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Long-Time Behavior of Space- and Time-Dependent Correlation Functions

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The long-time behavior of space- and time-dependent correlation functions is obtained including the ring contributions or correlated two-body effects. The latter give rise to anomalous hydrodynamic effects and persistent correlations in the nonhydrodynamic part.

I. INTRODUCTION

Attempts to establish the hydrodynamic equations of continuum mechanics from the principles of statistical mechanics have led in a variety of ways to the Green-Kubo expressions for transport coefficients in terms of time correlation functions of appropriate microscopic fluxes. More precisely, these expressions require time integrals of such functions. Recently, a number of investigations[1] have indicated that the long-time behavior of the correlation functions may be proportional to $t^{-3/2}$, much slower than an expected modulated exponential decay. In particular, Dorfman and Cohen[1] have come to this conclusion on the basis of a resummation of the divergent density expansion to account for the most divergent terms of the series. This selective resummation was suggested by Kawasaki and Oppenheim,[2] and includes sequences of correlated two-body collisions, or "ring events," as well as the usual Boltzmann contributions. The resulting time-correlation functions have a time dependence determined by the linearized Boltzmann operator, plus a "ring operator" arising entirely from the correlated two-body collisions. The latter is responsible for the anomalous long-time behavior. The correlation functions still decay fast enough to be integrable, so that the Navier-Stokes transport coefficients exist; however, the higher-order (Burnett) coefficients are not well defined. In this context it is then not clear in what sense the linear Navier-Stokes equations are a correct first approximation.

The correlation functions that determine the transport coefficients are space independent and do not directly reflect the hydrodynamic behavior of interest. It is more appropriate, then, for the investigation of hydrodynamics, to study certain space- and time-dependent correlation functions. In fact, under appropriate circumstances[3] these are the Green's functions for the macroscopic variables (e.g., local number density, local temperature, and local velocity). These correlation functions, or rather their Fourier-Laplace transforms, are calculated here in the ring approximation for hard spheres and for small $\vec{k}$ and ϵ ($\vec{k}$ is the Fourier transform variable associated with the space transform, and ϵ is the Laplace transform variable associated with the time transform). The conditions of small $\vec{k}$ and ϵ correspond, respectively, to small spatial gradients and long times, i.e., the situation for which hydrodynamic behavior might be expected. These calculations have already been carried out by McLennan[4] for the Boltzmann operator. His results show, for sufficiently small $\vec{k}$, the correlation functions can be written as the sum to two terms. The first, or hydrodynamic part, has simple poles at $\epsilon = -p_\alpha(k)$, where $p_\alpha(k)$ are the eigenvalues of the linearized hydrodynamic equations (Navier-Stokes equations). The second or microscopic part, has singularities that are bounded away from the hydrodynamic poles for small $\vec{k}$. The small ϵ behavior is dominated by the hydrodynamic part as expected, since the hydrodynamic poles lie closest to the origin. This means the space-time correlation functions asymptotically satisfy the linearized hydrodynamic equations, after some characteristic time, and is usually described as aging to hydrodynamics. The calculations of McLennan have been repeated here to include the ring operator, and qualitative differences appear. The "hydrodynamic part" no longer has simple poles but includes a branch cut as well.[5] The time dependence of the hydrodynamic part is thus different from the Boltzmann result, or that predicted by the usual linearized hydrodynamic equations. In addition, the microscopic part also has a branch cut extending into the region of the singularities of the hydrodynamic part. Although the singularities of the hydrodynamic part include a branch cut, there are also poles approximating the hydrodynamic poles, for small k. This is sufficient to give a long-time behavior approaching the hydrodynamic modes. The branch cut is more serious in the microscopic part, since deviations from the corresponding Boltzmann result increase for long times; for arbitrarily small but fixed, finite density there are times sufficiently large such that corrections to the Boltzmann result dominate. These contributions persist for long times, so there is no longer an exponential aging to hydrodynamics as in the Boltzmann case. The Green-Kubo expressions for the transport coefficients actually depend on only the microscopic parts of the appropriate correlation functions,[6] so it is this anomalous long-time behavior which is responsible for the difficulties encountered in Burnett order.

The long-time effects of correlated two-body collisions appear as a coupling of ordinary hydrodynamic modes in the spectrum of the (linear) collision operator. A similar coupling occurs in a perturbation solution to the ordinary Navier-Stokes equations if nonlinear convective terms are included. Results like those given here for the hydrodynamic part of the correlation functions have been obtained for more general systems using semiphenomenological arguments to include mode coupling through nonlinearities.[7] Many of the latter have been directed at the study of transport near the critical point and, while the ring approximation here is limited to low density, the qualitative similarity may be noteworthy. Correlation functions are related to hydrodynamic variables in Sec. II by linearizing in the initial deviations from equilibrium, a convergent procedure under reasonable conditions. This is sufficient to show deviations from solutions of the usual linear hydrodynamic equations, but comparison with solutions of modified linear equations or the nonlinear hydrodynamic equations is not considered.

A number of qualifications must be added to these comments. First, there is no assurance that the ring events give the most significant correction to the Boltzmann operator for long times. However, Dorfman and Cohen have included in addition certain "Enskog" contributions and found these do not change the long-time behavior in any qualitative way. Second, a perturbation theory used to calculate eigenfunctions and eigenvalues is known to have a finite radius of convergence for the Boltzmann operator, but nothing is known as yet about convergence when the ring operator is included; in addition, a variational principle is used to estimate the eigenvalues, the accuracy of which is firmly established again only for the Boltzmann case. Agreement with Dorfman and Cohen is maintained in the appropriate limits, but the results must be considered tentative.

II. CONNECTION WITH HYDRODYNAMICS

To motivate the study of space- and time-dependent correlation functions and aid interpretation, their role in the special case of initial local equilibrium will be considered. For sufficiently small deviations of the initial thermodynamic parameters from equilibrium, the correlation functions appear as Green's functions for the hydrodynamic variables, as follows:

A formal solution to the Liouville equation for initial local equilibrium is[3]

$$\rho(t)=\exp\Big\{-\Big[q+\int d\vec{x}\,\Big(\beta(\vec{x},0)\,u(\vec{x},t)-\sum_{\sigma=1}^{r}\big(\nu^{\sigma}(\vec{x},0)-\tfrac{1}{2}m\beta(\vec{x},0)\,U^{2}(\vec{x},0)\big)\,n^{\sigma}(\vec{x},t)-\beta(\vec{x},0)\,\vec{U}(\vec{x},0)\cdot\vec{p}(\vec{x},t)\Big)\Big]\Big\}\,, \qquad (2.1)$$

where $T=1/k_B\beta$ is the initial local temperature, $\mu^{\sigma}=\nu^{\sigma}/\beta$ is the initial local chemical potential for the σth component, and $\vec{U}$ is the initial local velocity. The phase functions $u(\vec{x},t)$, $n(\vec{x},t)$, and $\vec{p}(\vec{x},t)$ are, respectively, the local energy, number, and momentum densities, as functions of the phases at an earlier time $-t$. The constant q is determined by the condition that $\rho(t)$ be normalized to one.

The average local densities are obtained by averaging $n(\vec{x})$, $u(\vec{x})$, and $\vec{p}(\vec{x})$ over the ensemble $\rho(t)$. Nonequilibrium thermodynamics may be defined by requiring that the average local densities depend on the nonequilibrium thermodynamic variables in the same way as in equilibrium. The average flow velocity is defined as the average local momentum density divided by the average local mass density. For simplicity, the independent hydrodynamic variables will be taken as the average energy density, number density, and flow velocity denoted by, respectively, $\langle u(\vec{x});t\rangle$, $\langle n(\vec{x});t\rangle$, and $\vec{U}(\vec{x},t)$.

If the initial values $\beta(\vec{x},0)$, $\nu(\vec{x},0)$, and $\vec{U}(\vec{x},0)$ deviate only slightly from the final equilibrium values of the system, $\rho(t)$ may be expanded in these deviations to give

$$\rho(t)=f_0\Big[1-\int d\vec{x}\,\Big(\delta\beta(\vec{x},0)\,(u(\vec{x},t)-u_e)-\sum_{\sigma=1}^{r}\delta\nu(\vec{x},0)\,(n^{\sigma}(\vec{x},t)-n_e^{\sigma})-\beta_e\vec{U}(\vec{x},0)\cdot\vec{p}(\vec{x},t)\Big)+\cdots\Big]\,. \qquad (2.2)$$

Here f_0 is the equilibrium distribution function and quantities with subscript e denote equilibrium values. Only linear terms have been shown, and $\vec{U}_e$ has been taken to be zero. The linear contribution to the hydrodynamic variables is then

$$\langle n^{\sigma}(\vec{x});t\rangle=n_e^{\sigma}+\int d\vec{x}'\,\Big(\frac{1}{k_BT^2}\,\delta T(\vec{x}',0)\,\langle n^{\sigma}(\vec{x})\,(u(\vec{x}',t)-u_e)\rangle_0+\sum_{\sigma'=1}^{r}\delta\nu^{\sigma'}(\vec{x}',0)\,\langle n^{\sigma}(\vec{x})\,(n^{\sigma'}(\vec{x}',t)-n_e^{\sigma'})\rangle_0+\frac{1}{k_BT}\,U_i(\vec{x}',0)\,\langle n^{\sigma}(\vec{x})\,p_i(\vec{x}',t)\rangle_0\Big)\,,$$

$$\langle u(\vec{x});\, t\rangle = u_e + \int d\vec{x}'\left(\frac{1}{k_B T^2}\,\delta T(\vec{x}',0)\,\langle u(\vec{x})\,(u(\vec{x}',t)-u_e)\rangle_0 + \sum_{\sigma=1}^{r}\delta\nu^\sigma(\vec{x}',0)\,\langle u(\vec{x})(n^\sigma(\vec{x}',t)-n_e^\sigma)\rangle + \frac{1}{k_B T}\,U_i(\vec{x}',0)\,\langle u(\vec{x})p_i(\vec{x}',t)\rangle_0\right),$$

$$U_i(\vec{x},t) = \frac{1}{n_e m}\int d\vec{x}'\left(\frac{1}{k_B T^2}\,\delta T(\vec{x},0)\,\langle p_i(\vec{x})\,(u(\vec{x}',t)-u)\rangle_0 + \sum_{\sigma=1}^{r}\delta\nu^\sigma(\vec{x}',0)\,\langle p_i(\vec{x})\,(n^\sigma(\vec{x}',t)-n_e^\sigma)\rangle_0 + \frac{1}{k_B T}\,U_j(\vec{x}',0)\,\langle p_i(\vec{x})p_j(\vec{x}',t)\rangle_0\right). \tag{2.3}$$

The brackets $\langle\ \rangle_0$ indicate an equilibrium average. Equations (2.3) show that, in the linear approximation, appropriate correlation functions of the locally conserved phase functions $n(\vec{x})$, $u(\vec{x})$, and $\vec{p}(\vec{x})$ serve as Green's functions for the hydrodynamic variables. In particular, if the linear hydrodynamic equations are correct for long times, the correlation functions must reflect the familiar hydrodynamic modes for long times. Convergence of the expansion leading to (2.3) is discussed in Appendix A.

III. RING APPROXIMATION

The correlation functions will be calculated for a monatomic gas of hard spheres, although the results are expected to be similar for other short-range repulsive interactions. A general space-time correlation function of phase functions A and B is defined as

$$C_{AB}(\vec{r},t) = \langle A(\vec{O},O)B(\vec{r},t)\rangle_0, \tag{3.1}$$

where $B(\vec{r},t)$ is the phase function $B(\vec{r})$ at an earlier time $-t$, as determined by Hamilton's equations. The dependence of A and B on the positions and momenta of all the particles has not been made explicit, although dependence on the space point $\vec{r}$ has been indicated. The phase functions of principal interest are the locally conserved number density, energy density, and momentum density,

$$n(\vec{r}) = \sum_{\alpha=1}^{N}\delta(\vec{r}-\vec{q}_\alpha),$$

$$u(\vec{r}) = \sum_{\alpha=1}^{N}\frac{p^2\alpha}{2m}\,\delta(\vec{r}-\vec{q}_\alpha), \tag{3.2}$$

$$\vec{p}(\vec{r}) = \sum_{\alpha=1}^{N}\vec{p}_\alpha\delta(\vec{r}-\vec{q}_\alpha),$$

respectively (actually, only the kinetic part of the energy density has been included above for simplicity). Their associated fluxes, e.g., energy and momentum fluxes, will not be considered. In general, the phase functions A and B will always be taken to be sums of single-particle functions:

$$A(\vec{r}) = \sum_{\alpha=1}^{N}a(\vec{p}_\alpha)\delta(\vec{r}-\vec{q}_\alpha),$$

$$B(\vec{r}) = \sum_{\alpha=1}^{N}b(\vec{p}_\alpha)\,\delta(\vec{r}-\vec{q}_\alpha). \tag{3.3}$$

The correlation function simplifies to

$$C_{AB}(\vec{r},t) = n\int\int dv_1\,dq_1 \times f_0(\vec{v}_1)\,a(m\vec{v}_1)\,\delta(\vec{q}_1)\,\Phi_B(\vec{r}-\vec{q}_1,\vec{v}_1,t), \tag{3.4}$$

with

$$\Phi_B(\vec{r}-\vec{q}_1,\vec{v}_1,t) = \lim_{N\to\infty,\ \Omega\to\infty} f_0^{-1}(\vec{v}_1)m^{3/2} \times\int dp_2\,dq_2\cdots dp_N\,dq_N\,\Omega B(\vec{r},t)\,\rho_0. \tag{3.5}$$

Here, ρ_0 is the equilibrium canonical distribution function, $nf_0(\vec{v})$ is the Maxwell-Boltzmann function, Ω the volume and n is the density.

It is convenient to consider, instead of Eq. (3.4), its Fourier-Laplace transform,

$$C_{AB}(\vec{k},\epsilon) = \int_0^\infty dt\int d\vec{r}\,e^{i\vec{k}\cdot\vec{r}-\epsilon t}\,C_{AB}(\vec{r},t) = n\int d\vec{v}_1 f_0(\vec{v}_1)\,a(m\vec{v}_1)\,\Phi_B(\vec{k},\vec{v}_1,\epsilon), \tag{3.6}$$

with

$$\Phi_B(\vec{k},\vec{v}_1,\epsilon) = \int_0^\infty dt\int d\vec{r}\,e^{i\vec{k}\cdot\vec{r}-\epsilon t}\,\Phi_B(\vec{r},\vec{v}_1,t).$$

The "kinetic" equation satisfied by $\Phi_B(\vec{k},\vec{v}_1,\epsilon)$ can be determined only by a detailed analysis of the collision processes in the gas. We assume now that the relevant contributions for small ϵ (or long times) at sufficiently low densities are given by the ring approximation, for which $\Phi_B(\vec{k},\vec{v}_1,\epsilon)$ satisfies^8

$$(\epsilon + i\vec{k}\cdot\vec{v}_1 + nI_1 - nB)\Phi_B(\vec{k},\vec{v}_1,\epsilon) = \Phi_B(\vec{k},\vec{v}_1,t=0), \tag{3.7}$$

where nI_1 is the usual linearized Boltzmann operator,

$$-nI_1[g] = n\int dv_2 f_0(v_2)\,\langle 0,0\,|t|\,0,0\rangle\,[g(\vec{v}_1)+g(\vec{v}_2)] \tag{3.8}$$

and nB is the ring operator,

$$nB[g] = n\int\frac{d\vec{k}'}{(2\pi)^3}\int d\vec{v}_2 f_0(\vec{v}_2)\langle 0,0\,|t|\,0,0\rangle \times[\epsilon + i\vec{k}'\cdot\vec{v}_1 + i(\vec{k}-\vec{k}')\cdot\vec{v}_2 + nI_1 + nI_2]^{-1} \times\langle 0,0|t|0,0\rangle\,[g(\vec{v}_1)+g(\vec{v}_2)]. \tag{3.9}$$

The definition of the two-body t operators is given in Appendix B, with a discussion of the ring approximation. The dependence of B on $\vec{k}$, ϵ has been left implicit.

One final simplification will be made. The effects to be investigated are dynamical rather than statistical, so the initial condition $\Phi_B(\vec{k}, \vec{v}_1, t=0)$ will be evaluated only to lowest order in the density,

$$\Phi_B(\vec{k}, \vec{v}_1, t=0) = b(m\vec{v}_1) . \tag{3.10}$$

It is convenient to introduce the following notation:

$$(g, h) = \int d\vec{v}_1 f_0(\vec{v}_1) g^*(\vec{v}_1) h(\vec{v}_1) . \tag{3.11}$$

The correlation function (2.6) becomes, with Eqs. (2.7) and (2.10):

$$\begin{aligned} C_{AB}(\vec{k}, \epsilon) &= n(a, R(\vec{k}, \epsilon)b) , \\ R(\vec{k}, \epsilon) &= (\epsilon + i\vec{k}\cdot\vec{v}_1 + nI_1 - nB)^{-1} . \end{aligned} \tag{3.12}$$

The singularities of $C_{AB}(\vec{k}, \epsilon)$ are therefore determined from the spectrum of the operator $(i\vec{k}\cdot\vec{v}_1 + nI_1 - nB)$.

IV. SELF-DIFFUSION

The correlation functions just introduced involve sums of single-particle functions and describe many-particle correlations. The basic ideas will first be illustrated with the simple case of single-particle correlation functions, of interest in describing self-diffusion. The simplification is due to the fact that there is only one locally conserved single-particle function $n_1(\vec{r}) = \delta(\vec{r} - \vec{q}_1)$. The average of $n_1(\vec{r})$ may be interpreted as the probability density for the position of the diffusing particle, and is thus the only "hydrodynamic variable." The modifications of Eqs. (3.12) for single-particle correlations are

$$\begin{aligned} \overline{C}_{AB} &\equiv \lim \Omega C_{AB}(k, \epsilon) = (a, R'(k, \epsilon)b) , \\ R'(k, \epsilon) &= (\epsilon + i\vec{k}\cdot\vec{v}_1 + nJ_1 - nB_1')^{-1} , \\ -nJ_1[g] &= n\int dv_2 f_0 \langle 0, 0 | t | 0, 0 \rangle g(\vec{v}_1) , \\ nB'[g] &= n\int \frac{d\vec{k}'}{(2\pi)^3} \int dv_2 f_0(\vec{v}_2) \langle 0, 0 | t | 0, 0 \rangle \\ &\quad \times [\epsilon + i\vec{k}'\cdot\vec{v}_1 + i(\vec{k} - \vec{k}')\vec{v}_2 + nJ_1 + nI_2]^{-1} \\ &\quad \times \langle 0, 0 | t | 0, 0 \rangle g(v_1) , \end{aligned} \tag{4.1}$$

where nJ is the linearized Boltzmann-Lorentz operator. The subscripts 1 and 2 indicate that the domains of the operators are functions of $\vec{v}_1$ or $\vec{v}_2$, respectively.

Eigenfunctions and eigenvalues of $(i\vec{k}\cdot\vec{v}_1 + nJ_1 - nB')$ will be obtained by perturbation theory, treating $i\vec{k}\cdot\vec{v}_1$ as the perturbation, in a manner analogous to Ref. 4. The unperturbed operator has an eigenvalue 0 with eigenfunction 1 [the Fourier-transform of $n_1(\vec{r})$]. There are other (unknown) points in the spectrum of $nJ_1 - nB'$, so the correlation functions will be written as the sum of two parts—a hydrodynamic part arising from the perturbation of the zero eigenvalue, and a microscopic part due to the remaining spectrum. This terminology is justified when the Boltzmann-Lorentz operator alone is used, as mentioned in the Introduction, because the perturbed zero eigenvalue is smallest and determines the long-time behavior. (The perturbed zero eigenvalue and eigenfunction determine the Chapman-Enskog solution to the Boltzmann equation.) This dominance of the hydrodynamic part for long times is no longer assured here due to the ϵ dependence of nB'. Denoting the perturbed zero eigenvalue by $p(\vec{k}, \epsilon)$ and the corresponding eigenfunction by $g(\vec{k}, \epsilon)$, the first-order results are (for fixed ϵ)

$$\begin{aligned} g(\vec{k}, \epsilon) &= 1 - i\vec{k}\cdot\vec{V}(\epsilon) , \\ p(\vec{k}, \epsilon) &= D(\epsilon, \vec{k})k^2 , \end{aligned} \tag{4.2}$$

where $\vec{V}(\epsilon, \vec{k})$ satisfies $(1, V(\epsilon, \vec{k})) = 0$ and

$$(nJ_1 - nB_1)\vec{V}(\epsilon, k) = \vec{v}_1 ; \tag{4.3}$$

$D(\epsilon, \vec{k})$ is defined by

$$D(\epsilon, \vec{k}) = \tfrac{1}{3}(v_i , V_i(\epsilon, \vec{k})) . \tag{4.4}$$

The correlation function becomes

$$\overline{C}_{AB}(\vec{k}, \epsilon) = \frac{(a, g)(g, b)}{\epsilon + D(\epsilon, \vec{k})k^2} + (a_\perp, R'(\vec{k}, \epsilon)b_\perp) , \tag{4.5}$$

where $a_\perp$ and $b_\perp$ are the projections of a and b orthogonal to g:

$$a_\perp = a - g(g^*, a), \quad b_\perp = b - g(g^*, b).$$

The relevant correlation functions for self-diffusion are those formed from the locally conserved $n_1(\vec{r})$ and the associated flux $\vec{v}_1(\vec{r}) = \vec{v}_1\delta(\vec{r} - \vec{q})$. In the above approximation these are

$$\begin{aligned} \overline{C}_{n_1n_1}(\vec{k}, \epsilon) &= (\epsilon + Dk^2)^{-1} - \tfrac{1}{3}k^2(V_i , R'(\vec{k}, \epsilon)V_i) , \\ \overline{C}^{i}_{n_1v_1}(\vec{k}, \epsilon) &= \frac{-ik_i D}{\epsilon + Dk^2} + \tfrac{1}{3}ik_i(V_j , R'(\vec{k}, \epsilon)v_j) , \\ \overline{C}^{ij}_{v_1v_1}(\vec{k}, \epsilon) &= \frac{-k_ik_jD^2}{\epsilon + Dk^2} + (v_i , R'(\vec{k}, \epsilon)v_j) \end{aligned} \tag{4.6}$$

The $\vec{k}$, ϵ dependence of $D(\epsilon, \vec{k})$ has been left implicit.

In the Boltzmann case the functions corresponding to D and $\vec{V}$ can be estimated using a variational principle. A similar estimate will be used here. First, direct calculation shows that $nJ - nB'$ satisfies, for real f, h:

$$(f, (nJ - nB')h) = (h, (nJ - nB')f) . \tag{4.7}$$

Let $F(\overline{V}) = (\overline{V}_i , [2v_i - (nJ - nB')\overline{V}_i])$ for a real function $\overline{V}_i$ with $(\overline{V}_i , 1) = 0$. Varying $F(\overline{V})$ with respect to $\overline{V}$ locates the extremum,

$$F(\overline{V})=0=(\delta\overline{V}_i,\ [2v_i-(nJ-nB')\overline{V}_i])-(\overline{V}_i,\ (nJ-nB')\delta\overline{V}_i)$$

or

$$(\delta\overline{V}_i,\ [v_i-(nJ-nB')\overline{V}_i\ ])=0\ .$$

Therefore, $F(\overline{V})$ is an extremum when $\overline{V}_i=V_i$. As a trial function choose

$$\overline{V}_i=\alpha v_i\ , \tag{4.8}$$

where α is determined by the condition $\delta F(\alpha v_i)=0$. The result is

$$\alpha=\frac{3}{\beta m}\ [(v_i,\ (nJ-nB')v_i)\ ]^{-1},\quad \beta\equiv(k_BT)^{-1}\ . \tag{4.9}$$

Here, k_B is Boltzmann's constant. T is the temperature, and m is the mass. Use of Eq. (4.8) in (4.3) and (4.4) gives the desired approximations,[9]

$$D=(\beta m)^{-1}\alpha\ ,\quad (nJ-nB')v_i=\alpha^{-1}v_i\ . \tag{4.10}$$

The latter equation indicates that v_i is an approximate eigenfunction of $nJ-nB'$ with eigenvalue $\alpha^{-1}(\vec{k},\epsilon)$. Further, for small $\vec{k}$, the streaming term $i\vec{k}\cdot\vec{v}$ in $R'(\vec{k},\epsilon)$ may be neglected in calculating the microscopic part. This enables Eq. (4.6) to be further simplified to

$$\overline{C}_{nn}(\vec{k},\epsilon)=\frac{1}{\epsilon+D(\epsilon,\vec{k})k^2}-\frac{\beta mD^2(\epsilon,\vec{k})k^2}{\epsilon+[\beta mD(\epsilon,\vec{k})\ ]^{-1}}\ ,$$

$$\overline{C}^{\,i}_{nv}(\vec{k},\epsilon)=\frac{-ik_iD(\epsilon,\vec{k})}{\epsilon+D(\epsilon,\vec{k})k^2}+\frac{ik_iD(\epsilon,\vec{k})}{\epsilon+[\ \beta mD(\epsilon,\vec{k})\ ]^{-1}}\ ,$$

$$\overline{C}^{\,ij}_{vv}(\vec{k},\epsilon)=\frac{-k_ik_jD^2(\epsilon,\vec{k})}{\epsilon+D(\epsilon,\vec{k})k^2}+\frac{(\beta m)^{-1}\delta_{ij}}{\epsilon+[\ \beta mD(\epsilon,\vec{k})\ ]^{-1}}\ . \tag{4.11}$$

The evaluation of $D(\epsilon,k)$ from Eq. (4.9) requires $(v_i,\ nB'v_i)$ with B' defined in Eq. (4.1). The operator B' in turn contains $[\epsilon+i\vec{k}\cdot\vec{v}_i+i(\vec{k}-\vec{k}')\cdot\vec{v}_2+nJ_1+nI_2]^{-1}$. For small ϵ, only the small eigenvalues of $i\vec{k}'\cdot\vec{v}_1+i(k-k')\cdot\vec{v}_2+nJ_1+nI_2$ are required, and these are just the sum of the hydrodynamic eigenvalues of $(i\vec{k}'\cdot\vec{v}_1+nJ_1)$ and $[i(\vec{k}-\vec{k}')\cdot\vec{v}_2+nI_2]$ (the latter are given explicitly in Sec. V). The resulting expression is found to be

$$(v_i,\ nB'v_i)=\frac{2}{nD_0^2\beta^3m^3}\times\int\frac{d\vec{k}'}{(2\pi)^3}\left(\epsilon+D_0k'^2+\frac{\eta_0}{nm}(\vec{k}-\vec{k}')^2\right)^{-1},\quad k'<k_m$$

$$\equiv\frac{3}{(\beta m)^2D_0}\ \Delta(k,\epsilon)\ , \tag{4.12}$$

where D_0 is the diffusion constant determined by the Boltzmann-Lorentz operator and η_0 is the viscosity determined by the Boltzmann operator. The $\vec{k}'$ integration is cut off at some k_m, since only the small k part of the integrand has been calculated.

The function $D(\epsilon,k)$ is now

$$D(\epsilon,\vec{k})=D_0\,[1-\Delta(\epsilon,k)\ ]^{-1}\ . \tag{4.13}$$

The contribution from the correlated two-body collisions, Δ, becomes asymptotically

$$\lim_{\epsilon\to 0}\Delta(\epsilon)\to C-\frac{(\epsilon+\alpha k^2)^{1/2}}{6n\pi\beta mD_0\,(D_0+\eta_0/nm)^{3/2}}\ . \tag{4.14}$$

C is a constant depending on k_m. For small k and ϵ, $D(\epsilon,k)$ is

$$D(\epsilon,\vec{k})\to D-\beta mD^2\,a(\epsilon+\alpha k^2)^{1/2}\ ,$$

$$a\equiv[(\beta mD_0)^2\,6\pi n(D_0+\eta_0/nm)^{3/2}\ ]^{-1}\ , \tag{4.15}$$

$$\alpha=\eta_0\,D_0\,(nmD_0+\eta_0)^{-1}\ .$$

D is proportional to the Boltzmann diffusion constant D_0, and η_0 is the Boltzmann sheer viscosity.

The first terms on the right-hand side in Eqs. (4.11) are the hydrodynamic parts and the second terms are the microscopic parts. The Boltzmann result is regained on setting $a=0$, $D=D_0$. There are two essential modifications of the Boltzmann result in Eq. (4.11). The hydrodynamic part no longer represents a simple diffusion mode, due to the ϵ dependence of $D(\epsilon,\vec{k})$. In addition, the microscopic part, as well as the hydrodynamic part, has a branch cut extending to $-\alpha k^2$. The singularities of the two parts are then not well separated, and contributions from the microscopic part persist on the same time scale as those from the hydrodynamic part. As a specific example, $\overline{C}_{nn}(\vec{k},\epsilon)$ for small $\vec{k}$, ϵ is

$$\overline{C}_{nn}(\vec{k},\epsilon)=\frac{1}{\epsilon+Dk^2-\beta maD^2(\epsilon+\alpha k^2)^{1/2}}-\frac{\beta mD^2k^2}{\epsilon+(\ \beta mD)^{-1}+a(\epsilon+\alpha k^2)^{1/2}}\ . \tag{4.16}$$

For long times, the inverse transforms of the hydrodynamic and microscopic parts are, respectively,

$$\overline{C}^{\,h}_{nn}(r,t)\sim\frac{e^{-r^2/4Dt}}{(4\pi Dt)^{3/2}}\ ,$$

$$\overline{C}^{\,m}_{nn}(r,t)\sim\frac{3a(\beta mD)^3\alpha^{3/2}}{2\pi^2(2\alpha t)^4}\ e^{-r^2/4\alpha t}\ . \tag{4.17}$$

Therefore, while Eq. (4.11) shows the hydrodynamic part is not in general a solution to the usual diffusion equation, it approaches one for long times. However, the microscopic part also reflects a diffusion mode and decays only as t^{-4}.

Finally, the velocity autocorrelation function, from which the usual diffusion constant is determined, is

$$\frac{\langle\vec{v}\cdot\vec{v}(t)\rangle}{\langle v^2\rangle}=\lim_{k\to 0}\frac{1}{2\pi i}\ \frac{\beta m}{3}\int d\epsilon\,e^{\epsilon t}\,\overline{C}^{\,ii}_{vv}(\epsilon,\vec{k})\ . \tag{4.18}$$

The hydrodynamic part of $\overline{C}^{\,ii}_{vv}(\epsilon, k)$ does not contribute in the limit $k \to 0$, and the correlation function is[10]

$$\frac{\langle \vec{v} \cdot \vec{v}(t) \rangle}{\langle v^2 \rangle} = \frac{a(\beta m D)^{1/2}}{\pi} \times \int_0^\infty dy\, y^{1/2}\, \frac{e^{-yt/\beta m D}}{(y-1)^2 + \beta m D a^2 y} \; .$$

For short times the integral behaves as $e^{-t/\beta m D}$, which is the Boltzmann result. For asymptotically long times the velocity autocorrelation function is

$$\langle \vec{v} \cdot \vec{v}(t) \rangle / \langle v^2 \rangle \sim (\beta m D)^2 a / 2\pi^{1/2} t^{3/2} \, , \tag{4.19}$$

which agrees with Dorfman and Cohen.

V. CORRELATION OF LOCALLY CONSERVED QUANTITIES

The calculation of correlation functions constructed from the locally conserved number density, energy density, and momentum density is similar to that for the self-diffusion problem. Returning to Eq. (3.12), the eigenvalues and eigenfunctions of $(i\vec{k} \cdot \vec{v}_1 + nI_1 - nB)$ resulting from lowest-order perturbation on the zero eigenvalue of $nI_1 - nB$ are sought. The latter is fivefold degenerate with the two-particle summational invariants as eigenfunctions. The resulting perturbed eigenfunctions $g_\alpha(\vec{k}, \epsilon)$ and eigenvalues $P_\alpha(\vec{k}, \epsilon)$ are formally the same as those found by McLennan, except for the ϵ and k dependence:

$$\begin{aligned}
g_1 &= (\beta m)^{1/2} e_i^{(2)} \left(v_i - \frac{ik_j}{nm} \mathfrak{D}_{ij}(\vec{k}, \epsilon) \right) \; , \quad g_2 = (\beta m)^{1/2} e_i^{(3)} \left(v_i - \frac{ik_j}{nm} \mathfrak{D}_{ij}(\vec{k}, \epsilon) \right) \, , \\
g_3 &= (\tfrac{2}{5})^{1/2} \left[\beta u - \frac{5}{2} - \frac{\beta}{n} ik_i \left(\mathcal{S}_i(k, \epsilon) - \frac{2}{5} \frac{n v_i}{k_B} \lambda(\vec{k}, \epsilon) \right) \right] \, , \\
g_{4,5} &= (\tfrac{2}{15})^{1/2} \left\{ \beta u - \frac{\beta}{n} ik_i \left[\mathcal{S}_i(\vec{k}, \epsilon) + \frac{1}{2} \left(\eta(\vec{k}, \epsilon) - \frac{m}{5k_B} \lambda(\vec{k}, \epsilon) \right) v_i \right] \right\} \\
&\quad \pm \left(\frac{\beta m}{2} \right)^{1/2} e_i^{(1)} \left\{ v_i - \frac{ik_j}{nm} \left[\mathfrak{D}_{ij}(\vec{k}, \epsilon) - \tfrac{2}{15} e_j^{(1)} \left(\eta(\vec{k}, \epsilon) - \frac{7m}{5k_B} \lambda(\vec{k}, \epsilon) \right) \beta u - \frac{2m}{5k_B} \lambda(\vec{k}, \epsilon) \right] \right\} \, ,
\end{aligned} \tag{5.1}$$

and

$$P_1(\vec{k}, \epsilon) = \frac{\eta(\vec{k}, \epsilon)}{nm} k^2 = P_2(\vec{k}, \epsilon) \, , \quad P_3(\vec{k}, \epsilon) = \frac{2\lambda(\vec{k}, \epsilon) k^2}{5nk_B} \, , \quad P_{4,5}(\vec{k}, \epsilon) = \pm ikc + \Gamma(\vec{k}, \epsilon) k^2 \, . \tag{5.2}$$

The vectors $\vec{e}^{(1)}$, $\vec{e}^{(2)}$, and $\vec{e}^{(3)}$ are an orthonormal set with $e^{(1)}$ along the direction of $\vec{k}$. Also, $\mathcal{S}_i(\epsilon, \vec{k})$ and $\mathfrak{D}_{ij}(\epsilon, \vec{k})$ are orthogonal to the summational invariants and satisfy,

$$(I - B)\mathfrak{D}_{ij} = D_{ij} \equiv m(v_i v_j - \tfrac{1}{3} v^2 \delta_{ij}) \, , \quad (I - B)\mathcal{S}_i = S_i \equiv [u - (5/2\beta)] v_i \, . \tag{5.3}$$

Finally, we have

$$\begin{aligned}
&\lambda(\epsilon, \vec{k}) \equiv \tfrac{1}{3} k_B \beta^2 (S_i, \mathcal{S}_i) \, , \qquad u \equiv \tfrac{1}{2} m v^2 \, , \quad c \equiv (5/3\beta m)^{1/2} \, . \\
&\eta(\epsilon, \vec{k}) \equiv \tfrac{1}{10} \beta (D_{ij}, \mathfrak{D}_{ij}) \, , \quad \Gamma(\epsilon, \vec{k}) \equiv \frac{2}{3nm} \left(\eta(\epsilon, k) + \frac{1}{5} \frac{\lambda(\epsilon, k) m}{k_B} \right) \, ,
\end{aligned} \tag{5.4}$$

To this order in $\vec{k}$, the various correlation functions of the conserved local densities are found to be

$$C_{nn}(\vec{k}, \epsilon) = n \left(\frac{\frac{2}{5}}{\epsilon + P_3} + \frac{3}{5} \frac{\epsilon + \frac{4}{3}(P_1 + P_3)}{(\epsilon + P_4)(\epsilon + P_5)} + \frac{4}{3} \frac{k^4}{(\beta m)^2} g_2(\vec{k}, \epsilon) \right) \, , \tag{5.5}$$

$$C_{uu}(\vec{k}, \epsilon) = \frac{15n}{4\beta^2} \frac{\epsilon + \frac{4}{3} P_1}{(\epsilon + P_4)(\epsilon + P_5)} - \frac{5k^2 n}{2m\beta^3} g_1(\vec{k}, \epsilon) \; , \tag{5.6}$$

$$\begin{aligned}
C^{ij}_{pp}(\vec{k}, \epsilon) &= \left(\delta_{ij} - \frac{k_i k_j}{k^2} \right) \left(\frac{nm\beta^{-1}}{\epsilon + P_1} - \frac{k^2 n}{\beta^2} g_2(\vec{k}, \epsilon) \right) \\
&\quad + \frac{k_i k_j}{k^2} \left(\frac{nm}{\beta} \frac{\epsilon + \frac{2}{3} P_3}{(\epsilon + P_4)(\epsilon + P_5)} + \frac{2}{5} \frac{m^2 n P_3^2 k^{-2}}{\epsilon + P_3} - \frac{4k^2 n}{3\beta^2} g_2(\vec{k}, \epsilon) \right) \, ,
\end{aligned} \tag{5.7}$$

$$C_{nu}(k, \epsilon) = \frac{3n}{2\beta} \frac{\epsilon + \frac{2}{3} P_1 + P_3}{(\epsilon + P_4)(\epsilon + P_5)} \; , \tag{5.8}$$

$$C^{i}_{np}(k, \epsilon) = -ik_i n \left(\frac{2}{5} \frac{m P_3 k^{-2}}{\epsilon + P_3} + \frac{1}{\beta} \frac{1 - \frac{2}{5} \epsilon k^{-2} \beta m P_3}{(\epsilon + P_4)(\epsilon + P_5)} + \frac{4}{3} \frac{k^2 n}{m} g_2(\vec{k}, \epsilon) \right) \, , \tag{5.9}$$

$$C^i_{up}(k,\epsilon) = -ik_i\,\frac{5n}{2\beta^2}\,\frac{1-\frac{1}{5}\epsilon k^{-2}\beta m P_3}{(\epsilon+P_4)(\epsilon+P_5)}\ . \tag{5.10}$$

The microscopic parts, $g_1(\vec{k},\epsilon)$ and $g_2(\vec{k},\epsilon)$ are defined by

$$g_i(\vec{k},\epsilon) \equiv \tau_i^2(\epsilon+\tau_i^{-1})^{-1}\ ,\quad i=1,2 \tag{5.11}$$

and

$$\tau_1(\epsilon,\vec{k}) = (\beta m/n)(2/5k_B)\,\lambda(\epsilon,\vec{k})\ ,\qquad \tau_2(\epsilon,\vec{k}) = (\beta/n)\,\eta(\epsilon,\vec{k})\ . \tag{5.12}$$

The correlation functions are fully determined when $\lambda(\epsilon,\vec{k})$ and $\eta(\epsilon,\vec{k})$ are known. The small $\epsilon,\vec{k}$ behavior is found to be

$$\begin{aligned}\lambda(\epsilon,\vec{k}) &\to \lambda\{1-\beta m D_T[\,a_1(\epsilon+\alpha_1 k^2)^{1/2}+a_2(\epsilon+\tfrac{1}{2}\Gamma_0 k^2+ick)^{1/2}+a_2(\epsilon+\tfrac{1}{2}\Gamma_0 k^2-ick)^{1/2}]\}\ ,\\ \eta(\epsilon,k) &\to \eta\left\{1-\frac{\beta\eta}{n}\left[a_3\left(\epsilon+\frac{1}{2}\,\frac{\eta_0}{nm}\,k^2\right)^{1/2}+a_4\ (\epsilon+\tfrac{1}{2}\Gamma_0 k^2+ick)^{1/2}+a_4(\epsilon+\tfrac{1}{2}\Gamma_0 k^2-ick)^{1/2}\right]\right\}\ ,\end{aligned} \tag{5.13}$$

with

$$\begin{aligned}&\alpha_1 \equiv \frac{\eta_0\lambda_0}{nk_B}\left(\eta_0+\frac{2}{5}\,\frac{\lambda_0 m}{k_B}\right)^{-1}\ ,\quad a_1 \equiv \left[\left(\beta m D_{T0}\right)^2\,6n\pi\left(\frac{\eta_0}{nm}+\frac{2}{5}\,\frac{\lambda_0}{nk_B}\right)^{3/2}\right]^{-1}\ ,\quad a_2 \equiv [72\sqrt{2}(\beta m D_{T0})^2 n\pi\Gamma_0^{3/2}]^{-1}\ ,\\ &a_3 \equiv \left[\frac{120\sqrt{2}}{7}\left(\frac{\beta\eta_0}{n}\right)^2 n\pi\left(\frac{\eta_0}{nm}\right)^{3/2}\right]^{-1}\ ,\quad a_4 \equiv \left[240\sqrt{2}\left(\frac{\beta\eta}{n}\right)^2 n\pi\Gamma_0^{3/2}\right]^{-1}\ ,\quad D_T \equiv 2\lambda/5nK_B\ .\end{aligned} \tag{5.14}$$

The constants λ and η are proportional to, respectively, the Boltzmann thermal conductivity λ_0 and the Boltzmann sheer viscosity η_0. The proportionality constant depends on an undetermined cutoff such as that used in Eq. (4.12). Finally, we state without proof that evaluation of the flux-flux correlation functions occurring in the Green-Kubo expressions for the transport coefficients leads to

$$\lambda_{Gk} \equiv \lim_{\epsilon\to 0}\lim_{k\to 0}\lambda(\vec{k},\epsilon)\ ,\qquad \eta_{Gk} \equiv \lim_{\epsilon\to 0}\lim_{k\to 0}\eta(\vec{k},\epsilon)\ ,$$

with $\lambda(\epsilon,\vec{k})$ and $\eta(\epsilon,\vec{k})$ given by Eq. (5.13).

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APPENDIX A: CONVERGENCE OF EXPANSION ABOUT LOCAL EQUILIBRIUM

The formal solution to the Liouville equation for initial local equilibrium, Eq. (2.1), may be written as

$$\begin{aligned}\rho(t) = f_0(\beta_0,\nu_0,\vec{U}_0)\exp\{&-\delta q(\lambda)-\textstyle\int d\vec{x}'\,\delta\beta(x')u(x',t)\\ &-[\,\delta\nu(x')-\tfrac{1}{2}m\delta(\beta U^2)(x')\,]n(x')\\ &-\delta(\beta\vec{U})(x')\cdot\vec{p}(x',t)\}\ ,\end{aligned}$$

where $\delta\beta(x') \equiv [\,\beta(x',0)-\beta_0)$ is the deviation of the initial value $\beta(x'0)$ from the final equilibrium value β_0, with similar definitions for $\delta\nu(x')$, $\delta(\beta U^2)(x')$, $\delta(\beta\vec{U})(x')$, and δq. Expansion to lowest order in the deviations leads to Eq. (2.2). For simplicity, it will be assumed $\vec{U}_0 = \vec{U}(x',0) = 0 = \delta\nu(x')$; analysis of the more general case is similar. Let $\lambda = \max|\delta\beta(x',0)|$ and define $\delta\beta(x',0) = \lambda\delta\beta'(x',0)$. The average of a phase function $A(p_1\cdots p_N, q_1\cdots q_N)$ is then

$$\langle A;\,t\rangle = e^{-\delta q(\lambda)}\langle A\exp(-\lambda)\textstyle\int d\vec{x}'\,\delta\beta'(x',0)u(x',t)\rangle_0$$

and the following theorem holds:

Let $\langle A;\,t\rangle$ denote the average of the phase function A over a solution to the Liouville equation with initial local equilibrium for a system with repulsive interaction. Further, let the partition function Z and the equilibrium average of $|A|$ by analytic in β in some finite interval. Then $\langle A;\,t\rangle(\lambda)$ is analytic in λ about zero, and the expansion converges uniformly in time t.

Proof. Since the product of two analytic functions is analytic, it suffices to show $e^{-\delta q(\lambda)}$ and

$$\langle A\exp[-\lambda\textstyle\int dx'\,\delta\beta'(x')u(x',t)]\rangle_0$$

are each analytic in λ. Consider first $e^{\delta q(\lambda)}$. From normalization of $\rho(t)$,

$$\begin{aligned}e^{\delta q(\lambda)} &= \langle\exp[-\lambda\textstyle\int dx'\beta'(x')u(x',t)]\rangle_0\\ &= \sum_{n=0}^{\infty}\frac{(-\lambda)^n}{n!}\langle\Delta^n\rangle\ ,\\ \Delta &\equiv \int dx'\,\delta\beta'(x')u(x')\\ &\le \sum_{n=0}^{\infty}\frac{\lambda^n}{n!}\left\langle\left[\int d\vec{x}'u(\vec{x}')\right]^n\right\rangle_0\end{aligned}$$

$$= \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} \langle H^n \rangle_0 = Z(\beta - \lambda).$$

The expansion is bounded by that of the analytic function Z and is analytic. Since $e^{\delta q(0)} = 1$, $e^{-\delta q(\lambda)}$ is analytic for sufficiently small λ. Similarly,

$$\langle A \exp - \lambda \int d\vec{x}' \, \delta\beta'(\vec{x}') u(\vec{x}', t) \rangle_0$$

$$= \sum_{n=0}^{\infty} \frac{(-\lambda)^n}{n!} \left\langle A \left[\int d\vec{x}' \, \delta\beta'(\vec{x}') \, u(\vec{x}', t) \right]^n \right\rangle_0$$

$$\leq \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} \langle |A| H^n \rangle_0 = \langle |A| e^{\lambda H} \rangle_0$$

which shows convergence under the assumption that $\langle |A| \rangle_0$ is analytic in λ. The bound is independent of time, so the expansion converges uniformly.

APPENDIX B: RING APPROXIMATION

The ring approximation is discussed in detail in Ref. 8 (although in a slightly different context) and is only briefly summarized here. The "kinetic equation," Eq. (3.7), for $\Phi^{(1)}$ is obtained from an exact equation of the form

$$[\epsilon + \mathcal{H}^{(1)} + B(\epsilon)] \, \Phi^{(1)}(p_1, q_1, \epsilon) = b(p_1, q_1),$$

where $\mathcal{H}^{(1)} \equiv (p_1/m)(\partial/\partial q_1)$ and $B(\epsilon)$ is an operator on functions of p_1, q_1. If $B(\epsilon)$ is expanded in a power series in the density, the leading term is a Boltzmann operator. Terms cubic and higher in the density (four-body, or more, terms) diverge in the limit $\epsilon \to 0$, so convergence, at best, is not uniform. Since it is just the small ϵ behavior that is required to determine long-time behavior, the density expansion is not applicable. The ring approximation consists of a partial resummation, containing most divergent terms of each power of the density as $\epsilon \to 0$. This leads to[8]

$$B(\epsilon) = -f^{-1}(1) n \int dx_2 \, t_{12}(1,2)(1+P_{12}) R_0(1,2) - f^{-1}(1) n \int dx_2 \, t_{12}(1,2) \sum_{m=1}^{\infty} \{ n \int dx_3 [t_{13}(123)(1+P_{13})$$
$$\times R_0(123) + t_{23}(123) R_0(123)(1+P_{12})] f(3) \}^m \, t_{12}(12) R_0(12) f(1) f(2),$$

where

$$R_0(12) \equiv [\epsilon + \mathcal{H}^{(1)}(1) + \mathcal{H}^{(1)}(2)]^{-1},$$

$$R_0(123) = [\epsilon + \mathcal{H}^{(1)}(1) + \mathcal{H}^{(1)}(2) + \mathcal{H}^{(1)}(3)]^{-1}$$

and the t operators satisfy,

$$t_{ij}(ij) = \Theta_{ij} + t_{ij} R_0(ij) \Theta_{ij},$$

$$t_{ij}(ijk) = \Theta_{ij} + t_{ij} R_0(ijk) \Theta_{ij},$$

$$\Theta_{ij} \equiv \frac{\partial v(|\vec{r}_i - \vec{r}_j|)}{\partial \vec{r}_i} \left(\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j} \right),$$

Also, dx_i denotes $d\vec{p}_i \, d\vec{q}_i$ and P_{12} is a permutation operator, $P_{12} g(1,2) = g(2,1)$. Rearranging the expression for $B(\epsilon)$ gives

$$B(\epsilon) = -n \int dx_2 f(2) \tilde{t}_{12}(1+P_{12})$$
$$- n \int dx_2 f(2) \tilde{t}_{12} [\epsilon + \mathcal{H}^{(1)}(1)$$
$$+ \mathcal{H}^{(1)}(2) - L(1,2)]^{-1} \tilde{t}_{12}$$
$$\equiv -n \int dx_2 f(2) \tilde{t}_{12}(1+P_{12}) - n B^R(\vec{p}_1, \vec{q}_1, \epsilon)$$

with

$$L(1,2) = n \int dx_3 f(3) [\tilde{t}_{23}(123)(1+P_{23}) + \tilde{t}_{12}(1+P_{13})],$$

$$\tilde{t}_{ij} \equiv f^{-1}(i) f^{-1}(j) \, t_{ij} \, f(i) f(j).$$

Use has been made of the fact that $\int dx_2 \, t_{12} R_0 \, t_{12}$ vanishes for hard spheres. The equation satisfied by $\Phi^{(1)}(\vec{p}_1, \vec{q}_1, \epsilon)$ is now

$$[\epsilon + \mathcal{H}^{(1)} - n \int dx_2 f(2) \tilde{t}_{12}(1+P_{12}) - n B^R(\vec{p}_1, \vec{q}_1, \epsilon)]$$
$$\times \Phi(\vec{p}_1, \vec{q}_1, \epsilon) = b(\vec{p}_1, \vec{q}_1).$$

Fourier transforming this equation leads to, after some lengthy computation,

$$[\epsilon + i\vec{k} \cdot \vec{p}_1/m) - n \int d\vec{p}_2 f(2) \langle k, 0 | \tilde{t}_{12}(1+P_{12}) | k, 0 \rangle$$
$$- n B^R(k, \epsilon)] \, \Phi(\vec{p}_1, k, \epsilon) = b(\vec{p}_1, k).$$

Here, the notation is that of Ref. 3:

$$\langle k_1 k_2 | t_{12} | k_1' k_2' \rangle = \int d\vec{q}_1 d\vec{q}_2 \, e^{-i\vec{k}_1 \cdot \vec{q}_1 - \vec{k}_2 \cdot \vec{q}_2} \, t_{12} \, e^{i\vec{k}_1' \cdot \vec{q}_1 + i\vec{k}_2' \cdot \vec{q}_2},$$

and

$$B^R(p_1, k, \epsilon) \equiv \int \frac{d\vec{k}'}{(2\pi)^3} \, d\vec{p}_2 f(2) \langle k, 0 | \tilde{t}_{12} | k', k-k' \rangle$$
$$\times \left(e + i\vec{k}' \cdot \frac{\vec{p}_1}{m} + i(\vec{k} - \vec{k}') \cdot \frac{\vec{p}_2}{m} - L(k', k-k') \right)^{-1}$$
$$\times \langle k', k-k' | \tilde{t}_{12} | k, 0 \rangle,$$

$$L(k', k-k') \equiv \int d\vec{p}_3$$
$$\times f(3) [\langle k', k-k', 0 | \tilde{t}_{23}(1+P_{23}) | k', k-k', 0 \rangle$$
$$+ \langle k', k-k', 0 | t_{13}(1+P_{13}) | k', k-k', 0 \rangle].$$

The dependence of $\langle | t_{ij} | \rangle$ on k and ϵ for small k, ϵ is weak and may be reasonably neglected (this neglects space and time variations over distances of the order of the force range and overtimes of the order of the two-body collision time. With this approximation,

$$\int d\vec{p}_2 f(2) \langle 0, 0 | \tilde{t}_{12}(1+P_{12}) | 0, 0 \rangle$$

becomes the usual Boltzmann operator, and the resulting B^R is that used in Sec. III.

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[10] The author is indebted to Professor J. R. Dorfman for pointing out an error in this expression as it appeared in an earlier manuscript.

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Nonsymmetric Perturbation Calculations of Excited States of Helium[†]

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Perturbation-theoretic calculations are carried out for the lowest five states of the helium atom using a Hamiltonian which is not symmetric in the particle indices such that the zeroth-order spatial functions can be written as simple products of hydrogenic orbitals. The perturbation expansions are reasonably convergent except for the fifth state which is divergent as expected. By 19th order in the expansion the energies of the first two excited states are accurate to 2×10^{-4} and the expectation values of $\frac{1}{2}(1\pm P)$ are accurate to 1×10^{-4}.

I. INTRODUCTION

It is general practice to perform perturbation-theoretic calculations using spatial functions Φ_0 which possess the exact many-electron symmetry. Thus, for example, the energies of the first two excited states of helium have been calculated with

$$\Phi_0^{1,3} = 1s(1)\,2s(2) \pm 2s(1)\,1s(2)\,, \tag{1}$$

as the unnormalized singlet and triplet zeroth-order functions constructed from hydrogenic 1s and 2s functions.[1,2] The splitting between the two energies is called the exchange energy since in lowest (first) order it is given by

$$J_1 = 2\,\langle 1s(1)\,2s(2)\,|\,r_{12}^{-1}\,|\,2s(1)\,1s(2)\rangle\,, \tag{2}$$

although, in fact, J_1 is larger than the exact J itself by a factor of 3.

There are, however, some advantages to choosing the functions Φ_0 to be simple products of atomic orbitals as was first discussed by Heisenberg[3] and later by Hartree,[4] but further attempts have been discouraged by the generally accepted view[5,6] that a systematic treatment of perturbation theory is impossible unless the exact permutation symmetry is incorporated into Φ_0 itself. The contrary view was expressed by Musher[7,8] in a discussion of the hydrogen molecule where the rather obvious point was made that if perturbation theory converges then the particle symmetry will be introduced order by order by the action of the nonsymmetric perturbation. A necessary requirement for such a procedure