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Multispecies cluster expansion for the grand partition function*

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This paper studies the problem of a quantum gas of particles whose interparticle potential is attractive enough to support stable bound clusters. The approach to this problem is to employ the time-dependent two-Hilbert-space scattering theory—first developed by Faddeev to treat the three-body problem. From this theory the asymptotic completeness theorem is taken and utilized to give a new definition of the canonical partition function suitable for describing states that are a mixture of free particles and bound clusters. A multispecies cluster expansion is obtained for the grand partition function. The theory of few-particle time delay is employed to determine the values of these cluster integrals. From these solutions are obtained the multidensity virial equation of state, the internal energy, and a density expansion of the chemical mass-action law that gives the effect of interactions between particles and clusters. All of these solutions exhibit the fact that the only aspect of the collision process that has any effect on the macroscopic behavior of the system is the time delay. From another perspective this problem and the solutions obtained represent a specific nontrivial realization of the S-matrix description of statistical mechanics put forth by Dashen.

I. INTRODUCTION

This paper presents a theoretical description of the equilibrium statistical mechanics of a chemically reacting nonideal quantum gas. The physical system is that of N ($\simeq 10^{23}$) identical particles, bosons or fermions, which interact with one another via an arbitrary short range (non-Coulomb) potential. The potential is assumed to be attractive enough so that stable few-particle bound states are formed. This system, like many of the atomic or molecular systems it idealizes, creates through its own interaction new species types. Our goal will be to find explicit forms for the virial coefficients that occur in the multicomponent density expansion of the equation of state, the internal energy, and the chemical mass action law.

Our method for solving this problem is to apply Faddeev's time-dependent two-Hilbert-space theory of few-body scattering. In this context we will use the asymptotic completeness theorem to arrive at a definition of the canonical partition function that reflects the existence of stable clusters which may undergo chemical reaction. Next the theory of few-body time delay will be outlined and then used to compute an explicit formula for the multicomponent virial coefficients. This time delay approach to understanding the role of scattering in statistical mechanics finds its inception in the work of Smith. This paper will carry that program to completion. Although the first account of time-delay effects is given by Eisenbud and Wigner,[1] their work refers to a concept of time delay that is characteristic of a particle that is known to scatter through some fixed angle. Smith on the other hand gives a definition[2] which allows one to compute the total time advance or retardation experienced by a wave packet in the scattering process. Furthermore, Smith realized[3] that the virial coefficients should be in the form of a Laplace transform of the trace of the time-delay operator.

In contrast to the early work on this problem, the technical implementation of this program is strongly dependent on modern few-particle scattering theory. This is a necessity, since the equation of state will be one that involves many types of scattering—coalescence, rearrangement, breakup, and elastic scattering of both free particles and bound clusters. To describe all these processes one needs an appropriate multichannel scattering theory of the kind developed by Faddeev.[4] It is this theory that has been used to define a multichannel operator definition of time delay and to establish its relationship to the S matrix.[5] We already have used this approach to write down a general quantum theory of higher virial coefficients.[6] This first paper, hereafter referred to as I, did not treat the problem of chemical reactions and that is the subject of this paper.

Let us specify in greater detail the problem we study. The system is taken to be one of N identical spinless particles having mass m. To be concrete we will assume the particles are bosons. The time evolution of this system will be governed by the N-particle Hamiltonian H_N. We assume that the pairwise interaction between particles is such that stable two-particle clusters exist, but not three- or more-particle clusters. This restriction limits us to describing only the simplest of all chemical reactions—namely, two free particles combining to give a stable cluster. As one will see our analysis is not in principle confined to the case where there is only one type of elementary (i.e., Hamiltonian defining) particle and one composite cluster.

We further presume that the two-particle Hamiltonian has only a single bound state. That is, excited two-body bound states are absent. These states, where present, represent the rotational and vibrational modes of a two-particle cluster. The contribution of these modes to observables like the specific heat are already well understood. Again the addition of these states to our problem would complicate the mathematical description but not add new physical insights into the general behavior of multicomponent quantum gases.

One of the long-term aims of statistical mechanics is to derive all the equilibrium properties of a macroscopic system from the dynamical laws of the constituent quantum particles. For the problem studied here this aim is realized. We obtain closed-form solutions for the virial coefficients in terms of on-shell physical scattering amplitudes. These solutions indicate exactly the role of the collision process in the thermodynamic behavior of the system. In the analysis that follows the collision processes are treated without the introduction of any approximations. The one approximation used in this paper is to treat the free motion of stable fragments (clusters or particles) with Boltzmann statistics.

II. PARTITION FUNCTION AND STABLE CLUSTERS

The basic approach to this problem is to write down an appropriate Ursell cluster expansion for the grand partition function. Then a combination of time delay and scattering theory results are used to obtain explicit forms for the cluster integrals. We have found that the existence of a new species—formed of the stable two-particle bound clusters—requires that we modify the definition of the N-particle partition function.

At any given temperature T and volume V the N particles exist as N_1 free particles and N_2 bound clusters. Whatever N_1 and N_2 are they satisfy particle conservation, i.e.,

$$N = N_1 + 2N_2. \tag{2.1}$$

Let ρ_1 and ρ_2 be the densities N_1/V and N_2/V, respectively. The general form of the multispecies equation of state is

$$P/kT = \sum_{i+j\geq 1} a_{ij}(T)\rho_1^i\rho_2^j. \tag{2.2}$$

We develop a cluster expansion that will predict Eq. (2.2). In order to understand our modification of the cluster expansion it is useful to recall the customary treatment. The canonical partition function for l particles is proportional to the trace over the volume V of the probability operator

$$W_l(1,2,\ldots,l) = l!\,S(l)e^{-\beta H_{l,V}(1,2,\ldots,l)}. \tag{2.3}$$

The operator $S(l)$ is the symmetric wave-function projection operator containing the $l!$ distinct permutations of the particle labels $(1,2,\ldots,l)$. The Hamiltonian $H_{l,V}$ is for l particles including all their mutual interactions. The subscript V on $H_{l,V}$ comes from the boundary condition that the wave functions vanish on the surface of the volume. The Ursell operators $U_{l,V}$ are constructed from the W_l by the following equations[7]:

$$U_{1,V}(1) = W_1(1), \tag{2.4}$$

$$U_{2,V}(1,2) = W_2(1,2) - W_1(1)W_2(2), \tag{2.5}$$

$$\begin{aligned} U_{3,V}(1,2,3) = {} & W_3(1,2,3) - W_2(1,2)W_1(3) \\ & - W_2(1,3)W_1(2) - W_2(2,3)W_1(1) \\ & + 2W_1(1)W_1(2)W_1(3), \end{aligned} \tag{2.6}$$

etc. These equations mean that the physics derived from $U_{l,V}$ and W_l is the same, but $U_{l,V}$ have the technical advantage that the divergent behavior as $V\to\infty$ inherent in W_l is cancelled by the linear combinations that occur in (2.4)–(2.6).

The partition function for l particles is just the trace of W_l; thus the grand partition function for this system is

$$\Xi_1(V,T,z) = \sum_{l\geq 0} Q_l(V,T)z^l, \tag{2.7}$$

$$Q_l(V,T) = (1/l!)\,\mathrm{Tr}\,W_l. \tag{2.8}$$

The symbol $Q_l(V,T)$ is the partition function and the parameter z is the fugacity variable that will be eliminated when the equation of state is found. The equation

$$P/kT = (1/V)\ln\Xi_1 \tag{2.9}$$

gives the relation between statistical mechanics and thermodynamics. A second representation of Ξ_1 is the cluster integral expansion

$$\Xi_1(V,T,z) = \exp\left(V\sum_{l\geq 1} b_l(V,T)z^l\right). \tag{2.10}$$

The term $b_l(V,T)$ is the cluster integral. If we expand both Eqs. (2.7) and (2.10) as a power series in z and equate the coefficients of the different powers of z, then it is found that

$$b_l(V,T) = (1/Vl!)\,\mathrm{Tr}\,U_{l,V}. \tag{2.11}$$

In this same grand ensemble language the average number of particles in the system is given by

$$N = z\frac{\partial}{\partial z}\ln\Xi_1\big|_{V,T} \tag{2.12}$$

$$= V\sum_{l\geq 1} l b_l(V,T) z^l. \tag{2.13}$$

The last step is to write the equation of state as a density expansion:

$$P/kT = \sum_{l\geq 1} a_l(T)\rho^l. \tag{2.14}$$

The variable ρ is the particle space density NV^{-1}, and the a_l are the virial coefficients. These virials are found by placing Eqs. (2.9), (2.10), and (2.13) into Eq. (2.14) and equating the powers of the fugacity to find $a_1 = 1$; $a_2 = -b_2 b_1^{-2}$; $a_3 = 4a_2^2 - 2b_3 b_1^{-3}$; etc. These results are all standard[7] but are recounted here because they define our notation and serve as the point of departure for our development. For the case of distinguishable particles we computed in I $a_2(T)$ and $a_3(T)$ in terms of two- and three-body time delay.

The difficulty inherent in the one-fugacity grand partition function Ξ_1 is that it must lead to the single-density form of the equation of state rather than the two-species form Eq. (2.2). The reason for this is that the canonical partition functions $Q_N(V,T)$ do not reflect the existence of the stable clusters. The way to improve on this situation was suggested by Hill,[8] who argued that we must introduce two fugacities—z_1 for the free particles and z_2 for the stable clusters—and find a partition function for $i+2j$ particles wherein i is the number of free particles and j the number of clusters. Hill tried to implement this idea in the context of classical mechanics. Here we give a simple definition appropriate for quantum mechanics.

For l particles in a large volume V which are governed by the interacting Hamiltonian H_l, this system may exist in a number of distinct configurations. We can characterize these configurations by a pair of non-negative integers $[i,j]$ subject to the constraint $l = i + 2j$. The first integer i in $[i,j]$ represents the total number of free particles and the second integer j denotes the number of two-particle clusters. We seek the definition of a partition function $Q_{ij}(V,T)$ consistent with the state (or subspace of states) described by $[i,j]$.

Before proceeding farther it is necessary to give a general description of our particle coordinates, momenta, and Hamiltonians. Let $\vec{r}_i$ be the position of the ith particle in the volume V. The momentum $\vec{k}_i$ conjugate to $\vec{r}_i$ is

$$\vec{k}_i = -i\hbar\frac{\partial}{\partial \vec{r}_i}. \tag{2.15}$$

The center-of-mass variables of l particles are

$$\vec{R}_l = \frac{1}{l}\sum_{i=1}^{l}\vec{r}_i, \quad \vec{K}_l = \sum_{i=1}^{l}\vec{k}_i. \tag{2.16}$$

Complementary to these center-of-mass variables one may construct $l-1$ Jacobi coordinate variables. The resultant Jacobi coordinate system depends on the order in which the $\vec{r}_i$ are combined together. Suppose η is any permutation of $(1,2,3,\ldots,l)$. Then we define $\vec{x}_{i,\eta}, \vec{p}_{i,\eta}$ by the equations

$$\vec{x}_{i,\eta} = \vec{r}_{\eta(i+1)} - \frac{1}{i}\sum_{j=1}^{i}\vec{r}_{\eta(j)}, \quad i \leq l-1, \tag{2.17}$$

$$\vec{p}_{i,\eta} = -i\hbar\frac{2}{\partial \vec{x}_{i,\eta}}. \tag{2.18}$$

The Hamiltonian giving the total kinetic energy for the l particles is

$$H^0_{l,V} = \sum_{i=1}^{l}\frac{\vec{k}_i^2}{2m} = \frac{\vec{K}_l^2}{2lm} + h^0_{l,V}. \tag{2.19}$$

The Hamiltonian $h^0_{l,V}$ gives the relative kinetic energy of the system. It may also be written

$$h^0_{l,V} = \sum_{i=1}^{l-1}\frac{\vec{p}_{i,\eta}^2}{2m}\left(\frac{i+1}{i}\right). \tag{2.20}$$

This sum is independent of η. We will always use H to represent Hamiltonians that include the center-of-mass motion and h to indicate those where the center-of-mass kinetic energy has been subtracted. The absence of the subscript V will mean the Hamiltonian is defined on the infinite volume Hilbert space.

The potential is taken to be the sum of the real pairwise interactions v_{ij} between the l particles,

$$V_l(\vec{r}_1,\ldots,\vec{r}_l) = \sum_{i<j\leq l} v_{ij}(\vec{r}_i - \vec{r}_j). \tag{2.21}$$

The exact Hamiltonians are

$$H_{l,V} = H^0_{l,V} + V_l, \tag{2.22}$$

$$h_{l,V} = h^0_{l,V} + V_l. \tag{2.23}$$

However we shall also require the class of Hamiltonians that generate the time evolution of states consisting of a mixture of stable two-particle clusters and free particles. Let ξ be a partition of the l particles into ν subsets—each subset n_ν containing one or two particles subject to the overall constraint

$$\sum_{\nu} n_\nu = l. \tag{2.24}$$

The asymptotic potential is denoted V_l^ξ and given by

$$V_l^\xi = \sum_{(i<j)\in\xi} v_{ij}. \tag{2.25}$$

The restriction on the sum $(i<j)\in\xi$ requires that i and j occur in one of the two-particle subsets in the partition ξ. Clearly V_l^ξ describes the effective potential for a mixture of one- and two-particle clusters—each pair occurring in a two-body bound state has the two-particle potential needed to create this bound state. The corresponding asymptotic Hamiltonians specified by ξ are

$$H_{l,V}^{\xi}=H_{l,V}^{0}+V_l^{\xi}, \qquad (2.26)$$

$$h_{l,V}^{\xi}=h_{l,V}^{0}+V_l^{\xi}. \qquad (2.27)$$

We return now to the problem of defining the stable cluster canonical partition function. The construction of $Q_{ij}(V,T)$ rests on the asymptotic completeness theorem in few-particle scattering theory, whose content we shall now outline. Denote by $\mathcal{H}_l$ the l-particle Hilbert space appropriate for scattering theory—namely, square integrable functions defined on the $3l$ infinite volume coordinate space. On this space the symbol E_l will represent the identity operator. The asymptotic completeness theorem states that E_l has the orthogonal decomposition

$$E_l=\sum_{i+2j=l}\Lambda^{(+)}[i,j]. \qquad (2.28)$$

The $\Lambda^{(+)}[i,j]$ are a set of mutually orthogonal projection operators which span $\mathcal{H}_l$. The superscript (+) indicates that the scattering satisfies the outgoing radiation condition. The range of each $\Lambda^{(+)}[i,j]$ are all those states in $\mathcal{H}_l$ which are characterized by the motion of l particles which asymptotically (prior to the collision process) have i free particles and j free clusters.

The projection operators $\Lambda^{(+)}[i,j]$ are constructed from the N-body Moller wave operators.[4,9] For l-particle systems the wave operator is defined by the strong limit in the time variable t of

$$\Omega_{l;\xi}^{(\pm)}=\lim_{t\to\mp\infty}\exp(-ih_lt)\exp(+ih_l^{\xi})J_{l;\xi}. \qquad (2.29)$$

The center-of-mass motion is excluded from this definition. The partition ξ of the l particles, which is consistent with a stable grouping of particles into two- and one-particle clusters, defines the scattering channel. The operator $J_{l;\xi}$ will be defined in detail in Sec. III. Physically it ensures us that the wave function $\Omega_{l;\xi}^{(\pm)}$ acts on is consistent with ξ-channel stable cluster motion. When the partition ξ separates all the particles, $J_{l;\xi}$ is the identity. The superscript (+) or (−) on the wave operator indicates whether or not the scattering state satisfies an outgoing or incoming boundary condition. Let set $[i,j]$ denote all those partitions of l particles consistent with i free particles and j free clusters; then $\Lambda^{(+)}[i,j]$ is defined by the tensor product

$$\Lambda^{(+)}[i,j]=\sum_{\xi\in[i,j]}\Omega_{l;\xi}^{(+)}\Omega_{l;\xi}^{(+)\dagger}\otimes I_l, \quad (i,j)\neq(0,1). \qquad (2.30)$$

The operator I_l is just the identity on the center-of-mass space, $L^2(\vec{R}_l)$. The two-particle case is in this problem distinct from $l>2$ in that only the Hamiltonian h_2 has an eigenfunction.

A good illustration of how the asymptotic completeness theorem works can be derived by looking at the two- and three-particle cases. Consider $l=2$ first. Here the completeness statement is

$$E_2=\Lambda^{(+)}[2,0]+\Lambda^{(+)}[0,1]. \qquad (2.31)$$

The operator $\Lambda^{(+)}[2,0]$ is given by Eq. (2.30) and is the projection operator onto all the two-particle scattering states in $\mathcal{H}_2$. On the other hand $\Lambda^{(+)}[0,1]$ is the projection operator on the two-body bound states. Let ψ be the one permitted eigenstate of h_2 and let $-\epsilon_2$ be the bound-state energy; then

$$h_2\psi=-\epsilon_2\psi, \quad \|\psi\|=1. \qquad (2.32)$$

In terms of ψ the operator $\Lambda^{(+)}[0,1]$ is

$$\Lambda^{(+)}[0,1]=(\psi\otimes\overline{\psi})\otimes I_2. \qquad (2.33)$$

A standard proof of Eq. (2.31) may be found in Kato.[10]

The completeness theorem in the three-particle case is less trivial than that given above for two-particle scattering. Here the allowed partitions ξ are (1)(2)(3), (1)(23), (2)(13), and (3)(12). Let us identify these four sets respectively by $\alpha=(0,1,2,3)$. Thus the channel labeled by $\alpha=2$ implies that particle 2 is incident on the bound pair (13) having a wave function ψ given by Eq. (2.32). The index $\alpha=0$ describes the channel in which all three particles are initially free. The permited values of $[i,j]$ in this case are $[1,1]$ and $[3,0]$. The construction of the projection operator $\Lambda^{(+)}[1,1]$ has three scattering channels corresponding to $\alpha=1,2,3$. The operator $\Lambda^{(+)}[3,0]$ is given by one term, $\alpha=0$:

$$\Lambda^{(+)}[1,1]=\sum_{\alpha>0}\Omega_{3;\alpha}^{(+)}\Omega_{3;\alpha}^{(+)\dagger}\otimes I_3, \qquad (2.34)$$

$$\Lambda^{(+)}[3,0]=\Omega_{3;0}^{(+)}\Omega_{3;0}^{(+)\dagger}\otimes I_3. \qquad (2.35)$$

The three-particle completeness theorem reads

$$E_3=\Lambda^{(+)}[1,1]+\Lambda^{(+)}[3,0]. \qquad (2.36)$$

In Eq. (2.36) there is no bound-state projection operator like $\Lambda^{(+)}[0,1]$, because of the assumption of the absence of three-body bound states. The first proof of relation (2.36) was given by Faddeev[4] and another recently obtained by Thomas.[11] Although rigorous proofs for the asymptotic completeness theorem for arbitrary l have not yet been found we presume the theorem is universally valid. Even should this extension of the theorem fail in the sense that the sum of $\Lambda^{(+)}[i,j]$ for $i+2j=1$ does not span the entire l-particle Hilbert space $\mathcal{H}_l$, it would not significantly affect our analysis. In the case of the breakdown of the asymptotic completeness theorem, E_l on the left-hand side of Eq. (2.28) would be replaced by a projection operator on some subspace of $\mathcal{H}_l$. This subspace is the space of physical solutions for the Hamiltonian H_l. Thus in this situation the trace defining the partition on function $Q_l(V,T)$ in Eq. (2.8) should be summed over only states from this physical subspace.

The next step is to use this theorem together with its physical interpretation to define a stable-cluster canonical partition function. We shall carry out this process when the fundamental particles are taken to be bosons. For $l=i+2j$ set

$$Q_{ij}(V,T)=\mathrm{Tr}\,S(l)\Lambda^{(+)}[i,j]e^{-\beta H_{l,V}}. \tag{2.37}$$

To emphasize the interpretation of $Q_{ij}(V,T)$ recall that the trace is a sum of diagonal matrix elements over any complete orthonormal basis $\{\phi_n\}$. Thus Eq. (2.37) may be written as a sum of terms of the form

$$(\Lambda^{(+)}[i,j]S(l)\phi_n, \Lambda^{(+)}[i,j]e^{-\beta H_{l,V}}\phi_n). \tag{2.38}$$

In expressing this term we utilized the Hermitian and idempotent properties that projection operators have. Since the range of $\Lambda^{(+)}[i,j]$ is composed of only states that initially have i free particles and j free clusters, one sees that the sum in Eq. (2.37) is over states exclusively of this character. Demonstrating the necessary time reversal invariance of our defining procedure is a straightforward exercise.

Suppose z_1 to be the fugacity associated with the free particles and z_2 that of the two-particle clusters. The two-fugacity grand partition function is given by

$$\Xi_2(V,T,z_1,z_2)=\sum_{ij}Q_{ij}(V,T)z_1^i z_2^j. \tag{2.39}$$

Once Ξ_2 is known the equation of state is determined in the traditional way[7] by

$$P/kT=(1/V)\ln\Xi_2. \tag{2.40}$$

The ensemble averages of the number of free particles N_1 and the number of free clusters N_2 are given by

$$N_i=z_i\frac{\partial}{\partial z_i}\ln\Xi_2, \quad i=1,2. \tag{2.41}$$

Equations (2.40) and (2.41) furnish for us the equation of state (2.2) when z_1 and z_2 are eliminated in favor of N_1 and N_2.

Examine now the consistency of the two- and one-fugacity grand partition functions. When chemical equilibrium has been established then the chemical potential for free particles, μ_1, and that for bound pairs, μ_2, satisfy the relation

$$\mu_2=2\mu_1. \tag{2.42}$$

Restated in terms of fugacities, then

$$z_2=z_1^2. \tag{2.43}$$

The asymptotic completeness condition Eq. (2.28) implies

$$\sum_{i+2j=l}Q_{ij}(V,T)=Q_l(V,T). \tag{2.44}$$

This result, together with the restriction

$$z=z_1, \tag{2.45}$$

leads at once to

$$\Xi_1(V,T,z)=\Xi_2(V,T,z,z^2). \tag{2.46}$$

So when conditions (2.43) and (2.45) are valid one obtains the same values for the grand partition function and of course all the same thermodynamic predictions. Note also that the conditions (2.43) and (2.45) when combined with Eqs. (2.12) and (2.41) lead directly to the particle conservation relation (2.1).

The drawback, inherent in the structure of $\Xi_1(V,T,z)$, is that the possibility that the two species are *not* in equilibrium ($z_2\neq z_1^2$) cannot arise. Any attempt to obtain the multicomponent equation of state, Eq. (2.2), will fail because there are not enough independent fugacity variables to lead to explicit formulas for the a_{ij}. No such difficulty appears when Ξ_2 is used.

The two-fugacity grand partition function generates its own cluster integral expansion. The cluster expansion here takes the form

$$\Xi_2(V,T,z_1,z_2)=\exp\left(V\sum_{ij}b_{ij}(V,T)z_1^i z_2^j\right), \tag{2.47}$$

and the coefficients b_{ij} are determined by requiring that Eq. (2.47) be identical with Eq. (2.39). The results for these two-fugacity cluster integrals can be summarized in terms of an Ursell expansion. Define probability operators W_{ij} to be

$$W_{ij}(1,\ldots,l)=i!j!S(l)\Lambda^{(+)}[i,j]e^{-\beta H_{l,V}(1,\ldots,l)}, \tag{2.48}$$

where

$$Q_{ij}(V,T)=\frac{1}{i!j!}\mathrm{Tr}\,W_{ij}. \tag{2.49}$$

The Ursell operators $U_{ij,V}$ are then

$$U_{10,V}(1)=W_{10}(1), \tag{2.50a}$$

$$U_{01,V}(1,2)=W_{01}(1,2), \tag{2.50b}$$

$$U_{20,V}(1,2)=W_{20}(1,2)-W_{10}(1)W_{10}(2), \tag{2.50c}$$

$$U_{11,V}(1,2,3)=W_{11}(1,2,3) -\tfrac{1}{3}[W_{10}(1)W_{01}(2,3)+W_{10}(2)W_{01}(1,3) +W_{10}(3)W_{01}(1,2)], \tag{2.50d}$$

$$U_{30,V}(1,2,3)=W_{30}(1,2,3)+2W_{10}(1)W_{10}(2)W_{10}(3) -[W_{10}(1)W_{20}(2,3)+W_{10}(2)W_{20}(1,3) +W_{10}(3)W_{20}(1,2)], \tag{2.50e}$$

$$U_{02,V}(1,2,3,4)=W_{02}(1,2,3,4) -\tfrac{1}{3}[W_{01}(1,2)W_{01}(3,4) +W_{01}(1,3)W_{01}(2,4) +W_{01}(1,4)W_{01}(2,3)], \tag{2.50f}$$

etc. All the W_{ij} in these equations of course depend on the volume V. The b_{ij} are given by

$$b_{ij}(V,T)=\frac{1}{i!j!V}\operatorname{Tr}U_{ij,V}. \tag{2.51}$$

The fugacity form of the equation of state follows from Eq. (2.40) and Eq. (2.47). Thus

$$\frac{P}{kT}=\sum_{ij}b_{ij}(V,T)z_1^iz_2^j. \tag{2.52}$$

At the same time one may use Eq. (2.41) to find the densities ρ_1 and ρ_2 in terms of the fugacity variables,

$$\rho_1=\sum_{ij}ib_{ij}z_1^iz_2^j, \tag{2.53}$$

$$\rho_2=\sum_{ij}jb_{ij}z_1^iz_2^j. \tag{2.54}$$

The density form of the equation of state results from substituting Eqs. (2.52)–(2.54) into Eq. (2.2) and eliminating the z_1 and z_2 to find a_{ij}. The first few terms for these virials are found to be

$$a_{01}=1,\quad a_{10}=1, \tag{2.55a}$$

$$a_{02}=-b_{02}b_{01}^{-2}, \tag{2.55b}$$

$$a_{11}=-b_{11}b_{10}^{-1}b_{01}^{-1}, \tag{2.55c}$$

$$a_{20}=-b_{20}b_{10}^{-2}, \tag{2.55d}$$

$$a_{30}=-2b_{30}b_{10}^{-3}+4b_{20}^2b_{10}^{-4}. \tag{2.55e}$$

The fact that both a_{01} and a_{10} are unity express the law of partial pressures which is valid at low densities. Even this most elementary behavior is not evident in the one-density equation of state Eq. (2.14), although we know both Eq. (2.14) and Eq. (2.2) lead to the same values of P/kT.

In concluding this section we note that two-fugacity representations of the grand partition function have been used before by Pathria and Kawatra[12] but in a somewhat different physical context. Using the binary collision kernel method of Lee and Yang,[13] Pathria and Kawatra studied a two species gas consisting of two distinct fundamental particles. This system also leads to a multidensity equation of state having the form of Eq. (2.2). Our problem has a richer physical structure since the second species is a composite bound state formed from the first elementary particle species. The difference between the problems of course leads to differing definitions of $Q_{ij}(V,T)$. However, the Eqs. (2.55a)–(2.55e) that link a_{ij} to b_{ij} are the same for both problems.

III. CLUSTER INTEGRALS

In this section we shall study the cluster integrals as Laplace transforms of the trace of the few-body time-delay operator. We shall follow Mayer[14] in computing all our physical variables in the thermodynamic limit. For the problem studied here this means that the $V\to\infty$ limit of Eq. (2.52) exists and may be written

$$\frac{P}{kT}=\sum_{ij}\mathscr{b}_{ij}(T)z_1^iz_2^j, \tag{3.1}$$

where $\mathscr{b}_{ij}(T)$ is given by

$$\mathscr{b}_{ij}(T)=\lim_{V\to\infty}b_{ij}(V,T). \tag{3.2}$$

The double series in Eq. (3.1) is assumed to have a nonzero radius of convergence, and within this radius of convergence the equation of state obtained by combining Eq. (3.1) together with the $V\to\infty$ version of Eqs. (2.53)–(2.54) gives one the correct behavior of our system in the gas phase.

The reduction of the two-fugacity description to the standard one-fugacity treatment is easily obtained from the relation

$$b_l(V,T)=\sum_{i+2j=l}b_{ij}(V,T). \tag{3.3}$$

This equation follows from Eq. (2.44) and the definition of $b_{ij}(V,T)$ in Eq. (2.51). For potentials general enough to have bound states Ruelle[15] has established the existence of the thermodynamic limit. In the work of Bedeaux[16] one finds a proof of the limit $b_l(V,T)\to\mathscr{b}_l(T)$ as $V\to\infty$. All these results suggest it should be possible to rigorously establish the existence of the thermodynamic limit defined by the modified partition functions $Q_{ij}(V,T)$. However, in this paper we do not attempt a proof of the existence of the thermodynamic limit and merely assume its validity.

In the following we evaluate the Boltzmann-like contributions to $\mathscr{b}_{ij}(T)$. The projection operator $S(i+2j)$ is the sum of the $(i+2j)!$ permutations of $(i+2j)$ objects. These permutations are divided into two groups. The first are the direct terms. These are the permutations that leave the state with structure ξ invariant. This invariance is the result of the symmetry of the two-body bound-state wave functions. The remaining group of permutations are composed of those particle interchanges that remove particles from stable clusters and will be called exchange terms. The direct terms lead to a Boltzmann-like statistics. The exchange terms include all the symmetrizing effects of the Bose character of the system, with the exception of the two-body bound-state symmetry that is explicitly built into the definition of the direct terms.

Let us discuss why we expect the approximation of the direct term evaluation of b_{ij} to be accurate in the gas phase. Consider the two-body case. In this case the ideal-gas exchange term is known to be $\not{b}_2^0 = \lambda_1^{-3} 2^{-5/2}$. Here λ_1 is the thermal wavelength for one particle of mass m, i.e., $-(2\pi\hbar^2/mkT)^{1/2}$. We are interested in the behavior of the remainder of the exchange contributions to $\not{b}_2$. We denote these contributions by $\not{b}_2^{\text{ex}}$. For the case of hard-sphere scattering extensive studies have been made of this problem. Larsen *et al.*[17] and Lieb[18] have established that

$$\not{b}_2^{\text{ex}}(T) = \not{b}_2^0(T) \exp\{-\tfrac{1}{2}\pi^3 (a/\lambda_1)^2 + O[(a/\lambda_1)^{2/3}]\}, \tag{3.4}$$

where a in this formula is the hard-sphere radius. This equation means that the exchange contribution to $\not{b}_2(T)$ is exponentially suppressed as $T \to \infty$. In the specific case of helium atoms the exponential is roughly $e^{-T/2}$. Thus only within a few degrees Kelvin of absolute zero is the exchange term significant.[19]

Next consider the behavior of the three-body exchange terms. Here the ideal-gas contribution is $\not{b}_3^0 = \lambda_1^{-3} 3^{-5/2}$. In this problem, symmetrization of the wave function will involve single and double transpositions of particle labels. Both Bruch[20] and Hill[21] have studied this problem for hard-sphere scattering. Again, it is found that the exchange contributions decline exponentially in T. We interpret these results as arguing that all exchange terms become negligible relative to the contribution of the direct terms, provided that at short distances the force is strongly repulsive. It should be emphasized that the problem studied in this paper is more complex than the hard-sphere problem we mention above since we have stable bound clusters. To the best of our knowledge no systematic study has been made of exchange effects for cluster integrals when stable clusters are present.

We turn now to the evaluation of the direct-term contributions to b_{ij}. We will compute b_{20}, b_{11}, b_{30}, and b_{02}. This list of cluster integrals involves different few-body scattering processes. The first is a two-body scattering, the next two cluster integrals involve three-body scattering, and the last is a four-body problem.

In order to clarify the logical structure of the proofs that ensue we list the general physical features of scattering theory needed below. They are (a) the wave operator statement of energy conservation and (b) the operator definition of time delay. The proof will also exploit the cyclical invariance property of the trace. We, however, do not attach any physical interpretation to this mathematical property. Rather than develop an abstract general notation suitable to carry out a general evaluation of b_{ij}, it seems more instructive to study several specific cases. To illustrate the situation consider the forms (a) and (b) take in the two-particle problem.

First, (a) is technically known as the intertwining property and is given by the statement

$$h_2 \Omega_2^{(\pm)} = \Omega_2^{(\pm)} h_2^0. \tag{3.5}$$

The notation for the wave operator in Eq. (3.5) has omitted the partition label ξ, since in this case only the partition (1)(2) is possible. Consider the form property (b) takes in the two-body case. For any incident wave packet f the "freely" evolving system is

$$\Phi_2(t) = e^{-ih_2^0 t} f. \tag{3.6}$$

The exact solution $\Psi_2(t)$, whose time displacement is given by h_2, satisfies the boundary condition

$$\lim_{t \to -\infty} \| \Psi_2(t) - \Phi_2(t) \| = 0. \tag{3.7}$$

The $\Psi_2(t)$ determined by Eq. (3.7) is

$$\Psi_2(t) = e^{-ih_2 t} \Omega_2^{(+)} f. \tag{3.8}$$

Recall that $\vec{x}_1$ given by Eq. (2.17) is proportional to the spatial vector separation of the two particles. About the point $\vec{x}_1 = 0$ define a sphere of radius R and let $P(R)$ be the projection operator defined by this sphere: $P(R) f(\vec{x}_1) = f(\vec{x}_1)$ if $|\vec{x}_i| \le R$ and zero if $|\vec{x}_i| > R$. The quantity

$$T_2(R;f) = \int_{-\infty}^{\infty} [\, \| P(R) \Psi_2(t) \|^2 - \| P(R) \Phi_2(t) \|^2]\, dt \tag{3.9}$$

is the difference in transit times across the sphere R for the exact and "free" waves. The Hermitian operator that is related to $T_2(R;f)$ is determined to be

$$\langle \hat{p}_1' | q(E,R) | \hat{p}_1 \rangle = \pi m p \langle \vec{p}' | \Omega_2^{(+)\dagger} P(R) \Omega_2^{(+)} - P(R) | \vec{p} \rangle, \tag{3.10}$$

where

$$T_2(R;f)=2\int f^*(\vec{p}')\frac{\delta(E-E')}{mp}\times\langle\hat{p}'|q(E,R)|\hat{p}\rangle f(\vec{p})\,d\vec{p}\,d\vec{p}'. \qquad (3.11)$$

The momenta $\vec{p}$ appearing in these formula is that defined in (2.18) with $i=1$. The equivalence of expression (3.11) for $T_2(R;f)$ and that of Eq. (3.9) follows from using the intertwining property (3.5) and the evaluation of the time integral. In Eq. (3.10) the $\hat{p},\hat{p}'$ are unit vectors in the direction of $\vec{p}$ and $\vec{p}'$. On the right-hand side of (3.10) the vectors $\vec{p}$ and $\vec{p}'$ have lengths determined by the energy, $E=p_1^2/m=p_1'^2/m$. The family of operators given by the kernels $\langle\hat{p}'|q(E,R)|\hat{p}\rangle$ have a limit when $R\to\infty$ in the sense that there exists an operator $q(E)$ acting on the space of $L^2(\hat{p}_1)$ such that

$$\lim_{R\to\infty}T_2(R;f)=2\int f^*(\vec{p}')\frac{\delta(E-E')}{mp}\times\langle\hat{p}'|q(E)|\hat{p}\rangle f(\vec{p})\,d\vec{p}\,d\vec{p}'. \qquad (3.12)$$

Derivations of this and other two-body time-delay effects may be found in Refs. 2, 5, and 22–24.

We quote without proof the result for $\not{b}_{20}(T)$

$$b_{20}'(T)=\frac{2^{3/2}}{2!\lambda_1^3}\frac{1}{2\pi}\int_0^\infty e^{-\beta E}\operatorname{tr}q(E)\,dE. \qquad (3.13)$$

The prime on $b_{20}'(T)$ reminds us that we have evaluated only the direct part of $\not{b}_{20}(T)$.

The demonstration of Eq. (3.13) may be obtained using the arguments of I or taking the more complex proof of the form for b_{11} given below and tailoring it to the simpler problem here.

It is important to understand the physical character of formula (3.13). The time-delay operator $q(E)$ has a direct relation to the resolvent operators for complex energy z, $r_0(z)=(h_2^0-z)^{-1}$ and $r(z)=(h_2-z)^{-1}$, namely,

$$2\operatorname{Im}\operatorname{Tr}[r(E+i0)-r_0(E+i0)]=\operatorname{tr}q(E). \qquad (3.14)$$

The left-hand side of Eq. (3.14) is easily seen[25] to be the change of state density at energy E produced by the interaction V_2. Thus Eq. (3.13) is just the familiar Laplace transform of the change of state density.

It is useful to have a check on the result found in Eq. (3.13). If one defines an energy-dependent S matrix, $s(E)$, by the relations

$$S_2=\Omega^{(-)\dagger}\Omega^{(+)}, \qquad (3.15)$$

$$\langle\vec{p}'|S_2|\vec{p}\rangle=2(1/mp)\delta(E'-E)\langle\hat{p}'|s(E)|\hat{p}\rangle, \qquad (3.16)$$

then a known[22-24] form for the operator $q(E)$ is

$$q(E)=-is^\dagger(E)\frac{d}{dE}s(E). \qquad (3.17)$$

Placing representation (3.17) into Eq. (3.13) recovers the Beth-Uhlenbeck[26] phase-shift form of the second cluster integral valid for distinguishable particles. One also observes that when the S-matrix form of time delay is placed in Eq. (3.13) then the solution takes the form that Dashen *et al.*[27] describe. An additional feature peculiar to the two-body cluster integral is that we can avoid the direct term expansion and exactly evaluate $\not{b}_{20}$. However, when we go to cluster integrals involving three or more particles we have not yet found a way to represent all the symmetrization effects exactly. So we have chosen to treat all the cluster integrals in the same direct term expansion.

With the computation of the direct part of $\not{b}_{20}$ complete let us consider $\not{b}_{11}$ and $\not{b}_{30}$. Both of these cluster integrals involve three-particle scattering. The first involves a scattering that has two asymptotically free fragments—one fragment a two-particle cluster, another fragment an elementary particle. The second cluster integral involves three fragments, each an elementary particle. Before we can evaluate these cluster integrals it is necessary to understand in greater detail the two-Hilbert-space scattering theory for the three-body problem.

The coordinate systems for the three-body problem are given by Eqs. (2.17) and (2.18). We shall adopt a special notation for these coordinates. Consider the specification of the position of the particles in the center-of-mass frame. Let the permutation η of particles (1,2,3) take on the three cyclical choices—(1,2,3), (2,3,1), and (3,1,2). Then formulas (2.17)–(2.18) give us three sets of Jacobi coordinate variables—$(\vec{x}_{1\eta},\vec{x}_{2\eta})$. We shall relabel these three pairs of vectors, respectively, as $(\vec{y}_3,\vec{x}_3)$, $(\vec{y}_1,\vec{x}_1)$, and $(\vec{y}_2,\vec{x}_2)$. This change of labeling returns us to the notation used in Faddeev's work. Take α,β,γ to be cyclic over (1,2,3), then the variables $(\vec{y}_\alpha,\vec{x}_\alpha)$ have simple physical meanings. The variable $\vec{y}_\alpha$ is the vector separating particles β and γ, whereas $\vec{x}_\alpha$ is the spatial separation of particle α to the center of mass of the pair (β,γ). The momenta conjugate to $(\vec{y}_\alpha,\vec{x}_\alpha)$ will be $(\vec{q}_\alpha,\vec{p}_\alpha)$.

The two-Hilbert-space scattering formalism is the basis of our derivation of the values of $\not{b}_{11}$ and $\not{b}_{30}$. Let us define those features of this formalism used in the proof. As before the allowed partitions ξ of the three particles are (1)(2)(3), (1)(23), (2)(13), (3)(12), which we identify with $\alpha=(0,1,2,3)$. The time evolution of this system is controlled by the various three-body Hamiltonians h_3 and h_3^α, $(\alpha\geq 0)$. For the remainder of the description of the three-body problem we shall drop the ubiquitous subscript 3 appearing on all the Hamiltonians.

Long before or after the collision the motion of the system is determined by the asymptotic Hamiltonians h^α and consists of freely moving particles and clusters. We now want to describe the wave packets that characterize this asymptotic channel motion. Let us consider the α channel. The cluster $(\beta\gamma)$ will be described by the bound-state wave function $\psi(\vec{q}_\alpha)$ that satisfies Eq. (2.32). We shall need an additional function to describe the relative motion of α and the center of mass of the pair $(\beta\gamma)$. Clearly the appropriate variable is $\vec{p}_\alpha$ and we shall indicate the related wave packet by $f_\alpha(\vec{p}_\alpha)$. So the α channel motion is described by $f_\alpha(\vec{p}_\alpha)\psi(\vec{q}_\alpha)$. Since ψ is a known function all the nontrivial information about this channel is given by f_α. For f_α to be an acceptable wave packet it must lie in the space of square integrable functions, viz., $f_\alpha \in \mathfrak{h}_\alpha = L^2(\vec{p}_\alpha)$. Here the symbol $\mathfrak{h}_\alpha$ will represent the Hilbert space $L^2(\vec{p}_\alpha)$. The identity for this space will be represented by E^α. In effect the function f_α is like a two-particle wave packet except that one of the particles is the cluster $(\beta\gamma)$. For the three-free-particle state we have all six degrees of freedom present and the related wave-packet function will have the form $f_0(\vec{p},\vec{q})$. The space for f_0 will be $\mathfrak{h}_0 = L^2(\vec{p},\vec{q})$, and its identity E^0.

At this point it is useful to construct Hamiltonians that act in the channel spaces $\mathfrak{h}_\alpha$. These new Hamiltonians are suggested by the following considerations. The asymptotic motion of the cluster α is given by $f_\alpha(\vec{p}_\alpha)\psi(\vec{q}_\alpha)$. The corresponding Hamiltonian is h^α. One has then

$$h^\alpha f_\alpha(\vec{p}_\alpha)\psi(\vec{q}_\alpha) = \left(\frac{3}{4}\frac{p_\alpha^2}{m} + \frac{q_\alpha^2}{m} + v_\alpha\right) f_\alpha(\vec{p}_\alpha)\psi(\vec{q}_\alpha), \qquad (3.18)$$

where v_α is the two-particle potential for particles β and γ. Using Eq. (2.32) this may be written

$$h^\alpha f_\alpha(\vec{p}_\alpha)\psi(\vec{q}_\alpha) = \psi(\vec{q}_\alpha)\tilde{h}^\alpha f_\alpha(\vec{p}_\alpha). \qquad (3.19)$$

The operator $\tilde{h}^\alpha$ is called a channel Hamiltonian. It operates on the space $\mathfrak{h}_\alpha$ and by comparing Eqs. (3.18) and (3.19) is seen to be

$$\tilde{h}^\alpha = \tfrac{3}{4}p_\alpha^2/m - \epsilon_2, \qquad (3.20)$$

and physically corresponds to the total amount of energy available in the α channel. For the $\alpha = 0$ case there are no stable clusters so that

$$\tilde{h}^0 = h^0. \qquad (3.21)$$

The channel injection operator [denoted $J_{3;\alpha}$ in Eq. (2.29)] is defined as the mapping from the space $\mathfrak{h}_\alpha$ to $\mathfrak{h} = L^2(\vec{p}_\alpha, \vec{q}_\alpha)$ given by

$$[J_{3,\alpha} f_\alpha](\vec{p}_\alpha, \vec{q}_\alpha) = f_\alpha(\vec{p}_\alpha)\psi(\vec{q}_\alpha), \quad \alpha > 0, \qquad (3.22)$$

with $J_{3;0} = E^0$. The adjoint of J_α is easily found to be

$$[J_{3,\alpha}^\dagger f](\vec{p}_\alpha) = \int \psi(\vec{q}_\alpha)^* f(\vec{p}_\alpha, \vec{q}_\alpha)\, d\vec{q}_\alpha, \quad \alpha > 0. \qquad (3.23)$$

The operator $J_{3;\alpha}$ may be used to restate Eq. (3.19) so that it reads

$$h^\alpha J_{3;\alpha} = J_{3;\alpha}\tilde{h}_\alpha. \qquad (3.24)$$

Now the scattering problem may be given a simple statement. Let f_α specify some incident wave packet in channel α. The free evolution of the system is

$$\Phi_\alpha(t) = e^{-ih^\alpha t} J_{3;\alpha} f_\alpha. \qquad (3.25)$$

One seeks the exact solution of the time-dependent Schrödinger equation,

$$i\frac{\partial \Psi_\alpha(t)}{\partial t} = h\Psi_\alpha(t), \qquad (3.26)$$

that evolves from $\Phi_\alpha(t)$, i.e., that satisfies

$$\lim_{t\to-\infty} \| \Psi_\alpha(t) - \Phi_\alpha(t) \| = 0. \qquad (3.27)$$

The unique solution of this problem is given by

$$\Psi_\alpha(t) = e^{-iht}\Omega_{3;\alpha}^{(+)} f_\alpha. \qquad (3.28)$$

Equations (3.28), (3.27), and (3.25) are the basic ingredients from which the multichannel time-delay operator is constructed.

One may now state the technical form features (a) and (b) assumed in the three-particle case. The intertwining property (a) is

$$h\Omega_{3;\alpha}^{(+)} = \Omega_{3;\alpha}^{(+)}\tilde{h}^\alpha. \qquad (3.29)$$

This equation is the abstract form of energy conservation and means that the exact wave function (3.28) has the same energy as the incident wave function (3.25). The second feature of scattering theory (b) needed to construct the solution of the $\not{b}_{11}$ problem is the multichannel time delay. Let us define this observable and write down the Hermitian operator it generates.

Denote by R the radius of a six-dimensional sphere whose origin lies at the three-body center of mass. Associate with this sphere the projection operator $P(R)$ defined by

$$\begin{aligned} P(R)f(\vec{x}_\alpha, \vec{y}_\alpha) &= 0, \text{ if } \frac{1}{\sqrt{3}}x_\alpha^2 + \sqrt{3}y_\alpha^2 > R \\ &= f(\vec{x}_\alpha, \vec{y}_\alpha) \text{ otherwise.} \end{aligned} \qquad (3.30)$$

The combination of x_α^2 and y_α^2 is the radial distance of the point $(\vec{x}_\alpha, \vec{y}_\alpha)$ from the origin. The time delay for the state initiated by f_α is the integral

$$T_{3\alpha}(R; f_\alpha) = \int_{-\infty}^{\infty} [\, \|P(R)\Psi_\alpha(t)\|^2 - \|P(R)\Phi_\alpha(t)\|^2]\, dt. \qquad (3.31)$$

This has the same physical interpretation given earlier to Eq. (3.9). The time-independent operator that also constructs $T_{3\alpha}(R;f_\alpha)$ is[5]

$$\langle \hat{p}_\alpha | q_{\alpha\alpha}(E,R) | \hat{p}'_\alpha\rangle = \tfrac{4}{3}\pi m p_\alpha \langle \vec{p} | \Omega^{(+)\dagger}_{3;\alpha} P(R) \Omega^{(+)}_{3;\alpha} - J^\dagger_{3;\alpha} P(R) J_{3;\alpha} | \vec{p}'_\alpha\rangle, \tag{3.32}$$

where $\vec{p}_\alpha$ and $\vec{p}'_\alpha$ are constrained by energy conservation to be $E = \frac{3}{4}p^2_\alpha/m - \epsilon_2 = \frac{3}{4}p'^2_\alpha/m - \epsilon_2$ for $\alpha > 0$. In terms of the kernel (3.32) $T_{3\alpha}(R;f_\alpha)$ reads

$$T_{3\alpha}(R;f_\alpha) = \frac{3}{2m}\int f^*_\alpha(\vec{p}'_\alpha)\delta(E-E') \times \langle \hat{p}'_\alpha | q_{\alpha\alpha}(E,R) | \hat{p}_\alpha\rangle f_\alpha(\vec{p}_\alpha)\, d\vec{p}_\alpha\, d\vec{p}'_\alpha. \tag{3.33}$$

As in the two-particle case the $R\to\infty$ limit exists and may be represented by an operator $q_{\alpha\alpha}(E)$, viz.,

$$\lim_{R\to\infty} T_{3\alpha}(R,f_\alpha) = \frac{3}{2m}\int f^*_\alpha(\vec{p}'_\alpha)\delta(E-E') \times \langle \hat{p}'_\alpha | q_{\alpha\alpha}(E) | \hat{p}_\alpha\rangle f_\alpha(\hat{p}_\alpha)\, d\vec{p}_\alpha\, d\vec{p}'_\alpha. \tag{3.34}$$

An appealing aspect of the time-delay operator $q_{\alpha\alpha}(E)$ is its simple connection to the multichannel S matrix. Technically the S matrix is a mapping from the Hilbert space $\mathfrak{h}_\beta$ to $\mathfrak{h}_\alpha$ defined by

$$S_{\alpha\beta} = \Omega^{(-)\dagger}_{3;\alpha}\Omega^{(+)}_{3;\beta}. \tag{3.35}$$

From this basic definition one can obtain an energy-dependent family of equivalent reduced S-matrix operators by factoring out the energy δ function in S to give

$$\langle \vec{p}_\alpha | S_{\alpha\beta} | \vec{p}'_\beta\rangle = \frac{3}{2m}\frac{\delta(E-E')}{(p_\alpha p'_\beta)^{1/2}}\langle \hat{p}_\alpha | s_{\alpha\beta}(E) | \hat{p}'_\beta\rangle,$$
$$\langle \vec{p}_0 | S_{0\beta} | \vec{p}'_\beta\rangle = \frac{3^{3/4}}{\sqrt{2}m}\frac{\delta(E-E')}{(p_0 p'_\beta)^{1/2}}\langle \hat{p}_0 | s_{0\beta}(E) | \hat{p}'_\beta\rangle. \tag{3.36}$$

In the notation for momenta we have used $\vec{p}_0$ to represent the six-dimensional point $(\vec{q}_\alpha, \vec{p}_\alpha)$ and $(p_0, \hat{p}_0)$ to represent the spherical coordinate description of $\vec{p}_0$. The relation between the measures associated with $(\vec{p}_\alpha, \vec{q}_\alpha)$ and $\vec{p}_0$ is $p_0^5\, dp_0\, d\hat{p}_0 = d\vec{p}_\alpha\, d\vec{q}_\alpha$. The kernels on the right-hand sides of Eqs. (3.36) define the reduced S-matrix operators. In Ref. 5, it is shown that

$$q_{\alpha\alpha}(E) = -i\sum_{\gamma=0}^{3} s^\dagger_{\gamma\alpha}(E)\frac{d}{dE}s_{\gamma\alpha}(E), \quad \alpha > 0. \tag{3.37}$$

For the collection of channels that involve only two incident fragments, this equation gives us the basic link between $q_{\alpha\alpha}$ and $s_{\alpha\beta}$. This result is not used in the determination of the cluster integrals $\not{b}_{11}$ or $\not{b}_{30}$, but is required if we are to evaluate the time delay for specific potentials. This simple relation (3.37) is altered when one examines the three fragment channel, $\alpha = 0$.[6,30]

With the necessary elements of the three-body scattering formalism described we turn to the computation of $\not{b}_{11}$. The derivation starts from the definition of b_{11} found in Eqs. (2.50d) and (2.51). Thus

$$b_{11}(V,T) = V^{-1}\,\mathrm{Tr}_{(V)}\{S(3)\Lambda[1,1]e^{-\beta H_{3,V^{(\alpha,\beta,\gamma)}}} - (S(2)\Lambda[0,1]e^{-\beta H_{2,V^{(\alpha,\beta)}}})\otimes e^{-\beta H_{1,V^{(\gamma)}}}\}. \tag{3.38}$$

The subscript (V) on the trace means that the trace is evaluated only for coordinate positions that lie inside the volume V. Examine the trace in Eq. (3.38) for the direct terms. Look first at the second term, which basically involves only two-particle scattering. The two-body symmetric projection operator for particles α and β is $S(2) = 2^{-1}(E_2 + T_{\alpha\beta})$. The operator $T_{\alpha\beta}$ is the permutation that transposes α and β. Since the bound-state wave function of particles α and β [ψ in Eq. (2.32)] is symmetric, one has the identity

$$S(2)\Lambda[0,1] = \Lambda[0,1]. \tag{3.39}$$

As a consequence, the symmetry operator has no overall effect on this group of two-body terms. Note also that this term is independent of the particle labels that appear in $H_{2,V}$ and $H_{1,V}$. This is because the particles have identical masses and potential interactions.

The first term in Eq. (3.38) is a three-body scattering operator. Consider the effect of $S(3)$ on this term. The projection operator $S(3)$ is defined as

$$S(3) = (1/3!)(E_3 + T_{\alpha\beta} + T_{\alpha\gamma} + T_{\beta\gamma} + T_{\alpha\beta\gamma} + T^2_{\alpha\beta\gamma}). \tag{3.40}$$

Here $T_{\alpha\beta\gamma}$ is the cyclic permutation of α, β, γ. Again because of the symmetry of $\psi(\vec{q}_\gamma)$ we have

$$T_{\alpha\beta}J_{3;\gamma} = J_{3;\gamma}. \tag{3.41}$$

When Eq. (3.41) is combined with the relations $[T_{\alpha\beta}, h_3] = 0$ and $[T_{\alpha\beta}, h^\gamma_3] = 0$ it follows from the definition of $\Omega^{(+)}_{3;\gamma}$ that

$$T_{\alpha\beta}\Omega^{(+)}_{3;\gamma} = \Omega^{(+)}_{3;\gamma}. \tag{3.42}$$

Thus of the six permutations in $S(3)$, two—E_3 and $T_{\alpha\beta}$—give us the identity when they act on $\Omega^{(+)}_{3;\gamma}$. The other four lead to exchange terms. These exchange terms always transform at least one particle out of the two-body cluster in $\Omega^{(+)}_{3;\gamma}$. The direct term portion of $S(3)$ is then

$$S(3)\Lambda[1,1]=(2/3!)\Lambda[1,1]+\text{exchange terms.} \tag{3.43}$$

The infinite volume limit of the direct part of b_{11} can be written

$$b'_{11}(T)=\frac{3^{3/2}}{\lambda_1^3}\frac{1}{3}\sum_{\alpha=1}^{3}\operatorname{Tr}[\Omega_{3;\alpha}^{(+)}\Omega_{3;\alpha}^{(+)\dagger}e^{-\beta h}-J_{3;\alpha}J_{3;\alpha}^{\dagger}e^{-\beta h^\alpha}]. \tag{3.44}$$

The factor $3^{3/2}\lambda_1^{-3}$ comes from doing the infinite volume center-of-mass integration. The trace is now that of space $\mathfrak{h}_0$.

We connect this expression for b'_{11} to the time-delay operator by several simple steps. The projection operator $P(R)$ converges strongly to the identity E^0 on $\mathfrak{h}_0$. Thus we may insert $P(R)$ before the square bracket term in Eq. (3.44) if we take the $R\to\infty$ limit of the modified expression. So

$$b'_{11}(T)=\frac{3^{3/2}}{\lambda_1^3}\frac{1}{3}\lim_{R\to\infty}\sum_{\alpha=1}^{3}\operatorname{Tr}P(R)[\Omega_{3;\alpha}^{(+)}e^{-\beta\tilde{h}^\alpha}\Omega_{3;\alpha}^{(+)\dagger} -J_{3;\alpha}e^{-\beta\tilde{h}^\alpha}J_{3;\alpha}^{\dagger}]. \tag{3.45}$$

In writing representation (3.45) we have used the intertwining property in the two forms (3.24) and (3.29). Now invoke the cyclic invariance property of the trace to obtain the form of the time-delay operator found in Eq. (3.32). So one has

$$b'_{11}(T)=\frac{3^{3/2}}{\lambda_1^3}\frac{1}{3}\lim_{R\to\infty}\sum_{\alpha=1}^{3}\operatorname{Tr}[\Omega_{3;\alpha}^{(+)\dagger}P(R)\Omega_{3;\alpha}^{(+)} -J_{3;\alpha}^{\dagger}P(R)J_{3;\alpha}]e^{-\beta\tilde{h}^\alpha}. \tag{3.46}$$

The trace here is that appropriate for the space that defines the domain of $\Omega_{3;\alpha}^{(+)}$—namely, the Hilbert space $\mathfrak{h}_\alpha=L^2(\vec{\mathrm{p}}_\alpha)$. This trace may be expressed as an integral over $d\vec{\mathrm{p}}_\alpha$ so that Eq. (3.46) becomes

$$b'_{11}(T)=\frac{3^{3/2}}{\lambda_1^3}\frac{e^{\beta\epsilon_2}}{2\pi}\sum_{\alpha=1}^{3}\frac{1}{3}\int_0^\infty e^{-\beta E}\operatorname{tr}q_{\alpha\alpha}(E-\epsilon_2)\,dE. \tag{3.47}$$

Inside the integral we have the trace of the reduced operator $q_{\alpha\alpha}(E)$, viz.,

$$\operatorname{tr}q_{\alpha\alpha}(E)=\int\langle\hat{p}_\alpha|q_{\alpha\alpha}(E)|\hat{p}_\alpha\rangle d\hat{p}_\alpha. \tag{3.48}$$

Formula (3.47) is our principal result for b'_{11}.

A few general observations about this formula are in order. Like Eq. (3.13) for $b'_{20}(T)$, the form of the cluster integral is a Laplace transform of the trace of the time-delay operator for the scattering processes that are defined by the cluster configuration [1,1]. A new feature in formula (3.47) is that the cluster integral has an exponentially divergent behavior as $T\to 0$. This is a universal aspect of cluster integrals that involve scattering of one or more bound composite objects. Technically this behavior is a consequence of the fact that the scattering continuum of h_3 (which begins at $-\epsilon_2$) is shifted a finite amount from the unperturbed continuous spectrum of h_3^0 (which begins at 0). If one has n bound two-body clusters in the collision process then the factor $e^{\beta\epsilon_2}$ is replaced by $e^{n\beta\epsilon_2}$.

The remaining three-body cluster integral left to evaluate is $\not{b}_{30}$. The analysis in this instance differs from the two cases treated already. The collision involves three fragments all of which are initially free. The absence of stable clusters here makes the formalism look like an N-body extension of the two-body theory. The new element is that disconnected scattering is possible. For example, one may have initial physical states wherein particles β and γ collide, while the third particle is a spatially remote spectator. These states lead to scattering amplitudes characterized by generalized functions and need be analyzed with care.

Prior to finding $\not{b}_{30}$ we must introduce a mathematical description of the disconnected scattering events and provide a suitable definition of time delay in this channel. Let f_0 be any function (wave packet) in $\mathfrak{h}_0$. The free evolution of the system is given by $\Phi_0(t)$ from Eq. (3.25). Likewise the exact state vector for this initial state f_0 is $\Psi_0(t)$ as obtained from Eq. (3.28). Now let us write down time evolving states consistent with a spectator scattering process. Suppose particle α is remote from the pairwise collision of β and γ. Such a state would effectively evolve under the action of the Hamiltonian h_3^α. The time-dependent state vector is

$$\Psi_0^\alpha(t)=e^{-ih_3^\alpha t}W_\alpha^{(+)}f_0, \tag{3.49}$$

where again Ψ_0^α converges to Φ_0 as $t\to-\infty$:

$$\lim_{t\to-\infty}\|\Psi_0^\alpha(t)-\Phi_0(t)\|=0. \tag{3.50}$$

It is not difficult to see that the wave operator $W_\alpha^{(+)}$ must be

$$W_\alpha^{(+)}=E^\alpha\otimes\Omega_2^{(+)}(\beta,\gamma),\quad \alpha>0, \tag{3.51}$$

where E^α is the identity on $\mathfrak{h}_\alpha$ and $\Omega_2^{(+)}(\beta,\gamma)$ is the two-body Moller operator for particles β and γ. These spector wave operators $W_\alpha^{(+)}$ satisfy the intertwining relations

$$h_3^\alpha W_\alpha^{(+)}=W_\alpha^{(+)}h_3^0. \tag{3.52}$$

From these objects we construct the $\alpha=0$ channel three-particle time delay. The goal of our definition is to isolate the delay that is caused by genuine three-particle collisions with the effect of all two-body-like spectator processes removed. The time integral of the difference $\|P(R)\Psi_0(t)\|^2 - \|P(R)\Phi_0(t)\|^2$ would give one a delay that both the genuine and spectator collisions contribute to. On the other hand the integral of the difference $\|P(R)\Psi_0^\alpha(t)\|^2 - \|P(R)\Phi_0(t)\|^2$ is just the delay attributable to the α-spectator component in $\Psi_0(t)$. Removing the effect of all three spectator solutions leads to the definition

$$T(f_0)=\lim_{R\to\infty}\int_{-\infty}^{\infty}\left(\|P(R)\Psi_0(t)\|^2-\sum_{\alpha=1}^{3}\|P(R)\Psi_0^\alpha(t)\|^2+2\|P(R)\Phi_0(t)\|^2\right)dt. \tag{3.53}$$

The function $T(f_0)$ is the connected three-particle time delay for state f_0. This definition can be transformed into a time-independent form. In terms of the spherical coordinate representation $(p_0,\hat{p}_0)$ one finds

$$T(f_0)=\int f(\vec{p}_0)^*\,\frac{\delta(E-E')}{m_0p_0^4}\langle\hat{p}_0|q_{00}(E)|\hat{p}_0'\rangle\,f_0(\vec{p}_0')\,d\vec{p}_0\,d\vec{p}_0', \tag{3.54}$$

where operator $q_{00}(E)$ is the $R\to\infty$ weak limit of

$$\langle\hat{p}_0|q_{00}(E,R)|\hat{p}_0'\rangle=2\pi m_0p_0^4\langle\mathrm{p}_0|\,\Omega_{3;0}^{(+)\dagger}P(R)\Omega_{3;0}^{(+)}-\sum_{\alpha=1}^{3}W_\alpha^{(+)\dagger}P(R)W_\alpha^{(+)}+2P(R)\,|\vec{\mathrm{p}}_0'\rangle. \tag{3.55}$$

The length of the radial vector $\vec{\mathrm{p}}_0$ is given by

$$p_0^2/2m_0=\tfrac{3}{4}p_\alpha^2/m+q_\alpha^2/m=h_3^0\,, \tag{3.56}$$

where $m_0=3^{-1/2}\,m$.

All the necessary structures for the computation of $\not{b}_{30}(T)$ are in hand. Again the derivation will rest on (a) the intertwining property as stated in Eqs. (3.29) and (3.52) and (b) the definition of the connected three-particle time delay, Eq. (3.55). The formula for $b_{30}(V,T)$ given by Eqs. (2.50e) and (2.51) is

$$b_{30}(V,T)=\mathrm{Tr}_{(V)}\{S(3)\Lambda^{(+)}[3,0]e^{-\beta H_{3},V^{(\alpha,\beta,\gamma)}}+\tfrac{1}{3}e^{\beta H_3^0,V^{(\alpha,\beta,\gamma)}}-(S(2)\Lambda^{(+)}[2,0]e^{-\beta H_2,V^{(\alpha,\beta)}})\otimes e^{-\beta H_1,V^{(\gamma)}}\}. \tag{3.57}$$

Consider the direct and exchange term expansion of $b_{30}(V,T)$. Because there are no bound clusters the direct term for the symmetric projections $S(n)$ is $(1/n!)E_n$. All other terms are exchange terms. Thus the direct part of $\not{b}_{30}(T)$ in the infinite volume limit is

$$b_{30}'(T)=\frac{3^{3/2}}{\lambda_1^3}\,\frac{1}{3!}\mathrm{Tr}\left(\Omega_{3;0}^{(+)}\Omega_{3;0}^{(+)\dagger}e^{-\beta h}-\sum_{\alpha=1}^{3}W_\alpha^{(+)}W_\alpha^{(+)\dagger}e^{-\beta h^\alpha}+2e^{-\beta h^0}\right). \tag{3.58}$$

The center-of-mass integral in b_{30}' has been completed leading to the thermal wavelength factor $\lambda_1^{-3}3^{3/2}$. Now introduce the operator $P(R)$ and take limit $R\to\infty$. So Eq. (3.58) can be modified to read

$$b_{30}'(T)=\frac{3^{3/2}}{\lambda_1^3}\,\frac{1}{3!}\lim_{R\to\infty}\mathrm{Tr}P(R)\times\left(\Omega_{3;0}^{(+)}e^{-\beta h^0}\Omega_{3;0}^{(+)\dagger}-\sum_{\alpha=1}^{3}W_\alpha^{(+)}e^{-\beta h^0}W_\alpha^{(+)\dagger}+2e^{-\beta h^0}\right). \tag{3.59}$$

The cyclical invariance property of the trace allows us to write

$$b_{30}'(T)=\frac{3^{3/2}}{\lambda_1^3}\,\frac{1}{3!}\lim_{R\to\infty}\mathrm{Tr}\left(\Omega_{3;0}^{(+)\dagger}P(R)\Omega_{3;0}^{(+)}-\sum_{\alpha=1}^{3}W_\alpha^{(+)\dagger}P(R)W_\alpha^{(+)}+2P(R)\right)e^{-\beta h^0}. \tag{3.60}$$

By comparison with Eq. (3.55) and the introduction of the diagonal form for the trace gives the final result

$$b_{30}'(T)=\frac{3^{3/2}}{\lambda_1^3}\,\frac{1}{3!}\,\frac{1}{2\pi}\int_0^\infty e^{-\beta E}\,\mathrm{tr}q_{00}(E)\,dE, \tag{3.61}$$

where

$$\mathrm{tr}\,q_{00}(E)=\int\langle\hat{p}_0|q_{00}(E)|\hat{p}_0\rangle\,d\hat{p}_0. \tag{3.62}$$

If Eq. (3.61) is contrasted with the formula for $b_{11}'(T)$ we see that there is no exponential dependence on $\beta\epsilon_2$ in $b_{30}'(T)$. This is because the three fragments that appear in $b_{30}'(T)$ are all elementary and not stable clusters.

The result arrived at in Eq. (3.61) is similar to the one given by Bedeaux.[28] One difference is the Bedeaux considers only the problem of a quantum gas that does not have stable clusters, so he evaluates $\not{b}_3(T)$ instead of our modified cluster integral $b'_{30}(T)$. Also, of course, the time delay and S-matrix operators differ substantially in the two problems.

IV. THERMODYNAMICS

The previous section has demonstrated how to obtain explicit expressions for the multicomponent cluster integrals that appear in the two-fugacity grand partition function. This section begins with a brief consolidation of the cluster integral results. Then we present the forms of several of the functions that determine the thermodynamic behavior of the system. We compute formulas for the two-density virial coefficients that define the multicomponent equation of states. The chemical mass action law predicts the ratio of species as a function of temperature when the species are assumed to behave like an ideal gas. A general form of the chemical mass action law is found and the effect of the interactions between particles is determined in terms of a density expansion. The section also includes a study of the internal energy of the system. Again a virial-like density expansion for the internal energy is given and the coefficients in this expansion exhibited.

Consider a generalized notation for the cluster integrals. Two cluster integrals do not involve scattering. These are $\not{b}_{10}(T)$ and $\not{b}_{01}(T)$. Their values,

$$\not{b}_{10}(T)=\lambda_1^{-3}, \quad \not{b}_{01}(T)=\lambda_2^{-3}e^{\beta\epsilon_2}, \tag{4.1}$$

follow directly from their definitions. Here λ_2 is the thermal wave length for the bound cluster having mass $2m$. All other cluster integrals involve scattering. We claim the general solution may be written

$$b'_{ij}(T)=\frac{e^{j\beta\epsilon_2}}{\lambda_1^3}\frac{(i+2j)^{3/2}}{i\,!j!}L_{ij}(\beta), \tag{4.2}$$

where $L_{ij}(\beta)$ is the Laplace transform in the energy variable of the ij-channel time delay:

$$L_{ij}(\beta)=\frac{1}{2\pi}\int_0^\infty e^{-\beta E}t_{ij}(E)\,dE. \tag{4.3}$$

The real function $t_{ij}(E)$ is the trace of the time-delay operator for $n=i+2j$ body scattering for distinguishable particles. The boundary conditions for this n-body scattering is that it be initiated in one of the (identical) channels specified by $[i,j]$. We have demonstrated that

$$t_{20}(E)=\operatorname{tr}q(E), \tag{4.4a}$$

$$t_{11}(E)=\operatorname{tr}q_{\alpha\alpha}(E-\epsilon_2), \quad \alpha>0 \tag{4.4b}$$

$$t_{30}(E)=\operatorname{tr}q_{00}(E). \tag{4.4c}$$

In Eq. (4.4b) any value of $\alpha(=1,2,3)$ may be used since the fact that potentials are the same between all pairs of particles means that all $q_{\alpha\alpha}$ $(\alpha<0)$ have the same trace. We have also evaluated the result for b'_{02}, the four-body two-on-two channel. The proof has been omitted from Sec. III since it is nearly a copy of the proof for b'_{11}. One only need to replace the three-body channel injection operator $J_{3;\xi}$ by its four-body counterpart and use the analogous four-body wave operators.

Of course the formulas (4.3) give only the direct term contributions to $\not{b}_{ij}$—all cluster-destroying exchange terms have been dropped. We expect formulas (4.2), (4.3), and (4.4) to be valid for all values of i and j. This expectation is based on the observation that only two universal properties of two-Hilbert-space scattering theory—(a) the intertwining property and (b) the definition of a connected n-body time-delay operator—are needed to derive (4.4a)–(4.4c). A last comment concerns the statistical factor $1/(i!j!)$ appearing in Eq. (4.2). This factor is $1/n!$ of the number of different channels labeled by $[i,j]$ times the number of distinct permutation operators in $S(i+2j)$ that leave the $[i,j]$ cluster structure invariant. There are $n!/[i!(2!)^j j!]$ channels and 2^j invariant permutation operators.

Let us turn now to the virial equation of state. Using Eqs. (2.55a)–(2.55e) and substituting Eqs. (4.1)–(4.4) leads to

$$a_{20}(T)=-\lambda_1^3 2^{1/2}\frac{1}{2\pi}\int_0^\infty e^{-\beta E}t_{20}(E)\,dE, \tag{4.5}$$

$$a_{11}(T)=-\lambda_1^3\left(\frac{3}{2}\right)^{3/2}\frac{1}{2\pi}\int_0^\infty e^{-\beta E}t_{11}(E)\,dE, \tag{4.6}$$

$$a_{02}(T)=-\lambda_2^3 2^{1/2}\frac{1}{2\pi}\int_0^\infty e^{-\beta E}t_{02}(E)\,dE, \tag{4.7}$$

$$\begin{aligned}a_{30}(T)={}&\lambda_1^6 4\left(\frac{2^{3/2}}{2!}\frac{1}{2\pi}\int_0^\infty e^{-\beta E}t_{20}(E)\,dE\right)^2\\&-\lambda_1^6 2\,\frac{3^{3/2}}{3!}\frac{1}{2\pi}\int_0^\infty e^{-\beta E}t_{30}(E)\,dE,\end{aligned} \tag{4.8}$$

etc. A number of interesting features appear in these equations for $a_{ij}(T)$. The principal effect of the fact that b_{ij} is cluster integral with j separate two-body bound states is the exponential $e^{j\beta\epsilon_2}$ term in Eq. (4.2). This term diverges as $T\to 0$ and so dominates the behavior of Eq. (4.2) for small $(kT\ll\epsilon_2)$ T. We note, however, in all the formulas for a_{ij} that the exponential behavior and all dependence on ϵ_2 is cancelled out. Basically the effect of a factor $e^{j\beta\epsilon_2}$ is to control the relative amounts of N_1 and N_2 and has no effect on the multispecies virial. By way of contrast examine the one density equation of state (2.2). Here the virial is

$$a_2(T)=-\lambda_1^3\left(2^{3/2}e^{\beta\epsilon_2}+\frac{2^{3/2}}{2!}\frac{1}{2\pi}\int_0^\infty e^{-\beta E}t_{20}(E)\,dE\right). \quad (4.9)$$

This equation retains the exponential in ϵ_2 because the equation of state (2.2) does not reflect the two-species character of the system.

An attractive feature of our formulas for the virials $a_{ij}(T)$ is that each depends on just the scattering process determined by its ij label. For example, $a_{11}(T)$ is controlled by the scattering of one free particle from one free cluster. Another conclusion emerging from these equations is obtained by comparing $a_{20}(T)$ and $a_{02}(T)$. These virials both relate to the scattering of two fragments. In the first, $a_{20}(T)$, the fragments are elementary. In the second they are composite two-body clusters. Nevertheless the structure of the formula for the two virials is identical if one changes the thermal wavelength to include the mass of the fragment. All of the composite effects in the four-body $a_{02}(T)$ are confined to the function $t_{02}(E)$—the four-body time delay.

The formulas (4.5)–(4.8) also provide a simple physical picture of the role of the microscopic scattering process in determining the behavior of the equation of state. If V and T are held fixed, then for $t_{ij}(E)>0$ the pressure is decreased relative to the multispecies ideal gas law. If $t_{ij}(E)<0$, the case for repulsive potentials, then the pressure is increased. The condition $t_{ij}(E)>0$ implies the fragments may stay together in the collision process longer than the same fragments but evolve without interfragment interactions. Thus the interactions are effectively creating extra space for the particles to exist in relation to free-particle dynamics. This is a quantum version the co-volume approximation used in obtaining the van der Waals equation of state. Here the equivalent prohibited co-volume is the relative velocity of the fragments multiplied by the time delay. This effective restricted volume depends on the energy of the collision process and may be both positive and negative in magnitude.

The next thermodynamic function that we shall discuss is the internal energy of our system. The energy U is defined from the grand partition function to be

$$U=\frac{-\partial}{\partial\beta}\ln\Xi_2\Big|_{z_1,z_2}. \quad (4.10)$$

In terms of the cluster integrals the energy per unit volume is determined from Eq. (4.10) to have the form

$$\frac{U}{V}=-\sum_{ij}^{\infty}\frac{\partial}{\partial\beta}\not{b}_{ij}z_1^iz_2^j. \quad (4.11)$$

The fugacity dependence z_1 and z_2 will be eliminated and Eq. (4.11) replaced by a density expansion in ρ_1 and ρ_2. Two identities control the following results:

$$\frac{\partial}{\partial\beta}\frac{1}{\lambda_1^3}=-\frac{1}{\lambda_1^3}(\tfrac{3}{2}kT), \quad (4.12)$$

$$\frac{\partial}{\partial\beta}\not{b}_{ij}=j\epsilon_2\not{b}_{ij}-\tfrac{3}{2}kT\not{b}_{ij}+\not{b}_{ij}\frac{\partial}{\partial\beta}\ln L_{ij}(\beta). \quad (4.13)$$

The first follows from the definition of the thermal wavelength, the second from the relation (4.2).

We define the general form of a multidensity expansion of the internal energy to be

$$\frac{U+\epsilon_2N_2}{V}=\sum_{ij}c_{ij}(T)\rho_1^i\rho_2^j, \quad (4.14)$$

and seek to determine the coefficients $c_{ij}(T)$. If we substitute Eq. (4.13) and the fugacity density expansions (2.53) and (2.54) we find that Eq. (4.14) becomes

$$\sum_{ij}\not{b}_{ij}\;\frac{3}{2}kT-\frac{\partial}{\partial\beta}\ln L_{ij}\;z_1^iz_2^j$$
$$=\sum_{ij}c_{ij}\left(\sum_{i'j'}i'b_{i'j'}z_1^{i'}z_2^{j'}\right)^i\left(\sum_{i''j''}j''b_{i''j''}z_1^{i''}z_2^{j''}\right)^j. \quad (4.15)$$

Equating the coefficients of the linear terms in z_1 and z_2 leads at once to

$$c_{10}=c_{01}=\tfrac{3}{2}kT. \quad (4.16)$$

Thus Eq. (4.14) becomes

$$U(T)=\tfrac{3}{2}kT(N_1+N_2)-N_2\epsilon_2+V\sum_{i+j\geq 2}c_{ij}(T)\rho_1^i\rho_2^j. \quad (4.17)$$

The first two terms here provide us with the result of the equipartition theorem. The third term is the energy stored in the N_2 bound clusters. The last term is clearly the energy of interaction of all the particles in the gas and vanishes as the density of the system N/V goes to zero.

Let us compute quadratic terms in this density expansion, that is, all c_{ij} with $i+j=2$. Equating the coefficients of z_1^2, z_1z_2, and z_2^2 in Eq. (4.15) determines, these quadratic c_{ij}. A little algebra shows

$$c_{ij}(T)=\lambda_1^3d_{ij}\frac{1}{2\pi}\int_0^\infty(E-\tfrac{3}{2}kT)e^{-\beta E}t_{ij}(E)\,dE; \quad (4.18)$$

where

$$d_{20}=d_{11}=\sqrt{2},\quad d_{02}=4,\quad i+j=2. \quad (4.19)$$

So again we have found that density deviations of the internal energy from that of a two-component ideal gas is proportional to a Laplace transform of the weighted time-delay structure $(E - \frac{3}{2}kT) \times t_{ij}(E)$. In calculating specific heats from Eq. (4.17) one must recall that both N_1 and N_2 are temperature dependent.

The last thermodynamic aspect we treat is the chemical mass action law. For the simple chemical reaction in this problem this law states that ρ_1^2/ρ_2 is a constant dependent only on temperature. This is strictly true only in the limit of ideal gases. We shall express the deviations from this ideal-gas behavior by a density expansion. Computing the ratio ρ_1^2/ρ_2 by employing the cluster integral expansions (2.53) and (2.54) will give us series expressions in the fugacity variables z_1 and z_2. To eliminate these variables in favor of density variables consider the inverse of Eqs. (2.53) and (2.54), viz.,

$$z_1 = \frac{\rho_1}{b_{10}} - 2\frac{b_{20}}{b_{10}^3}\rho_1^2 - \frac{b_{11}}{b_{10}^2 b_{01}}\rho_1\rho_2 + \cdots , \tag{4.20}$$

$$z_2 = \frac{\rho_2}{b_{01}} - 2\frac{b_{02}}{b_{01}^3}\rho_2^2 - \frac{b_{11}}{b_{10} b_{01}^2}\rho_1\rho_2 + \cdots . \tag{4.21}$$

Now find ρ_1^2/ρ_2 by computing the ratio of $b_{01}z_2\rho_2$ and $(b_{10}z_1\rho_1)^2$. Use the fact that at equilibrium $z_1^2 = z_2$. After a little algebra one obtains

$$\frac{\rho_1^2}{\rho_2} = \frac{e^{-\beta\epsilon_2}}{2^{3/2}\lambda_1^3}\left[1 + \left(4\frac{b_{20}}{b_{10}^2} - \frac{b_{11}}{b_{10}b_{01}}\right)\rho_1 + \left(\frac{2b_{11}}{b_{10}b_{01}} - \frac{2b_{02}}{b_{01}^2}\right)\rho_2 + \cdots\right]. \tag{4.22}$$

The temperature-dependent factors multiplying ρ_1 and ρ_2 are

$$4\frac{b_{20}}{b_{10}^2} - \frac{b_{11}}{b_{10}b_{01}} = \frac{\lambda_1^3}{2\pi}\int_0^\infty e^{-\beta E}[2^{5/2}t_{20}(E) - (\tfrac{3}{2})^{3/2}t_{11}(E)]\,dE , \tag{4.23}$$

$$\frac{2b_{11}}{b_{10}b_{01}} - \frac{2b_{02}}{b_{01}^2} = \frac{\lambda_1^2}{2\pi}\int_0^\infty e^{-\beta E}[2(\tfrac{3}{2})^{3/2}t_{11}(E) - t_{02}(E)]\,dE . \tag{4.24}$$

Equation (4.22) represents our expansion of the chemical mass action law. The first term gives just the standard ideal-gas result. The density-dependent terms exhibit the deviation from the ideal behavior produced by the collision processes in the gas. The term proportional to ρ_1 is dominant at high temperatures ($kT \gg \epsilon_2$) and the ρ_2 term dominant at low temperatures ($kT \ll \epsilon_2$). In this calculation we find again that the coefficients of the expansion are independent of the cluster binding energy ϵ_2. This bound-state energy only enters the multiplicative factor in representation (4.22).

Consider for a moment the relation between the equation of state Eq. (2.2) and the expansion (4.22). If one wants to compute the pressure P from Eq. (2.2), knowledge of the virials $a_{ij}(T)$ is insufficient. One must also know ρ_1 and ρ_2 as a function of temperature. Since the total density $\rho = N/V$ is independent of temperature one may use

$$\rho = \rho_1 + 2\rho_2 \tag{4.25}$$

to write Eq. (4.22) as an equation in one variable, say ρ_1. Thus Eq. (4.22) determines ρ_1 and ρ_2. As a consequence the state of the system is only completely determined when the multispecies equation of state Eq. (2.2) is combined with the generalized chemical mass action law Eq. (4.22).

V. CONCLUSIONS

We have provided a thorough investigation of an interacting quantum gas, wherein the bound-state and continuum behavior of this N-particle system are treated simultaneously. Basically the existence of the stable clusters has forced on us a modified definition of the canonical partition function that rests on the n-particle asymptotic completeness theorem. We obtain the cluster integral expansion for this multispecies gas and evaluate these cluster integrals in terms of appropriate Laplace transforms of the trace of the multichannel time-delay operators. In exhibiting the equation of state, the internal energy, and the nonideal version of the chemical mass action law, the role of the bound cluster has been completely described.

In the two-particle cluster integral problem Uhlenbeck and Beth[26] long ago constructed a solution that employs just the derivatives of partial-wave phase shifts. In the three-body cluster integral problem for the case where there are no two-body bound states (and thus no multichannel aspect), Larsen and Mascheroni[29] found a representation of the solution in terms of three-body phase shifts. We note, however, that when a stable two-particle cluster exists then these phase shift solutions for $\not{b}_3(T)$ must fail or undergo substantial modification. Collision processes like breakup, where the initial and final state differ by three continuous degrees of freedom, have not yet been given any phase shift description. What is taking place in this example for the term $b_{11}(T)$ is that the trace of the time delay operator is replacing the phase shift as the general descriptor of the scattering process.

At a fundamental level our solution for the multispecies equation of state and the other thermodynamic functions exhibit the precise relationship between the details of the microscopic quantum scattering and the macroscopic behavior of the system. Our solutions show that the only aspect of the collision process that has any effect on the thermodynamic behavior of the system is time delay. In the scattering channels where there are only two asymptotic fragments a simple relationship with the S matrix as indicated in Eqs. (3.17) and (3.37) exists. Here the time-delay operator may be thought of as the logarithmic energy derivative of the multichannel S matrix. The case of three free fragments shows that the time delay must be expressed as a connected group of logarithmic S-matrix operators[6] plus a term due to the known three-body rescattering singularities. The appropriate formulas are given by Buslaev and Merkuriev.[30] These formulas indicate that the three fragment channel has a time delay that is still just a function of S-matrix operators. Thus all the cluster integrals may be written as functions of S-matrix operators. This important fact has been stressed by Dashen *et al.*[27] Through the cluster representation of the grand partition function one now has an S-matrix definition of statistical mechanics. In high-energy particle physics often one will have an S-matrix description of systems for which there is no Hamiltonian. In this case we may use the S-matrix form of the grand canonical partition function as a natural although admittedly *ad hoc* extension of statistical mechanics.

At a practical level we anticipate that our solutions will be an appropriate starting point for realistic calculations of the higher virials. Equations (4.2) and (4.3) would seem to be the place to introduce either classical or semiclassical approximations for the cluster integrals. Note that one can use either the time delay or S-matrix realizations of our results in attempting to find new approximations. As a simple example consider the computation of $a_{02}(T)$. This virial coefficient dominates the equation of state at low temperatures where $\rho_2 \gg \rho_1$. To find a_{02} exactly one needs to solve the four-body scattering problem. However, for low collision energies $kT < e_2$, the two clusters will scatter without breaking up. Thus we can introduce an effective intercluster potential and treat the scattering as a two-body problem. From this two-body problem we can compute the phase shifts from Schrödinger's equation and so arrive at an expression for the four-body time delay

$$t_{02}(E) = 2\sum_{l=0} (2l+1)\frac{d\delta^l_{02}(E)}{dE} . \tag{5.1}$$

This procedure in fact is the one followed in introducing the Lennard-Jones potential to approximate the atom-atom interaction in treating nonideal gases. Clearly this approach ignores the composite character of the atoms.

A second practical calculation to be expected from these results is to use them to predict the high-temperature behavior of the virials $a_{ij}(T)$. One can on the basis of the spectral property for time delay develop few-body Levinson's theorems valid for the scattering of an entire wave without the introduction of a partial-wave analysis.[31] It is then expected that these theorems will dominate the high-temperature behavior of the virial coefficients.

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