mathbf{p}_\alpha{}'', z-q_\alpha{}'^2)\langle\mathbf{p}_\alpha{}''\mathbf{q}_\alpha{}'|\sum_{\beta\neq\alpha}T_\beta|\mathbf{p}_\alpha\mathbf{q}_\alpha\rangle|}{z-p''_\alpha{}^2-q_\alpha{}'^2}. \quad (4.13)$$

We call the last integral $\langle\mathbf{q}_\alpha{}'|R_{l_\alpha m_\alpha}(\mathbf{p}_\alpha\mathbf{q}_\alpha)\rangle$; from (3.15) it is seen to satisfy

$$\langle\mathbf{q}_\alpha{}'|R_{l_\alpha m_\alpha}(\mathbf{p}_\alpha\mathbf{q}_\alpha)\rangle = 2\sum_{l_\alpha m_\alpha}\int d\mathbf{q}'_\beta\langle\mathbf{q}'_\alpha|\vartheta_{l_\alpha m_\alpha,l_\beta m_\beta}|\mathbf{q}'_\beta\rangle \times[\sigma_{l_\alpha m_\alpha}(\mathbf{p}_\alpha\mathbf{q}_\alpha)+\langle\mathbf{q}'_\beta|R_{l_\beta m_\beta}(\mathbf{q}_\alpha\mathbf{q}_\beta)\rangle]. \quad (4.14)$$

We assume that (4.14) has been solved and find, upon substituting (4.14) into (3.27),

$$b'_{3,2}=8\lambda^{-3}\sum_{l_\beta m_\beta}\int\int d\mathbf{p}_\alpha d\mathbf{q}_\alpha\frac{1}{2\pi i}\oint_C\frac{e^{-\beta z}}{(z-p_\alpha{}^2-q_\alpha{}^2)^2}dz \times\sum_\gamma\{\sigma_{l_\alpha m_\alpha}(\mathbf{p}_\gamma, z-q_\gamma{}^2)+\sigma_{l_\alpha m_\alpha}(-\mathbf{p}_\gamma, z-q_\gamma{}^2)\} \times\langle\mathbf{q}_\gamma|R_{l_\alpha m_\alpha}(\mathbf{p}_\alpha\mathbf{q}_\alpha)\rangle. \quad (4.15)$$

Notice again that angular integrations for the $\gamma=\alpha$ part of the bracketed expression could be performed explicitly. Regarding the remaining part, the same remark is in order as was made above for the bound-state contributions.

The resulting expression for $b_{3,2}{}'$, Eq. (4.15), is a three-fold integral. Two variables will be p_α, q_α, the third some real x as in (3.7). Again we find that after solution of the Faddeev equations we are left with a few feasible quadratures.

Before closing this section we wish to outline the necessary steps in an actual calculation of the third virial or cluster coefficient. One starts, of course, with a determination from the second virial coefficient of the parameters characterizing a potential well of given functional shape. In the case of He^4 such a well will just produce a bound state or not. We wish to stress that this is actually immaterial for the following step, namely, the choice of some separable t matrix associated with the two-body potential. The approximate t matrix changes continuously if the bound-state pole moves to the neighboring unphysical sheet. Its contribution there will be considered as important as that of a truly bound state. This observation makes it necessary to investigate whether additional resonances exist in other partial waves.

A choice

$$\langle\mathbf{k}|t(z)|\mathbf{k}'\rangle\sim\sum_i\frac{g_i(\mathbf{k})g_i(\mathbf{k}')}{z-\epsilon_i{}^{(2)}}, \quad (4.16)$$

with g eventually z-dependent in order to satisfy off-energy-shell unitarity,[14] would be the simplest conceivable. One then has to solve the partial-wave integral equations (4.8) and (4.3), after which the calculation of the bound-state and continuum contributions (4.9) and (4.15) is reduced to repeated quadratures. Calculations along these lines are in progress.

V. DISCUSSION

We presented above a theoretical framework for the calculation of the third virial coefficient of a boson gas, which incidentally can be generalized to any virial coefficient of a boson or fermion gas. Of the three cluster coefficients which determine the third coefficient, the first two are well-known expressions valid for any temperature.

The third cluster coefficient contains three-particle correlations of statistical, dynamical or mixed nature The first is of course the expression for an ideal gas. The mixed part, on the other hand, though containing only the interactions between a single pair, is already of non-elementary nature. Its magnitude may be expressed in terms of a single off-energy-shell two-body scattering matrix which is in principle calculable. The possibility of a two-body bound state offers no difficulty, and its contributions can in fact be isolated. We note that since no approximation is involved, the mixed correlation term can also be calculated for any temperature.

The major stress in this paper lies on $b_{3,2}$, the dynamical part of the third cluster coefficient, which embodies all interactions except the single one contained in the mixed term. It has been shown that the Faddeev theory for the three-body scattering problem provides a closed formulation of the dynamical correlation problem.

In principle all there is to be done is the solution of coupled integral equations and several quadratures. Though conceptually simple, the computational difficulties are enormous and one has for the moment to resort to approximations. It is for instance simpler to solve the Faddeev equations for any factorizable two-body off-energy-shell scattering matrix. The corresponding theory of the third cluster coefficient has been discussed and its validity for low temperatures seems assured.

It is appropriate to compare the Faddeev approach with the application of the Lee-Yang theory of cluster coefficients by Pais and Uhlenbeck[3] and by Larsen.[4] We have already discussed the unmistakable advantages of the former, which is an exact theory in what appears as an essentially closed formalism. None of the inherent difficulties in series expansions, like slow or dubious convergence in the presence of bound states, appears. The Faddeev approach, for instance, treats in a perfectly natural way two- or three-body states if present. One and the same formalism is used for two-body forces which are repulsive, too weak to give binding but sufficient to produce a resonance, or for attractive forces. This is in constrast with the formalism of Pais and Uhlenbeck, which requires different treatments for qualitatively different binding properties of the interaction.

Guided by the exact theory of the second virial coefficient in terms of bound-state energies and scattering phase shifts, Pais and Uhlenbeck[3] posed the question whether all virial coefficients may be determined from scattering data. In fact already the multiple-scattering expansion (and therefore also the binary-collision expansion) provides a hint: The basic element in the theory is the off-energy-shell scattering matrix, which apart from special values of momenta and energies is not measurable. One learns, however, from the very example of the second virial coefficient that the argument is inconclusive. To our knowledge it has as yet not been demonstrated how the known expression for the second cluster coefficient results if one starts from a form in terms of a off-energy-shell t matrix.[16] It would repay the effort to find the manipulations leading to the known answer. It may teach us how to compute other cluster coefficients or parts of them in terms of quantities on the energy shell in spite of their appearances as functionals of off-energy-shell scattering matrices.

Note added in proof. B. Baumgarth has recently expressed the 2 integral in (3.5) in terms of the t matrix on the energy shell and its derivative.

It is remarkable that the separable approximations discussed actually provide in some remote sense an answer to the question of Pais and Uhlenbeck. The elements one retains in a separable t matrix are in essence known and consist of energies and form factors of bound states and resonances. The latter may be considered as measurable properties of the off-energy-shell t matrix, to be contrasted with phase shifts, which follow from t on the energy shell. This holds for a simple choice [Eq. (4.16)] as well as for more sophisticated ones.[14] If is further satisfactory to see that nearby singularities on the second sheet, through their energies, widths, and resonance form factors, play a role equivalent to their bound-state partners.

ACKNOWLEDGMENTS

It is a pleasure to thank J. M. Blatt for useful discussions. A discussion with P. Martin on the singular behavior in the zero-temperature limit has been very enlightening.