Moderately dense gas quantum kinetic theory: Aspects of pair correlations

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A recently formulated density corrected quantum Boltzmann equation emphasizes the need to explicitly include pair correlations and the conversion of kinetic energy to potential energy as important effects in the kinetic theory of moderately dense gases. This paper first considers an appropriate evolution equation for the pair correlations which includes their decay via interactions with other particles in the gas. The molecular description is given of such a gas close to local thermal equilibrium, together with expressions for the associated hydrodynamic variables. Wigner functions are used to uniquely separate macroscopic and microscopic properties. An accompanying paper solves the combination of linearized Boltzmann and correlated pair equations to obtain expressions for the transport coefficients. © 1996 American Institute of Physics. [S0021-9606(96)51032-9]

I. INTRODUCTION

One of the authors has proposed[1] that pair correlations should be explicitly taken into account when formulating density corrections to the quantum Boltzmann equation. Essentially this recognizes that the singlet density operator $\rho^{(1)}$ represents particles that are correlated with other particles in the gas as well as particles that are free. This is written for particle labelled 1 as

$$\rho_1^{(1)} = \rho_{f1} + \rho_{c1}. \tag{1}$$

At equilibrium, the free particle contribution ρ_f is Maxwellian while the correlated pair contribution ρ_c includes a second virial coefficient type of contribution.[2] The modification of the quantum Boltzmann equation that includes *all* pair particle effects is then written

$$i\hbar \frac{\partial(\rho_{f1} + \rho_{c1})}{\partial t} = [H_1^{(1)}, \rho_{f1} + \rho_{c1}]_- $$
$$+ \mathrm{Tr}_2[V, \Omega \rho_{f1}\rho_{f2}\Omega^\dagger]_-, \tag{2}$$

where Ω is the Møller operator for binary collisions arising from the potential V and $H_1^{(1)}$ is the one particle Hamiltonian for particle 1. It was argued[1] that binary correlations arise from isolated bimolecular collisions so that the correlations between particles 1 and 2 are given by

$$\rho_{c12} = \Omega \rho_{f1}\rho_{f2}\Omega^\dagger - \rho_{f1}\rho_{f2} \tag{3}$$

and the correlated contribution to the singlet is

$$\rho_{c1} = \mathrm{Tr}_2\rho_{c12}. \tag{4}$$

[Tr_2 is the trace over all states of particle 2.] Equation (2) thus constitutes an equation for the free density operator ρ_f, from which the full singlet density operator can be calculated using Eqs. (1), (3) and (4).

Laloë and Mullin[3] have also arrived at the notion that one must explicitly distinguish a free particle density operator from the singlet density operator. Their method of formulating this distinction differs from what was proposed in Ref. 1, specifically they consider that the pair density operator used for collisions should be such that it factors both before and after the collision. We see this as being contrary to the spirit of the Boltzmann Stosszahlansatz and that a factorization before the collision is all that should be required. However in attempting to use Eq. (2) to calculate transport coefficients, it was discovered that the pair correlation density operator of Eq. (3) gives rise to divergent contributions when the gas is inhomogeneous. These are directly attributable to the long time persistence of correlations once they have been created. Laloë and Mullin's approach would eliminate such problems. Our alternate approach, as proposed in the present work, is to recognize that Eq. (3) for the pair correlation is an approximation, specifically ignoring the presence of other particles in the gas, whose effect would be, in part, to cause the pair correlations to decay to their local equilibrium values by means of the interaction with other particles in the gas. Explicitly this work incorporates a correlation decay rate into the formula for the pair correlation density operator so as to model this effect. Since the pair correlations are dynamic associations of a pair of particles without having a definite molecular structure, the equation governing the operator ρ_{c12} representing a correlated pair, see Sec. II, is written as a dynamic equation whose out-of-equilibrium solution should be solved by a steady state approximation method, see the following paper.

Equations of change for the number density n, stream velocity $\mathbf{v}_0$ and kinetic energy ε^K are easily derived from the density corrected quantum Boltzmann equation using operator methods. The explicit operator definitions of these quantities and the equations of change are given in Ref. 1. In later sections it will be more useful to have the equivalent phase space expressions for the various fluid dynamic quantities and these are developed in Sec. III. But the equations of change are independent of the detailed method of how the

various quantities are to be expressed and these are summarized as follows: the equation of continuity

$$\frac{\partial n}{\partial t} = -\nabla \cdot (n \mathbf{v}_0), \tag{5}$$

the equation of motion

$$nm \frac{\partial \mathbf{v}_0}{\partial t} + nm \mathbf{v}_0 \cdot \nabla \mathbf{v}_0 = -\nabla \cdot \mathsf{P} \tag{6}$$

where P is the pressure tensor and m is the particle mass; and the kinetic energy equation

$$\frac{\partial n \varepsilon^K}{\partial t} = -\nabla \cdot (n \mathbf{v}_0 \varepsilon^K + \mathbf{q}^K + \mathbf{q}_{\text{coll}}) - \mathsf{P}^t : \nabla \mathbf{v}_0 + \sigma^K. \tag{7}$$

Here the transpose P^t of the pressure tensor P enters to couple the convective energy to the ''internal'' kinetic energy per particle ε^K while heat flux contributions associated with ''kinetic'' $\mathbf{q}^K$ and ''collisional'' $\mathbf{q}_{\text{coll}}$ motion describe the conductive flow of kinetic energy. Finally there is a ''production'' term σ^K which allows the transfer between kinetic and potential energy. While the equations of continuity and motion are consistent with the conservation of number of particles and total momentum, the presence of the production term in the kinetic energy implies that the total kinetic energy is not conserved because of possible conversion to potential energy. Thus it is necessary to look at the equation of change for the potential energy per particle ε^V. In Ref. 1 this was obtained in a manner consistent with pair particle interactions and shown to be of the form

$$\frac{\partial n \varepsilon^V}{\partial t} = -\nabla \cdot (n \mathbf{v}_0 \varepsilon^V + \mathbf{q}^V) - \sigma^K, \tag{8}$$

where the productions of potential and kinetic energy exactly cancel and there is the added heat flux contribution $\mathbf{q}^V$ associated with conductive potential energy flow.

In this work the gas is treated as having only small deviations from local equilibrium and the Chapman-Enskog[4–8] approach is used in the following paper to get estimates for the deviations of the free density operator ρ_f and of the correlated pair operator ρ_{c12} from local equilibrium. This is then used to obtain expressions for the transport coefficients including the collisional transfer contributions. There are other density corrections which arise from triple collision and bound state effects, but these are not considered in the present treatment. Rather the emphasis is to understand the role of pair correlations in gas transport theory. There is a close parallel to an earlier[9] classical treatment of the inhomogeneous corrections to the Boltzmann collision operator, but at that time no distinction was made between total and free single particle distribution functions, nor was the potential energy equation included in that treatment. Yet that theory is the basis of recent[10] successful estimates of the density corrections to the transport coefficients after inclusion of three body and atom-bound state collisional contributions.

The development of this formulation requires in particular an expansion about local equilibrium in powers of the position gradient. As an operator formalism complicates this expansion because position and momentum do not commute, it is useful to use a representation in which such an expansion can be more easily carried out. The Wigner function[11] formulation is very convenient for this purpose so it is used for the description of local equilibrium and the gradient deviations from local equilibrium, for both the free particles and the center of mass motion of the correlated pairs. In contrast, the relative motion of correlated pairs and of collision processes are written in operator form. The essential reason for this difference in description is that the Wigner function allows the specification of both the macroscopic position dependence of the density, stream velocity and temperature that parameterize the density operators and the microscopic local Maxwellian momentum distribution. In contrast, the relative motion is a purely local (microscopic) effect, so needs no distinction in character between its position and momentum dependence.

II. EQUATION FOR THE PAIR CORRELATIONS

Dilute gas kinetic theory is based on the Boltzmann equation, which essentially treats all particles as being independent (free) except when they are in the midst of a collision. Reference 1 takes the approach that for describing density corrections to dilute gas behaviour, it is necessary to explicitly account for pair correlation effects. Inherent in this description is the notion that the gas can be thought of, except during isolated collision processes, as consisting of free particles and *independent* correlated pairs. Specifically a correlated pair is neither correlated nor interacting with any third particle, except again during an isolated collision event. For an N-particle gas this implies that, except during collisions, the N-particle density operator can be considered to have the structure, called the binary correlation approximation in Ref. 1,

$$\rho^{(N)} \approx \sum_{N_c=0}^{[N/2]} \sum_{\alpha, \gamma} \prod_{i \epsilon \alpha} \rho_{fi} \prod_{(jk) \epsilon \gamma} \rho_{cjk}, \tag{9}$$

where α is a listing of which particles are free, γ a listing of which N_c pairs are correlated, and the sums are over all possible listings and over all possible numbers of correlated pairs, up to the maximum, the integer less than or equal to $N/2$. Reference 1 considered the pair correlations as arising from binary collisions and emphasized how the interaction between two *free* particles leads to correlations with Eq. (3) as the result. However, in trying to implement that work it was found that divergent effects arise when the free density operator is inhomogeneous. In contrast, the present approach is to consider that the pair correlations are determined dynamically by a kinetic equation that includes their decay due to interactions with other (third) particles. The object of this section is to present a kinetic equation appropriately describing these effects. Since pair correlations represent a loose association of a pair of molecules, it is reasonable that their dynamics is described by aspects of the quantum Liouville equation, in particular their interaction with a third particle, rather than in terms of isolated collision events. Thus the

decay terms are modelled here by a linear relaxation rate towards equilibrium, due to interactions with the more abundant freely moving particles.

For the present purposes it is necessary to recognize that three particle correlations, density operator ρ_{c123}, need to be taken into account. Thus the obvious changes must be made to Eq. (9) to include all possible ways of distributing particles between free, pair correlations and triple correlations. It is understood that the correlation density operators always describe *isolated* sets of correlated particles. The singlet, pair and triplet density operators deduced from this structure are

$$\rho_1^{(1)} \equiv N\text{Tr}_{2\ldots N}\rho^{(N)} = \rho_{f1} + \text{Tr}_2\rho_{c12} + \tfrac{1}{2}\text{Tr}_{23}\rho_{c123}, \quad (10)$$

$$\rho_{12}^{(2)} \equiv N(N-1)\text{Tr}_{3\ldots N}\rho^{(N)} = \rho_1^{(1)}\rho_2^{(1)} + \rho_{c12} + \text{Tr}_3\rho_{c123}, \quad (11)$$

and

$$\rho_{123}^{(3)} \equiv N(N-1)(N-2)\text{Tr}_{4\ldots N}\rho^{(N)}$$
$$= \rho_1^{(1)}\rho_2^{(1)}\rho_3^{(1)} + \rho_{c12}\rho_3^{(1)} + \rho_{c23}\rho_1^{(1)}$$
$$+ \rho_{c13}\rho_2^{(1)} + \rho_{c123}, \quad (12)$$

where some simplifications have been made based on taking N very large. These equations are interpreted as being an appropriate description of the gas between interactions of the different groups of correlated particles.

Equations of change for the reduced density operators are given by the BBGKY hierarchy.[4–7] The first BBGKY equation together with Eqs. (3) and (10) were used in Ref. 1 to obtain the modified Boltzmann equation (2). Here it is the second BBGKY equation

$$i\frac{\partial\rho_{12}^{(2)}}{\partial t} = \mathscr{L}_{12}^{(2)}\rho_{12}^{(2)} + \text{Tr}_3(\mathscr{V}_{13} + \mathscr{V}_{23})\rho_{123}^{(3)}, \quad (13)$$

that is used to derive an equation for the pair correlation density operator. The superoperators $\mathscr{L}^{(n)}$ and $\mathscr{V}_{jk}$ are defined according to $\mathscr{L}^{(n)}A = \hbar^{-1}[H^{(n)}, A]_-$ and $\mathscr{V}_{jk}A = \hbar^{-1}[V_{jk}, A]_-$, for an n-particle Hamiltonian $H^{(n)}$ consisting of a sum of 1-particle kinetic K_j and pairwise additive potential V_{jk} contributions. On inserting the expansions (10)–(12) for the singlet and pair density operators into the second BBGKY equation, an equation for the time evolution of the correlation density operators is obtained

$$i\frac{\partial(\rho_{c12} + \text{Tr}_3\rho_{c123})}{\partial t} = \mathscr{L}_{12}^{(2)}\rho_{c12} + \mathscr{V}_{12}\rho_{f1}\rho_{f2} + \text{Tr}_3\{(\mathscr{V}_{13}$$
$$+ \mathscr{V}_{23})\rho_{123}^{(3)} + \mathscr{L}_{12}^{(2)}\rho_{c123}$$
$$- \mathscr{V}_{13}\rho_{13}^{(2)}\rho_2^{(1)} - \mathscr{V}_{23}\rho_{23}^{(2)}\rho_1^{(1)}$$
$$+ \mathscr{V}_{12}(\rho_{c13}\rho_2^{(1)} + \rho_{c23}\rho_1^{(1)})\}. \quad (14)$$

All contributions to the trace are considered as interaction terms and it is useful to express all of these in terms of the full reduced density operators rather than their correlation components. At the same time it is argued that the trace term appearing in the time derivative should be dropped because this is of higher order in the density and that the resulting

equation then describes the time evolution of the pair correlation operator taking into account three particle (isolated) collisions. The result can be organized as

$$i\frac{\partial\rho_{c12}}{\partial t} = \mathscr{L}_{12}^{(2)}\rho_{c12} + \mathscr{V}_{12}\rho_{f1}\rho_{f2} + \text{Tr}_3\{\mathscr{L}_{123}^{(3)}\rho_{123}^{(3)}$$
$$- (\mathscr{L}_{12}^{(2)} + \mathscr{L}_3^{(1)})\rho_{12}^{(2)}\rho_3^{(1)} - (\mathscr{L}_{13}^{(2)} + \mathscr{L}_2^{(1)})\rho_{13}^{(2)}\rho_2^{(1)}$$
$$- (\mathscr{L}_{23}^{(2)} + \mathscr{L}_1^{(1)})\rho_{23}^{(2)}\rho_1^{(1)} + 2(\mathscr{L}_1^{(1)} + \mathscr{L}_2^{(1)} + \mathscr{L}_3^{(1)})$$
$$\times \rho_1^{(1)}\rho_2^{(1)}\rho_3^{(1)}\}. \quad (15)$$

For an *isolated* three particle interaction, each factorized term in the trace represents an independent set of particles. As such, at thermal equilibrium each density operator in the trace should be of Boltzmann form, namely $\rho^{(n)} \propto e^{-H^{(n)}/kT}$. It is easy to show that the trace term, associated with interactions of the pair 12 with other particles in the gas, vanishes under these conditions. It is now *assumed* that this "interaction" term acts to drive the pair correlation to its local homogeneous equilibrium form as determined by the density, temperature and mean velocity of the free particle density operator, namely

$$\rho_{c12}^e = \int\int d\mathbf{P}\, d\mathbf{R}\, \Delta(\mathbf{R},\mathbf{P})\, \tfrac{1}{8}n_f^2\Lambda_r^6(T_f)$$
$$\times e^{-(\mathbf{P}-2m\mathbf{v}_f)^2/4mkT_f}U(T_f), \quad (16)$$

with n_f, $\mathbf{v}_f$ and T_f all evaluated at the center of mass position $\mathbf{R}$ and time t, including the temperature dependence of the relative motion Ursell operator. $\Lambda_r = h/(\pi mkT)^{1/2}$ is the thermal deBroglie wavelength for relative motion. See Sec. III for the definition of U and Δ as well as how the Wigner function allows the simultaneous dependence on position and momentum while preserving the proper interpretation of noncommuting operators. For small deviations from equilibrium the interaction term is modeled as a linear decay rate

$$i\frac{\partial\rho_{c12}}{\partial t} = \mathscr{L}_{12}^{(2)}\rho_{c12} + \mathscr{V}_{12}\rho_{f1}\rho_{f2} + i\frac{\rho_{c12}^e - \rho_{c12}}{\tau}. \quad (17)$$

This equation is used in the following paper to determine the state of the pair correlations when the gas is out of equilibrium.

III. LOCAL EQUILIBRIUM WITH SMALL GRADIENTS

The Chapman–Enskog[4–8] theory of gas transport properties is based on the idea that the gas is locally close to equilibrium with a local number density n, temperature T and stream velocity $\mathbf{v}_0$, each of which is a function of the macroscopic position $\mathbf{r}$ and time t. For a free (monatomic) particle, the local equilibrium distribution is a Maxwellian centered at the local stream momentum $m\mathbf{v}_0(\mathbf{r},t)$. This mix of momentum and position dependence is most easily described in a phase space, Wigner function,[11] representation of the density operator.

The Wigner function $f^{(1)}(\mathbf{r},\mathbf{p},t)$ associated with single particle density operator $\rho^{(1)}(t)$ is obtained by the Fourier transform

$$f^{(1)}(\mathbf{r},\mathbf{p},t)=h^{-3}\int d\mathbf{q}\; e^{i\mathbf{q}\cdot\mathbf{r}/\hbar}\langle\mathbf{p}+\tfrac{1}{2}\mathbf{q}|\rho^{(1)}(t)|\mathbf{p}-\tfrac{1}{2}\mathbf{q}\rangle$$

$$=\mathrm{Tr}\Delta(\mathbf{r},\mathbf{p})\rho^{(1)}(t), \tag{18}$$

where the trace Tr is over the translational states and the operator[12] Δ is defined by

$$\Delta(\mathbf{r},\mathbf{p})\equiv h^{-3}\int d\mathbf{q}\; e^{i\mathbf{q}\cdot\mathbf{r}/\hbar}|\mathbf{p}-\tfrac{1}{2}\mathbf{q}\rangle\langle\mathbf{p}+\tfrac{1}{2}\mathbf{q}|$$

$$=h^{-3}\int d\mathbf{R}\; e^{i\mathbf{p}\cdot\mathbf{R}/\hbar}|\mathbf{r}+\tfrac{1}{2}\mathbf{R}\rangle\langle\mathbf{r}-\tfrac{1}{2}\mathbf{R}| \tag{19}$$

in both momentum and position representations. The inverse transformation

$$\rho^{(1)}(t)=h^3\int\int d\mathbf{p}\; d\mathbf{r}\;\Delta(\mathbf{r},\mathbf{p})f^{(1)}(\mathbf{r},\mathbf{p},t) \tag{20}$$

enables the density operator to be obtained from the Wigner function. It is also useful to know that

$$\mathrm{Tr}\; AB=h^3\int\int d\mathbf{r}\; d\mathbf{p}[\mathrm{Tr}\; A\Delta(\mathbf{r},\mathbf{p})][\mathrm{Tr}\;\Delta(\mathbf{r},\mathbf{p})B] \tag{21}$$

as well as the trace properties

$$\int\int\Delta(\mathbf{r},\mathbf{p})d\mathbf{r}\; d\mathbf{p}=1;\quad\mathrm{Tr}\;\Delta(\mathbf{r},\mathbf{p})=h^{-3};$$

$$\mathrm{Tr}\;\Delta(\mathbf{r},\mathbf{p})\Delta(\mathbf{r}',\mathbf{p}')=\delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{p}-\mathbf{p}')/h^3 \tag{22}$$

and the relation between individual particle and center of mass–relative phase space representations

$$\Delta_1(\mathbf{r}_1,\mathbf{p}_1)\Delta_2(\mathbf{r}_2,\mathbf{p}_2)$$

$$=\Delta_{\mathrm{CM}}\!\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2},\mathbf{p}_1+\mathbf{p}_2\right)\Delta_{\mathrm{rel}}\!\left(\mathbf{r}_2-\mathbf{r}_1,\frac{\mathbf{p}_2-\mathbf{p}_1}{2}\right). \tag{23}$$

The local equilibrium Wigner function for the free particles (equivalent to the density operator ρ_f^{le}) is to be Maxwellian

$$f_f^{le}(\mathbf{r},\mathbf{p},t)=\frac{n_f}{(2\pi mkT_f)^{3/2}}e^{-(\mathbf{p}-m\mathbf{v}_f)^2/2mkT_f} \tag{24}$$

with free particle density $n_f(\mathbf{r},t)$, free particle stream velocity $\mathbf{v}_f(\mathbf{r},t)$ and free particle temperature $T_f(\mathbf{r},t)$. The position and time dependence of these local parameters are to be understood in the following even when they are not explicitly expressed, and it is noted that f_f^{le} depends on $\mathbf{r}$ and t only through these local parameters. For purposes of the Chapman Enskog expansion, deviations of f_f from local equilibrium are associated with linear gradients in $\mathbf{v}_f$ and T_f so that

$$f_f(\mathbf{r},\mathbf{p},t)=f_f^{le}(\mathbf{r},\mathbf{p},t)(1+\phi), \tag{25}$$

with the perturbation ϕ linear in the gradients and otherwise a function of n_f,T_f and the dimensionless velocity $\mathbf{W}\equiv(\mathbf{p}-m\mathbf{v}_f)/\sqrt{2mkT_f}$. The standard form[4,5] for ϕ is

$$\phi=-\mathbf{A}\cdot\nabla\ln T_f-\mathsf{B}:[\nabla\mathbf{v}_f]^{(2)}-C\nabla\cdot\mathbf{v}_f, \tag{26}$$

wherein $\mathbf{A}$, B and C are vector, tensor and scalar functions of $\mathbf{W}$. Here

$$[\nabla\mathbf{v}_f]^{(2)}\equiv\tfrac{1}{2}[\nabla\mathbf{v}_f+(\nabla\mathbf{v}_f)^t]-\tfrac{1}{3}\mathsf{U}\nabla\cdot\mathbf{v}_f \tag{27}$$

is the traceless symmetric second rank tensor formed from the velocity gradient while U is the second rank identity tensor.

At equilibrium the pair correlations are governed by the Ursell[13] operator

$$U(T)\equiv e^{-H_{\mathrm{rel}}/kT}-e^{-K_{\mathrm{rel}}/kT} \tag{28}$$

involving the relative free motion and total Hamiltonians $K_{\mathrm{rel}}\equiv\mathbf{p}_{\mathrm{op}}^2/m$ and $H_{\mathrm{rel}}=K_{\mathrm{rel}}+V$, times a Maxwellian for the center of mass motion. At local equilibrium, the hydrodynamic variables of correlation density $n_c(\mathbf{R},t)$, temperature $T_c(\mathbf{R},t)$ and mean velocity $\mathbf{v}_c(\mathbf{R},t)$ are to be localized at the position $\mathbf{R}$ of the center of mass of the pair, so the local equilibrium state is most conveniently written in terms of a Wigner function for the center of mass motion and an operator for relative motion, thus

$$f_{c12}^{le}(\mathbf{R},\mathbf{P},t)=\frac{n_c}{\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\frac{e^{-(\mathbf{P}-2m\mathbf{v}_c)^2/4mkT_c}}{(4\pi mkT_c)^{3/2}}U(T_c). \tag{29}$$

Since it is not inherently clear whether the local temperatures for the free particle and pair correlations should be equal or different, here they are allowed to differ so that any possible effect of these differences can be examined.

Of prime importance for the Boltzmann equation (2) is the correlation contribution to the local equilibrium singlet Wigner function

$$f_{c1}^{le}(\mathbf{r},\mathbf{p},t)\equiv\mathrm{Tr}_{12}\;\Delta_1(\mathbf{r},\mathbf{p})\rho_{c12}^{le}$$

$$=8\int\int d\mathbf{r}_{21}\; d\mathbf{p}_{21}\;\mathrm{Tr}_{\mathrm{rel}}\Delta_{\mathrm{rel}}(\mathbf{r}_{21},\mathbf{p}_{21})$$

$$\times f_{c12}^{le}(\mathbf{r}+\tfrac{1}{2}\mathbf{r}_{21},2\mathbf{p}+2\mathbf{p}_{21},t)\simeq f_{c1}^{lh}+f_{c1}^{lc}, \tag{30}$$

with an expansion of the dependence on the center of mass position in powers of the relative position $\mathbf{r}_{21}$. The notation f_{c1}^{lh} denotes the "locally homogeneous" contribution calculated as if the gas was homogeneous, but with the values of $n_c,\mathbf{v}_c$ and T_c associated with the macroscopic position $\mathbf{r}$ of particle 1, namely

$$f_{c1}^{lh}(\mathbf{r},\mathbf{p},t)=\frac{n_c\Lambda_{rc}^3}{h^3\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\int d\mathbf{q}\; e^{-(\mathbf{q}+\mathbf{p}-m\mathbf{v}_c)^2/mkT_c}$$

$$\times\langle\mathbf{q}|U(T_c)|\mathbf{q}\rangle. \tag{31}$$

Here $\Lambda_{rc}\equiv h/(\pi mkT_c)^{1/2}$ is the *relative motion* thermal de-Broglie wavelength at temperature $T_c(\mathbf{r},t)$. It is convenient to recognize that the exponential factor in Eq. (31) is associated with the center of mass motion since $2(\mathbf{p}+\mathbf{p}_{\mathrm{op}})=\mathbf{P}_{\mathrm{op}}$ is the center of mass momentum operator associated with particle 1 having momentum $\mathbf{p}$ and relative momentum (operator) $\mathbf{p}_{\mathrm{op}}$. On introducing the notation $K_{\mathrm{CM}}\equiv(\mathbf{P}_{\mathrm{op}}-2m\mathbf{v}_c)^2/4m=(\mathbf{p}+\mathbf{p}_{\mathrm{op}}-m\mathbf{v}_c)^2/m$, the integration over relative momentum can be written as a trace. With the

notation Tr_r to emphasize that the trace over relative motion is to be carried out keeping the momentum of particle 1 fixed, Eq. (31) can be rewritten as

$$f_{c1}^{lh}(\mathbf{r},\mathbf{p},t)=\frac{n_c\Lambda_{rc}^3}{h^3\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT_c}U(T_c). \tag{32}$$

The inhomogeneous contribution f_{c1}^{lc} is formally obtained by expanding the (center of mass) position dependence of $n_c,\mathbf{v}_c$ and T_c about the position $\mathbf{r}$ (of particle 1) that appears as a parameter in f_{c1}. Only the first order gradient term needs retaining, compare the treatment of Baerwinkel et al.[14] and of Thomas et al.[15] for obtaining the phase space representation of the corresponding collision integral. This is labelled ''lc'' for ''local center of mass correction factor'' since it is associated with the fact that the center of mass of the correlated pair is displaced from the macroscopic position $\mathbf{r}$, this implying a common gradient contribution $\frac{1}{2}\mathbf{r}_{\mathrm{op}}\cdot\nabla$ acting on all the local parameters, where $\mathbf{r}_{\mathrm{op}}$ is the relative position operator (particle 2 minus particle 1) and $\nabla\equiv\partial/\partial\mathbf{r}$ is the gradient with respect to the macroscopic position. This inhomogeneity term is thus

$$f_{c1}^{lc}(\mathbf{r},\mathbf{p},t)=\nabla\cdot\frac{n_c\Lambda_{rc}^3}{4h^3\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT_c}[\mathbf{r}_{\mathrm{op}},U(T_c)]_+$$

$$=\mathsf{F}_{cn}^c\cdot\nabla\ln n_c+\ \mathsf{F}_{cv}^c:\nabla\mathbf{v}_c+\mathsf{F}_{cT}^c\cdot\nabla\ln T_c, \tag{33}$$

where

$$\mathbf{F}_{cn}^c=\frac{n_c\Lambda_{rc}^3}{2h^3\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT_c}[\mathbf{r}_{\mathrm{op}},U(T_c)]_+, \tag{34}$$

$$\mathsf{F}_{cv}^c=\frac{n_c\Lambda_{rc}^3}{2kT_ch^3\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\mathrm{Tr}_r(\mathbf{p}+\mathbf{p}_{\mathrm{op}}-m\mathbf{v}_c)$$

$$\times e^{-K_{\mathrm{CM}}/kT_c}[\mathbf{r}_{\mathrm{op}},U(T_c)]_+, \tag{35}$$

and

$$\mathbf{F}_{cT}^c=\frac{n_c\Lambda_{rc}^3}{4h^3\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT_c}$$

$$\times\left[\mathbf{r}_{\mathrm{op}},\left(\frac{K_{\mathrm{CM}}}{kT_c}-3\right)U(T_c)+T_cU_{T_c}(T_c)\right]_+, \tag{36}$$

using the definition $U_T\equiv\partial U/\partial T$ for the temperature derivative of U.

Parallel to the treatment of f_f, for purposes of the Chapman Enskog expansion, deviations of f_{c12} from local equilibrium are associated with linear gradients in $\mathbf{v}_c$ and T_c so that

$$f_c(\mathbf{R},\mathbf{P},t)=f_c^{\mathrm{le}}(\mathbf{R},\mathbf{P},t)(1+\Phi), \tag{37}$$

with the pertubation Φ linear in the gradients and otherwise a function of n_c,T_c, operators $H_{\mathrm{rel}},K_{\mathrm{rel}}$ and the dimensionless velocity $\mathscr{G}\equiv(\mathbf{P}-2m\mathbf{v}_c)/\sqrt{4mkT_c}$. By analogy with the free particle case, Φ is written as

$$\Phi=-\mathbf{A}_c\cdot\nabla\ln T_c-\ \mathsf{B}_c:[\nabla\mathbf{v}_c]^{(2)}-C_c\nabla\cdot\mathbf{v}_c. \tag{38}$$

IV. MACROSCOPIC VARIABLES

The macroscopic variables inherently depend both on the free density operator and the density operator for correlated pairs. Also, at equilibrium they must agree with equilibrium statistical mechanics, whose relations for a moderately dense gas are reviewed in the Appendix. The various macroscopic variables appearing in Eqs. (5)–(7) are discussed in turn.

It follows from Eqs. (1), (24) and (32) that the particle density is

$$n(\mathbf{r},t)\equiv\int d\mathbf{p}\ f^{(1)}(\mathbf{r},\mathbf{p},t)$$

$$=\int d\mathbf{p}\ f_f^{le}(1+\phi)+8\int\int\int d\mathbf{p}\ d\mathbf{r}_{21}\ d\mathbf{p}_{21}$$

$$\times\mathrm{Tr}_{\mathrm{rel}}\Delta_{\mathrm{rel}}(\mathbf{r}_{21},\mathbf{p}_{21})f_{c12}^{le}(\mathbf{r}+\tfrac{1}{2}\mathbf{r}_{21},2\mathbf{p}+2\mathbf{p}_{21},t)$$

$$\times(1+\Phi)=n_f+n_c \tag{39}$$

with the ''Chapman Enskog'' constraint (auxiliary condition) that the pertubation from local equilibrium does not contribute to any hydrodynamic variables, in particular

$$\int d\mathbf{p}f_f^{le}\phi+\int\mathrm{Tr}_{\mathrm{rel}}f_c^{le}(\mathbf{r},\mathbf{P},t)\Phi d\mathbf{P}=0. \tag{40}$$

The stream velocity is the average velocity of the particles,

$$n\mathbf{v}_0(\mathbf{r},t)\equiv\int d\mathbf{p}\frac{\mathbf{p}}{m}f^{(1)}(\mathbf{r},\mathbf{p},t)=n_f\mathbf{v}_f+n_c\mathbf{v}_c \tag{41}$$

subject to the auxiliary condition

$$\int d\mathbf{p}\frac{\mathbf{p}}{m}f_f^{le}\phi+\mathrm{Tr}_{\mathrm{rel}}\int\frac{\mathbf{P}-2\mathbf{p}_{\mathrm{op}}}{2m}f_c^{le}(\mathbf{r},\mathbf{P},t)\Phi\ d\mathbf{P}=\mathbf{0}. \tag{42}$$

Clearly, if the gas was in internal equilibrium it would have a common convective motion, so that $\mathbf{v}_f=\mathbf{v}_c=\mathbf{v}_0$. Thus any difference in these velocities must be associated with non-equilibrium processes. Ignoring for the moment the possible contribution from the perturbations, the local equilibrium kinetic energy density is

$$n\varepsilon^{K,le}(\mathbf{r},t)\equiv\int d\mathbf{p}\frac{(\mathbf{p}-m\mathbf{v}_0)^2}{2m}f^{(1),le}(\mathbf{r},\mathbf{p},t)$$

$$=n_f\left[\frac{3}{2}kT_f+\frac{m}{2}(\mathbf{v}_f-\mathbf{v}_0)^2\right]+n_c\left[\frac{3}{4}kT_c\right.$$

$$+\frac{m}{2}(\mathbf{v}_c-\mathbf{v}_0)^2$$

$$\left.+\frac{1}{2\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\mathrm{Tr}_{\mathrm{rel}}\frac{\mathbf{p}_{\mathrm{op}}^2}{m}U(T_c)\right]. \tag{43}$$

Note that n_c is the (effective) number of particles that are correlated so that $\frac{3}{4}kT_c$ is the average center of mass energy per particle. Similarly, the $\frac{1}{2}$ multiplying the kinetic energy of relative motion partitions this quantity between the two correlated particles. The terms involving $(\mathbf{v}_f-\mathbf{v}_0)^2$ and

$(\mathbf{v}_c - \mathbf{v}_0)^2$ are second order in gradients and so will be dropped from further consideration. Since the collisions are to be treated as nonlocal, there is a conversion between kinetic and potential energy and only total energy is required to be conserved. The potential energy is determined by the pair density operator which, to second order in density, involves both the product of free density operators and the pair correlation density operator, thus the local equilibrium contribution is

$$n\varepsilon^{V,le}(\mathbf{r},t) \equiv \frac{1}{4}\mathrm{Tr}_{12}[\delta(\mathbf{r}-\mathbf{r}_{\mathrm{op},1})+\delta(\mathbf{r}-\mathbf{r}_{\mathrm{op},2})]V\rho_{12}^{(2),le}$$

$$=\frac{1}{2}n_f^2\int V d\mathbf{r}_{\mathrm{rel}}+\frac{1}{2}n_c\frac{\mathrm{Tr}_{\mathrm{rel}}VU(T_c)}{\mathrm{Tr}_{\mathrm{rel}}U(T_c)}. \tag{44}$$

The auxiliary condition for the energy involves the total energy, so requiring

$$\int \frac{(\mathbf{p}-m\mathbf{v}_0)^2}{2m}f_f^{le}\phi \, d\mathbf{p}+\frac{1}{2}\int\int\int V_{12}f_{f1}^{le}f_{f2}^{le}(\phi_1$$

$$+\phi_2)d\mathbf{r}_{12}\, d\mathbf{p}_1\, d\mathbf{p}_2$$

$$+\tfrac{1}{2}\mathrm{Tr}_{\mathrm{rel}}\int\left(\frac{(\mathbf{P}-2m\mathbf{v}_0)^2}{4m}+H_{\mathrm{re}};\right)f_c^{le}\Phi \, d\mathbf{P}=0. \tag{45}$$

Provided the equilibrium conditions $n_c=n_f^2\Lambda_r^3\mathrm{Tr}_{\mathrm{rel}}U(T)$, $T_f=T_c=T$ and $\mathbf{v}_f=\mathbf{v}_c=\mathbf{v}_0$ are satisfied to order n^2, ε^K reduces to the thermodynamic kinetic energy per particle, Eq. (A7) and ε^V to the potential energy, Eq. (A8). The individual contributions appearing in Eqs. (43) and (44) can be understood with the help of Eq. (A6).

The pressure tensor and the heat flux have contributions arising from several mechanisms. In particular the kinetic contribution to the pressure tensor is

$$\mathsf{P}^K(\mathbf{r},t) \equiv \int d\mathbf{p}\frac{(\mathbf{p}-m\mathbf{v}_0)(\mathbf{p}-m\mathbf{v}_0)}{m}f^{(1)}(\mathbf{r},\mathbf{p},t)$$

$$=n_f[kT_f\mathsf{U}+m(\mathbf{v}_f-\mathbf{v}_0)(\mathbf{v}_f-\mathbf{v}_0)]$$

$$+n_c\left[\frac{1}{2}kT_c\mathsf{U}+m(\mathbf{v}_c-\mathbf{v}_0)(\mathbf{v}_c-\mathbf{v}_0)\right.$$

$$\left.+\frac{\mathrm{Tr}_{\mathrm{rel}}(\mathbf{p}_{\mathrm{op}}^2/m)U(T_c)}{3\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\mathsf{U}\right]$$

$$+\int d\mathbf{p}\frac{(\mathbf{p}-m\mathbf{v}_0)(\mathbf{p}-m\mathbf{v}_0)}{m}f_f^{le}\phi$$

$$+\mathrm{Tr}_{\mathrm{rel}}\int d\mathbf{P}\left[\frac{(\mathbf{P}-2m\mathbf{v}_0)(\mathbf{P}-2m\mathbf{v}_0)}{4m}+\frac{\mathbf{p}_{\mathrm{op}}\mathbf{p}_{\mathrm{op}}}{m}\right]f_c^{le}\Phi \tag{46}$$

while the collisional transfer contribution is

$$\mathsf{P}_{\mathrm{coll}}(\mathbf{r},t) \equiv \frac{-1}{2}\mathrm{Tr}_{12}\mathbf{r}_{\mathrm{op}}\boldsymbol{\nabla}V\delta(\mathbf{R}_{\mathrm{op}}-\mathbf{r})\Omega\rho_{f1}\rho_{f2}\Omega^\dagger$$

$$=-\frac{n_f^2\Lambda_r^3}{6}\mathrm{Tr}_{\mathrm{rel}}\mathbf{r}_{\mathrm{op}}\cdot\boldsymbol{\nabla}Ve^{-H_{\mathrm{rel}}/kT}\mathsf{U}+\frac{-n_f^2\Lambda_r^3}{4kT}$$

$$\times\mathrm{Tr}_{\mathrm{rel}}\mathbf{r}_{\mathrm{op}}\boldsymbol{\nabla}V\Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+\Omega^\dagger :\boldsymbol{\nabla}\mathbf{v}_f$$

$$-\frac{n_f^2\Lambda_r^6}{16h^3}\mathrm{Tr}_{\mathrm{rel}}\int d\mathbf{P}e^{-K_{\mathrm{CM}}/kT}\mathbf{r}_{\mathrm{op}}\boldsymbol{\nabla}V$$

$$\times\Omega e^{-K_{\mathrm{rel}}/kT}(\phi_1+\phi_2)\Omega^\dagger. \tag{47}$$

The local equilibrium collisional transfer contribution to the pressure is of virial form which, when combined with the kinetic contribution gives the standard expression $P=nkT_f+n_f^2kT_fB$ for the total pressure. See the Appendix for more detail. Since T_f and T_c differ only by gradient terms and since the present theory is restricted to linear in gradient effects, such differences are ignored in the terms involving the perturbations. Thus these expressions have been written in terms of a common local temperature T.

The kinetic contribution to the heat flux is

$$\mathbf{q}^K(\mathbf{r},t) \equiv \int d\mathbf{p}\left(\frac{\mathbf{p}}{m}-\mathbf{v}_0\right)\frac{(\mathbf{p}-m\mathbf{v}_0)^2}{2m}f^{(1)}(\mathbf{r},\mathbf{p},t)$$

$$=\frac{5}{2}n_fkT_f(\mathbf{v}_f-\mathbf{v}_0)+\frac{5}{2}n_c\left[\frac{kT_c}{2}+\frac{\mathrm{Tr}_{\mathrm{rel}}(\mathbf{p}_{\mathrm{op}}^2/m)U}{3\mathrm{Tr}_{\mathrm{rel}}U}\right]$$

$$\times(\mathbf{v}_c-\mathbf{v}_0)+\int d\mathbf{p}\left(\frac{\mathbf{p}}{m}-\mathbf{v}_f\right)\frac{(\mathbf{p}-m\mathbf{v}_f)^2}{2m}f_f^{le}$$

$$\times(\mathbf{r},\mathbf{p},t)\phi+\mathrm{Tr}_{\mathrm{rel}}\int d\mathbf{P}\left[\frac{(\mathbf{P}-2m\mathbf{v}_c)^2}{4m}+\frac{\mathbf{p}_{\mathrm{op}}^2}{m}\right.$$

$$\left.-\frac{(\mathbf{P}-2m\mathbf{v}_c)\cdot\mathbf{p}_{\mathrm{op}}}{m}\right]\frac{(\mathbf{P}-2m\mathbf{v}_c-2\mathbf{p}_{\mathrm{op}})}{4m}f_c^{le}\Phi. \tag{48}$$

The collisional transfer of kinetic energy is given by

$$\mathbf{q}_{\mathrm{coll}}\equiv-\frac{1}{4m}\mathrm{Tr}_{12}\delta(\mathbf{R}_{\mathrm{op}}-\mathbf{r})\mathbf{r}_{\mathrm{op}}(\mathbf{P}-2m\mathbf{v}_0)\cdot\boldsymbol{\nabla}V\Omega\rho_{f1}\rho_{f2}\Omega^\dagger$$

$$=-\frac{n_f^2\Lambda_r^3}{8m}\mathrm{Tr}_{\mathrm{rel}}\mathbf{r}_{\mathrm{op}}\boldsymbol{\nabla}V\cdot\Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+\Omega^\dagger\cdot\boldsymbol{\nabla}\ln T$$

$$-\frac{n_f^2\Lambda_r^3}{6}(\mathbf{v}_f-\mathbf{v}_0)\mathrm{Tr}_{\mathrm{rel}}\mathbf{r}_{\mathrm{op}}\cdot\boldsymbol{\nabla}Ve^{-H_{\mathrm{rel}}/kT_f}-\frac{n_f^2\Lambda_r^6}{32mh^3}\mathrm{Tr}_{\mathrm{rel}}$$

$$\times\int d\mathbf{P}e^{-K_{\mathrm{CM}}/kT}\mathbf{r}_{\mathrm{op}}(\mathbf{P}-2m\mathbf{v}_0)\cdot\boldsymbol{\nabla}V\Omega e^{-K_{\mathrm{rel}}/kT_f}(\phi_1$$

$$+\phi_2)\Omega^\dagger. \tag{49}$$

The potential heat flux is

$$\mathbf{q}^V=\frac{1}{4m}\mathrm{Tr}_{12}[\mathbf{p}_{op,1}-m\mathbf{v}_0,\delta_1]_+V_{12}\rho_{12}^{(2)}$$

$$=\frac{1}{4m}\mathrm{Tr}_{12}(\mathbf{P}-2m\mathbf{v}_0)\delta(\mathbf{R}_{\mathrm{op}}-\mathbf{r})V\rho_{12}^{(2)}$$

$$=\frac{1}{2}\left[n_f^2(\mathbf{v}_f-\mathbf{v}_0)\int Vd\mathbf{r}+\frac{n_c}{\mathrm{Tr}_{\mathrm{rel}}U}(\mathbf{v}_c-\mathbf{v}_0)\mathrm{Tr}_{\mathrm{rel}}VU\right]$$

$$+\frac{\Lambda_r^3}{32mh^3}\mathrm{Tr}_{\mathrm{rel}}\int d\mathbf{P}e^{-K_{\mathrm{CM}}/kT}(\mathbf{P}-2m\mathbf{v}_0)V$$

$$\times\left[n_f^2\Lambda_r^3 e^{-K_{\rm rel}/kT}f(\phi_1+\phi_2)+\frac{n_c}{{\rm Tr}_{\rm rel}U}U\Phi\right]. \qquad (50)$$

Clearly the leading terms of each of these quantities vanish if $\mathbf{v}_f=\mathbf{v}_c=\mathbf{v}_0$, leaving only the perturbation contributions.

There remains the kinetic energy production term

$$\sigma^K=-\frac{1}{4m}{\rm Tr}_{12}\{[\,\delta(\mathbf{r}-\mathbf{r}_{op,1})+\delta(\mathbf{r}-\mathbf{r}_{op,2})]$$

$$\times(\mathbf{p}_{op}\cdot\boldsymbol{\nabla}V+\boldsymbol{\nabla}V\cdot\mathbf{p}_{op})\}_s\Omega\rho_{f1}\rho_{f2}\Omega^{\dagger}. \qquad (51)$$

Here the subscript $\{\ \}_s$ signifies the properly symmetrized operator. This completes the formal expressions for the hydrodynamic variables in terms of the free ϕ and correlation Φ perturbation functions.

V. DISCUSSION

A recently proposed[1] density corrected quantum Boltzmann equation involves both free and pair correlation contributions. This paper has discussed the expansion of both about local equilibrium. In order to even formulate such properties requires a means of distinguishing between macroscopic and microscopic motion. This has been accomplished in the present work by expressing the quantum density matrix in the Wigner equivalent representation. In particular, for the Wigner function of a single particle, the position dependence is necessarily related to macroscopic motion while the momentum dependence is of microscopic origin. For the pair particle correlations, the analogous position dependence of the macroscopic motion is associated with the position of the center of mass of the pair.

In the original formulation,[1] the pair correlation density operator was determined entirely by the free density operator, see Eq. (3). This expression is an obvious extrapolation of the equilibrium relation. As mentioned in Sec. I, it was found by computation that this led to certain divergences and transport coefficients that were inconsistent with the well documented dilute gas expressions. The present work treats the correlations as governed by a dynamical equation, see Sec. II, that includes their decay due to interactions with other particles in the gas.

The following paper linearizes the pair of equations (the Boltzmann equation and the pair correlation equation) about local equilibrium and solves them, essentially in a steady state approximation, using what is believed to be the simplest physically reasonable set of approximations. This yields expressions for the transport coefficients which are the quantum generalizations of the classical expressions,[9] including also contributions from pair correlation effects.

There are other closures of the BBGKY hierarchy that could also be used for formulating correlation contributions. Dufty and Kim[16] have used a particular closure for the second BBGKY equation that can be expressed in terms of a relation between ρ_{c12} and ρ_f, see the Appendix in Ref. 17. The related closure of Klimontovich[18] might also be used. But whichever closure, the role of pair correlations is required in order to evaluate their contribution to the singlet density operator and the transport coefficients. It is of course

the closure of Reference 1 that is explored here and in the following paper. An alternate possible approach is that the free and pair correlations are considered as independent with a closure at the third BBGKY equation level. That has not been explored in this work.

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APPENDIX: EQUILIBRIUM STATISTICAL MECHANICS RELATIONS

To second order in the density $n=N/W$, and thus including pair correlations, the equilibrium pressure is given by $P=nkT(1+nB)$. Here, W will be used for the volume since the symbol V denotes the potential energy. The second virial coefficient $B(T)$ is related to the kinetic K and total $H=K+V$ Hamiltonians for the *relative* motion of a pair of particles through the Ursell operator

$$U(T)\equiv e^{-H/kT}-e^{-K/kT} \qquad (A1)$$

and the *relative* thermal deBroglie wavelength $\Lambda_r\equiv h/(\pi mkT)^{1/2}$ by

$$B=-\tfrac{1}{2}\Lambda_r^3{\rm Tr}_{\rm rel}U. \qquad (A2)$$

Note that in this Appendix, H and K are Hamiltonians for relative motion and the subscript ''rel'' appearing in the main text has been dropped. $B(T)$ exists provided the potential vanishes rapidly enough for large distances. It follows from standard thermodynamic relations and the ideal gas limiting behaviour that the Helmholtz function is

$$A(N,W,T)=-NkT\ln\frac{eW}{N\Lambda^3}+\frac{N^2kTB}{W}. \qquad (A3)$$

Here, $\Lambda\equiv h/(2\pi mkT)^{1/2}=\Lambda_r/\sqrt{2}$ is the single particle thermal deBroglie wavelength. Immediate consequences of this is that the energy per particle is

$$\varepsilon=\frac{1}{N}\left[A-T\left(\frac{\partial A}{\partial T}\right)_{N,W}\right]=\frac{3}{2}kT-nkT^2\frac{dB}{dT} \qquad (A4)$$

and the corresponding heat capacity (at constant volume) is

$$C_v\equiv\left(\frac{\partial\varepsilon}{\partial T}\right)_n=\frac{3}{2}k-2nkT\frac{dB}{dT}-nkT^2\frac{d^2B}{dT^2}. \qquad (A5)$$

In terms of molecular quantities the energy per particle can be explicitly expressed in a number of different ways

$$\varepsilon = \frac{3}{2}kT + \frac{3}{2}nkTB + \frac{n}{2}\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}[He^{-H/kT} - Ke^{-K/kT}]$$

$$= \frac{3}{2}kT + \frac{n}{2}\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}\left[\left(H - \frac{3}{2}kT\right)e^{-H/kT} - \left(K - \frac{3}{2}kT\right)\right.$$

$$\left.\times e^{-K/kT}\right]$$

$$= \frac{3}{2}kT + \frac{n}{2}\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}\left[\left(K - \frac{3}{2}kT\right)U + Ve^{-H/kT}\right]$$

$$= \frac{3}{2}kT + \frac{3}{2}nkTB + \frac{n}{2}\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}[HU + Ve^{-K/kT}]$$

$$= \frac{3}{2}kT + \frac{3}{2}nkTB + \frac{n}{2}\left[\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}HU + \int V d\mathbf{r}_{\mathrm{rel}}\right]. \quad (A6)$$

While the first form is what arises by direct differentiation of Eqs. (A2) and (A4), the second form demonstrates how each of total and free particle relative energies deviate from $(3/2)kT$. It should be recognized that the trace of the individual exponential terms in each of these forms are separately infinite and only the difference has a finite trace. In contrast, as written, the individual contributions to the trace in each of the remaining forms are separately finite, under the same conditions as for the existence of a finite second virial coefficient. The third form splits the energy into kinetic

$$\varepsilon^K \equiv \frac{3}{2}kT + \frac{n}{2}\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}\left(K - \frac{3}{2}kT\right)U = \frac{3}{2}kT + \frac{1}{2}nkT\varepsilon_1,$$
$$(A7)$$

and potential

$$\varepsilon^V = (n/2)\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}} V e^{-H/kT} \quad (A8)$$

energy parts. The kinetic energy consists of the usual classical value of $(3/2)kT$ plus a quantum correction from the noncommutation of position and momentum in the Ursell operator which is expressed in terms of ε_1, a notation introduced by Imam–Rahajoe and Curtiss.[19] The fourth form arises from a different association of which Hamiltonian is to multiply U. Since the product $Ve^{-K/kT}$ factors into separate position and momentum parts its trace can be reduced to separate integrals over the two parts, leading to the fifth and last form given in Eq. (A6) for writing the energy. It is this last form which is closest in structure to that which arises from the division into free and correlated contributions, compare Eqs. (43) and (44). The corresponding molecular formula for the heat capacity C_v is conveniently written in the second structural form of Eq. (A6) as

$$C_v = \frac{3}{2}k(1 + nB) + \frac{n\Lambda_r^3}{2kT^2}\mathrm{Tr}_{\mathrm{rel}}$$

$$\times\left[\left(H - \frac{3}{2}kT\right)^2 e^{-H/kT} - \left(K - \frac{3}{2}kT\right)^2 e^{-K/kT}\right].$$
$$(A9)$$

An alternate view of the structure of the gaseous system is to consider

$$Q^U(T) \equiv \tfrac{1}{2}\mathrm{Tr}_{\mathrm{rel}}U(T) \quad (A10)$$

to be the partition function for the pair correlations. The corresponding energy is then

$$E^U(T) = kT^2 \frac{\partial \ln Q^U}{\partial T} = \frac{\mathrm{Tr}_{\mathrm{rel}}(He^{-H/kT} - Ke^{-K/kT})}{\mathrm{Tr}_{\mathrm{rel}}U}$$

$$= \frac{3}{2}kT + \frac{kT^2}{B}\frac{dB}{dT} = \frac{3}{2}kT + \frac{\varepsilon - \frac{3}{2}kT}{-nB}. \quad (A11)$$

This quantity enters naturally in the kinetic theory treatment.

Next consider the question of how many particles act as if they are essentially free, and how many are correlated into pairs. On the basis that the number of freely acting particles is proportional to the absolute activity λ and the number of correlated pairs is proportional to the square of λ, it is inherent first to identify the absolute activity. This is given in terms of the chemical potential μ according to

$$\ln \lambda = \frac{\mu}{kT} = \frac{1}{kT}\left(\frac{\partial A}{\partial N}\right)_{T,W} = \ln(n\Lambda^3) + 2nB. \quad (A12)$$

It follows that the equation for the absolute activity

$$\lambda \simeq n\Lambda^3(1 + 2nB) \quad (A13)$$

can be inverted to give

$$n \simeq \frac{\lambda}{\Lambda^3} - \frac{2\lambda^2}{\Lambda^6}B = n_f + n_c, \quad (A14)$$

identifying the densities of free and correlated particles as the two terms in the λ expansion of the density. At equilibrium, it is seen that there is an effective equilibrium constant

$$\frac{n_c}{n_f^2} = -2B = \Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}U. \quad (A15)$$

Lastly there are the various expressions for the pressure. The standard result $P = nkT(1 + nB)$, with which this Appendix began, is reproduced by

$$P = -\left(\frac{\partial A}{\partial W}\right)_{N,T}. \quad (A16)$$

However, if the (finite) volume dependence is scaled $W \to sW$ with a scale factor s, then the volume derivative can be replaced by the scale derivative. Applying this scaling to all position dependence $\mathbf{r}_{\mathrm{op}} \to s^{1/3}\mathbf{r}_{\mathrm{op}}$ in the Ursell operator (note that to retain the commutation relations the momentum operator scales according to $\mathbf{p}_{\mathrm{op}} \to s^{-1/3}\mathbf{p}_{\mathrm{op}}$), gives the ''virial'' equation of state, namely

$$P = nkT + n^2kTB + \frac{n^2}{2}\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}[\tfrac{2}{3}KU - \tfrac{1}{3}\mathbf{r}_{\mathrm{op}}\cdot\boldsymbol{\nabla}Ve^{-H/kT}]. \quad (A17)$$

Clearly the trace term must vanish, see Ref. 2, but the last term,

$$P_{\mathrm{virial}} = -\frac{n^2}{6}\Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}\mathbf{r}_{\mathrm{op}}\cdot\boldsymbol{\nabla}Ve^{-H/kT} \quad (A18)$$

is the ''virial'' form for the pressure due to collisions (equivalently, interactions). This is what arises naturally from the Boltzmann collision term if the collisions are treated as nonlocal, compare Ref. 15. The other terms in the virial equation of state are associated with the kinetic contribution to the pressure. This combination can be written in a number of different ways

$$P^K = P - P_{\text{virial}} = \left(n - \frac{1}{2} n_c\right) kT + \frac{n^2}{3} \Lambda_r^3 \text{Tr} KU$$

$$= nkT + \frac{n^2}{3} \Lambda_r^3 \text{Tr} \left(K - \frac{3}{2} kT\right) U$$

$$= nkT + \frac{1}{3} n^2 kT \varepsilon_1 = \frac{2}{3} n \varepsilon^K. \tag{A19}$$

Since $n = n_f + n_c$, the first form for P^K can be compared with Eq. (46) while the later forms stress the nonclassical (quantum) corrections to the kinetic contribution to the pressure, particularly through the Imam–Rahajoe– Curtiss[19] correction factor ε_1.

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