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Bound-state and finite-collision-time effects in the binary-collision approximation

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The kinetic theory for time-correlation functions at low density is studied for potentials with bound states and finite collision times. The contribution to the binary-collision operator from bound pairs of atoms with arbitrarily large interaction times is shown to exist and to vanish for times large compared to the characteristic scattering time, justifying the Boltzmann limit for potentials with attractive parts. The effects of such bound states and finite collision times on the short-time behavior of correlation functions are illustrated by a detailed calculation of the velocity-autocorrelation function for a square-well potential. Good agreement with the corresponding results from molecular dynamics is obtained.

I. INTRODUCTION

The description of time-correlation functions for a low-density gas in terms of the Boltzmann equation results from several limiting conditions on the phenomena to be described. At sufficiently low density it is expected that only the first term in a formal cluster expansion for the dynamics of the system is required, leading to the binary-collision approximation.[1] The Boltzmann description results from the binary-collision approximation with two further limits: (1) neglect of spatial variations associated with the relative distance between a colliding pair of atoms, and (2) neglect of the time variation associated with the interaction time of a pair of atoms. These conditions effectively restrict application of the Boltzmann result to spatial variations over distances large compared to the force range and times long compared to the interaction time. For most transport phenomena the relevant space and time scales are the mean free path and mean time between collisions, both considerably larger than the corresponding force range and interaction time at low density. Consequently, calculations based on the Boltzmann equation are adequate for a wide variety of problems in gas dynamics.[2] However, a complete description of low-density time-correlation functions over all space and time scales requires the detailed description of the binary-collision approximation. The effects associated with spatial variations over distances of the order of the force range have been discussed elsewhere.[3] The objective here is to study the time dependence of spatially homogeneous correlation functions for short as well as long times in the binary-collision approximation.

One motivation for this study is to investigate the dependence of the short-time dynamics of the gas on the potential model. To illustrate this dependence consider, for example, the velocity-autocorrelation function. For a hard-sphere gas the correlation function has an exponential decay for all times, whereas for a Lennard-Jones gas the initial decay is a Gaussian followed by exponential decay at long times. The reason for this difference is that the Lennard-Jones potential allows a finite interaction time for a pair of atoms while the hard-sphere interaction time is zero. The short-time behavior of the correlation function thus provides a more detailed picture of the binary dynamics for a given potential than can be obtained from transport data. Such effects are easily observed in dense gases or liquids, where they are often modeled in terms of parameters determined from the first few initial time derivatives of the correlation function.[4] The low-density gas is a prototype case where these effects can be studied at a more fundamental level. Even at low density, such finite-collision-time effects are important to describe observed line shapes in pressure or collisional broadening.[5] Furthermore, computer simulations of gases at low densities are now available[6] to provide a detailed test of linear kinetic theory beyond the Boltzmann approximation.

In practice, the origin of finite collision times is largely associated with the existence of an attractive part of the pair potential. For such potentials the binary-collision approximation leads to contributions from bound pairs of atoms describing trajectories bounded in space and characterized by an infinite interaction time. In contrast, the Boltzmann description has no such contribution and contains information only about the asymptotic scattered states. There is a technical problem, therefore, as to how the Boltzmann limit is obtained when the possibility for bound states exists. As noted above, the Boltzmann description is expected to result from the binary-collision approximation for times long compared to the interaction time. For the scattering states the interaction time is of the order of $\tau \equiv \sigma/v$, where σ is the force range and v is the average velocity. In this case it is easily shown that the binary-collision rate rapidly approaches its asymptotic limit for $t > \tau$. However, since the interaction time for bound states is infinite it is unclear what results for long times from their contribution to the binary-collision approximation. The fact that the time dependence for the bound states cannot be scaled by the collision time, τ, has been a persistent difficulty in the many-body analysis needed to justify the Boltzmann limit at low density, and most such discussions are accompanied by a restriction to short-ranged repulsive potentials. An exception[7] is the discussion of Kirkwood for the time-averaged single-particle reduced distribution function. Its relationship to the present work is given in Appendix C. The analysis of the bound-state contribution to the binary-collision approximation presented here indicates that there are no fundamental problems, at least at the low-density level. More specifically, the bound-state contribution to the correlation function is shown to exist for all times, and to vanish on a time scale of the order of τ as required by the Boltzmann limit, although considerably more slowly than the scattering-state contribution. Detailed calculations are performed here only for the special case of a square-well potential, but the same qualitative behavior is indicated for more general potentials.

Another motivation for the study of finite collision-time effects in the binary-collision approximation is their importance at higher densities when multiple collisions are accounted for. Preliminary investigations based on a "repeated ring" kinetic equation indicate that part of the density dependence of transport coefficients is due to collisional damping during a binary collision due to collisions with other particles of the fluid.[8,9] A close relationship between the short-time two-particle dynamics described here and higher-order-density effects is found; these results will be described elsewhere.[10]

In the next section the binary-collision approximation for spatially homogeneous time-correlation functions is recalled. The collision operator is described for a general continuous potential and for the special case of a square-well potential. In particular, the velocity-autocorrelation function for a continuous potential is considered in Sec. III. The associated collision integral is separated into bound state and scattering contributions. The bound-state dynamics are represented as a series of contributions from portions of trajectories between successive turning points. A more detailed analysis of the velocity-autocorrelation function for the square-well potential is given in Sec. IV. Uniform convergence (with respect to time) of the bound-state series is proved for a typical one of the collision integrals. The Laplace transformed series is also summed to illustrate the analytic behavior of the bound-state dynamics. In general, a countably infinite number of poles equally spaced on the imaginary axis, corresponding to partial collisions at the edges of the well, are found for fixed impact parameter and relative velocity. Both bound state and scattering contributions are evaluated numerically and their rate of approach to the Boltzmann limit demonstrated. The velocity-autocorrelation function is calculated for short times and much of the structure observed at low temperatures in recent computer simulations is identified as due to bound-state dynamics.

II. BINARY-COLLISION APPROXIMATION

The correlation functions to be considered are either self-correlation functions

$$F^s_{AB}(t) \equiv \lim_{V\to\infty} \frac{1}{V}\langle Nab(t)\rangle, \tag{2.1}$$

where $\langle\cdots\rangle$ denotes an equilibrium average, N is the number of particles, V is the volume, and $a(\vec{p}_1)$ and $b(\vec{p}_1)$ are single-particle functions of the momentum; or, total correlation functions

$$F^T_{AB}(t) \equiv \lim_{V\to\infty} \frac{1}{V}\langle AB(t)\rangle, \tag{2.2}$$

where A and B are sums of single-particle functions

$$A = \sum_i^N a(\vec{p}_i), \quad B = \sum_i^N b(\vec{p}_i). \tag{2.3}$$

It is also convenient to define the average of b or a to vanish. In the kinetic theory approach the correlation functions are expressed in terms of an average over the single-particle phase space, obtained by first averaging over all degrees of freedom except one to give

$$F^s_{AB}(t) = \int d\vec{p}_1 b(p_1)\psi^{(s)}_a(\vec{p}_1; t), \tag{2.4}$$

$$F^T_{AB}(t) = \int d\vec{p}_1 b(p_1)\psi^{(T)}_A(\vec{p}_1; t). \tag{2.5}$$

The functions $\psi^{(s)}_a$ and $\psi^{(T)}_A$ are the first members of sets of functions ($1 \leq l \leq N$)

$$\psi^{(s)}_a(1\ldots l; t) \equiv \sum_{N\geq l} \frac{N!}{(N-l)!}\int dx_{l+1}\cdots dx_N \rho a(p_1(-t)), \tag{2.6}$$

$$\psi_A^{(T)}(1\ldots l;t)\equiv\sum_{N\geq l}\frac{N!}{(N-l)!}\int dx_{l+1}\cdots dx_N\rho A(-t)\,. \tag{2.7}$$

The time dependence of the reduced distribution functions $\psi_a^{(s)}(p_1,t)$ and $\psi_A^{(T)}(p_1,t)$ is governed by the first equation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy (with specified initial conditions). A formally exact closure of this hierarchy is possible,[11] leading to exact kinetic equations for $\psi_a^{(s)}$ and $\psi_A^{(T)}$. This procedure is briefly described in Appendix A, along with a derivation of the binary-collision approximation to the exact kinetic equation. The result is that both the self-correlation and total correlation functions may be written in the form

$$F_{AB}(t)=\int d\vec{p}_1 f_0(p_1)b(\vec{p}_1)y(\vec{p}_1,t)\ , \tag{2.8}$$

where $f_0(p_1)$ is the Maxwell-Boltzmann distribution and $y(\vec{p}_1,t)$ satisfies the "kinetic equation"[12]

$$\frac{\partial y(p_1,t)}{\partial t}=-\int_0^t d\tau\, M(t-\tau)y(\vec{p}_1,\tau) \tag{2.9}$$

with the initial condition $y(p_1,t=0)=a(\vec{p}_1)$. The operator $M(t)$ is defined by

$$M(t)=\int\frac{dz}{2\pi i}e^{zt}\tilde{M}(z)\ , \tag{2.10}$$

$$\tilde{M}(z)\equiv -z\int_0^\infty dt\, e^{-zt}f_0^{-1}(p_1)\int d\vec{p}_2 d\vec{r}_2[z+L_0(12)](e^{-L(12)t}-e^{-L_0(12)t})f_0(12)(1+\lambda P_{12})\,. \tag{2.11}$$

Here $f_0(12)$ is the low-density two-particle equilibrium distribution function, and $L(12)$ and $L_0(12)$ are the generators for two-particle dynamics with and without interaction, respectively. The parameter λ equals zero for the self-correlation function, $F^{(s)}$, or equals 1 for the total correlation function $F^{(T)}$. Finally, P_{12} is the permutation operator that changes the argument of the function on which it operates from $\vec{p}_1$ to $\vec{p}_2$.

It is often convenient to associate the domain of the collision operator, $\tilde{M}(z)$, with elements of a Hilbert space whose scalar product is defined by

$$(a,b)\equiv\frac{1}{n}\int d\vec{p}f_0(\vec{p})a^*(\vec{p})b(\vec{p})\,. \tag{2.12}$$

(The factor of $1/n$ has been introduced to make the scalar product independent of the density.) The correlation function may then be expressed in terms of its Laplace transform

$$F_{AB}(t)=\int\frac{dz}{2\pi i}e^{zt}\tilde{F}(z)\,, \tag{2.13}$$

$$\tilde{F}(z)=n(b,[z+\tilde{M}(z)]^{-1}a)\,. \tag{2.14}$$

Furthermore, let $\{\psi_\alpha\}$ be a complete set of functions in this space (e.g., Hermite polynomials). Then $\tilde{M}(z)$ may be represented in terms of its matrix elements with respect to this set,

$$\tilde{M}_{\alpha\beta}(z)\equiv(\psi_\alpha,\tilde{M}(z)\psi_\beta)=\frac{-z}{n}\int_0^\infty dt\, e^{-zt}\int d\vec{G}d\vec{g}d\vec{r}\,\psi_\alpha^*(\vec{G}-\tfrac{1}{2}\vec{g})[z+\bar{L}_0(12)]$$
$$\times(e^{-\bar{L}(12)t}-e^{-\bar{L}_0(12)t})f_0(12)[\psi_\beta(\vec{G}-\tfrac{1}{2}\vec{g})+\lambda\psi_\beta(\vec{G}+\tfrac{1}{2}\vec{g})]\,. \tag{2.15}$$

Here a transformation to relative and center-of-mass variables has been performed $[\vec{G}\equiv(\vec{p}_2+\vec{p}_1)/2$, $\vec{g}\equiv\vec{p}_2-\vec{p}_1$, $\vec{r}\equiv\vec{r}_2-\vec{r}_1]$. Also $\bar{L}(12)$ and $\bar{L}_0(12)$ are the two-particle Liouville operators for the relative coordinates. In particular, $\bar{L}_0(12)$ is given by

$$\bar{L}_0(12)=\vec{g}\cdot\vec{\nabla}_r/m\,. \tag{2.16}$$

There are well-developed methods[3,13] by which the scalar product in Eq. (2.13) can be calculated from knowledge of the matrix elements, $\tilde{M}_{\alpha\beta}(z)$. Consequently, it is sufficient to restrict further attention to the properties of these functions.

The right-hand side of Eq. (2.14) may be rewritten in a form useful for the purposes of the next two sections as

$$\tilde{M}_{\alpha\beta}(z)=-\frac{1}{n}\int d\vec{G}d\vec{g}f_0(1)f_0(2)\int d\vec{r}\bigg(\frac{\vec{g}\cdot\vec{\nabla}_r}{m}e^{-\beta V(r)}\psi_\alpha^*(\vec{G}-\tfrac{1}{2}\vec{g})\bar{\psi}_\beta'(\vec{g},\vec{G};\lambda)$$
$$+ze^{-\beta V(r)}\psi_\alpha^*(\vec{G}-\tfrac{1}{2}\vec{g})[\bar{\psi}_\beta'(\vec{g},\vec{G};\lambda)-\bar{\psi}_\beta(\vec{g},\vec{G};\lambda)]\bigg)\,, \tag{2.17}$$

where $V(r)$ is the pair potential and

$$\bar{\psi}'_\beta \equiv z\int_0^\infty dt\, e^{-zt} e^{-\bar{L}(12)t}\bar{\psi}_\beta(\vec{g},\vec{G};\lambda),$$
$$\bar{\psi}_\beta(\vec{g},\vec{G};\lambda)\equiv \psi_\beta(\vec{G}-\tfrac{1}{2}\vec{g})+\lambda\psi_\beta(\vec{G}+\tfrac{1}{2}\vec{g}). \qquad (2.18)$$

Equations (2.9) and (2.16) define the binary-collision approximation for space-independent time-correlation functions. These results have been expressed in a form such that the force does not appear explicitly and consequently they apply for both continuous and discontinuous potentials. In the next section (2.17) is further discussed for a general continuous potential with an attractive and a repulsive part. The detailed analysis for the square-well potential is described in Sec. IV.

III. CONTINUOUS POTENTIALS

In this section it will be assumed that the potential is continuous, differentiable, and of short range. Without loss of generality it will also be assumed that the potential is negligibly small for $r>R_0$. The second term of Eq. (2.17) can then be transformed to a surface integral over a spherical surface of radius, $R>R_0$, which thus refers to relative distances such that the particles are initially free. $\tilde{M}_{\alpha\beta}(z)$ can then be written as the sum of a scattering state and a bound-state contribution, distinguishing the two regions of phase space giving rise to different kinds of trajectories. Let $V(r)$ be a central intermolecular potential characterized by an attractive and a repulsive part and two turning points R_1 and R_2. The pair will be bound if its initial position and velocity satisfy

$$R_1 \leq r \leq R_2, \qquad (3.1)$$

$$\left(\frac{4}{m}[E_0 - V(r)]\right)^{1/2} \leq v \leq \left(\frac{4}{m}[E_2 - V(r)]\right)^{1/2}, \qquad (3.2)$$

where E_0 and E_2 are the values of the effective potential

$$V'(r) = V(r) + mv^2b^2/r^2 \qquad (3.3)$$

at $r=R_m$ (the minimum of the potential) and $r=R_2$, respectively, and b is the impact parameter of the pair. When the initial position and velocity are outside the range defined by Eqs. (3.1) and (4.2) the pair will be free. The matrix elements of Eq. (2.17) may be written as the sum of scattering and bound-states contributions,

$$\tilde{M}_{\alpha\beta}(z) = \tilde{M}^{\rm sc}_{\alpha\beta}(z) + \tilde{M}^{\rm bs}_{\alpha\beta}(z), \qquad (3.4)$$

with

$$\tilde{M}^{\rm sc}_{\alpha\beta}(z) = \frac{-1}{n}\int d\vec{G}\, d\vec{g}\, f_0(1) f_0(2) \times \int d\vec{r}\, R_{\rm sc}(\vec{r},g)\left(\frac{\vec{g}}{m}\cdot\vec{\nabla}_r e^{-\beta V(r)}\psi^*_\alpha \bar{\psi}'_\beta + z e^{-\beta V(r)}\psi^*_\alpha(\bar{\psi}'_\beta - \bar{\psi}_\beta)\right) \qquad (3.5)$$

and

$$\tilde{M}^{\rm bs}_{\alpha\beta}(z) = \frac{-z}{n}\int d\vec{G}\, d\vec{g}\, f_0(1) f_0(2)\int d\vec{r}\, R_{\rm bs}(\vec{r},g) \times e^{-\beta V(r)}\psi^*_\alpha(\bar{\psi}'_\beta - \bar{\psi}_\beta), \qquad (3.6)$$

where $\bar{\psi}'_\beta$ is defined in Eq. (2.18) and the functions $R_{\rm sc}(\vec{r},g)$ and $R_{\rm bs}(\vec{r},g)$ represent the restriction on the integration:

$$R_{\rm bs}(\vec{r},g) = \theta(R_2 - r)\theta(r - R_1) \times \theta(g - [4m(E_0 - V)]^{1/2})\theta([4m(E_2 - V)]^{1/2} - g) \qquad (3.7)$$

and

$$R_{\rm sc}(\vec{r},g) = 1 - R_{\rm bs}, \qquad (3.8)$$

where θ is the step function.

To be more specific, the following will be limited to a discussion of the velocity-autocorrelation function:

$$F(t) = \langle v_{1x} v_{1x}(t)\rangle / \langle v_{1x}^2\rangle. \qquad (3.9)$$

The normalized x component of the momentum may be taken as the first member of the complete set $\{\psi_\alpha\}$,

$$\psi_1 = p_x/[(p_x, p_x)]^{1/2} = p_x/(mkT)^{1/2}. \qquad (3.10)$$

The Laplace transform of the velocity-autocorrelation function is then given by Eq. (2.13) with $a = b = \psi_1$,

$$\tilde{F}(z) = n(\psi_1, [z + \tilde{M}(z)]^{-1}\psi_1). \qquad (3.11)$$

It is known that the corresponding Boltzmann-Lorentz collision operator has the momentum as an approximate eigenfunction,[14] and this will be assumed to be true also for the more general binary-collision operator considered here. The correlation function is then determined entirely in terms of the single matrix element, $\tilde{M}_{1,1}(z)$,

$$\tilde{F}(z) \sim \frac{1}{z + \tilde{M}_{1,1}(z)}. \qquad (3.12)$$

Before proceeding with the analysis of $\tilde{M}_{1,1}(z)$ it is noted that the binary-collision approximation preserves the symmetries of the underlying dynamics, including time-reversal invariance. As a consequence it may be shown that $\tilde{M}^*(z) = \tilde{M}(z^*)$. It then follows that Eqs. (2.13) and (3.12) may be transformed to

$$F(t)=2\,\mathrm{Re}\int_0^\infty \frac{d\omega}{\pi}\cos(\omega t)\frac{1}{i\omega+\tilde{M}_{1,1}(i\omega)}, \quad (3.13)$$

providing the analytic extension of $\tilde{M}_{1,1}(z)$ to $z=i\omega$ exists.

Substitution of (3.10) into (2.17) allows integration over the total momentum and the angular part of the relative momentum with the result

$$\tilde{M}_{1,1}(z)=\frac{-n}{24\sqrt{\pi}}\left(\frac{m}{kT}\right)^{5/2}\int_0^\infty dv\, v^2 e^{-\beta m v^2/4}\times\int d\vec{r}[\vec{v}\cdot\vec{\nabla}_r e^{-\beta V(r)}(\vec{v}\cdot\vec{v}')+z e^{-\beta V(r)}\vec{v}\cdot(\vec{v}'-\vec{v})], \quad (3.14)$$

where $\vec{v}'$ is the "scattered" relative velocity [Eq. (2.18) with $\lambda=0$]

$$\vec{v}'=z\int_0^\infty dt\, e^{-zt}e^{-\bar{L}(12)t}\vec{v}. \quad (3.15)$$

The collision integral $\tilde{M}_{1,1}(z)$ can be separated in the sum of a scattering-states and a bound-states contribution, as in Eqs. (3.5) and (3.6),

$$\tilde{M}_{1,1}(z)=\tilde{M}^{sc}_{1,1}(z)+\tilde{M}^{bs}_{1,1}(z), \quad (3.16)$$

$$\tilde{M}^{sc}_{1,1}(z)=\frac{-n}{24\sqrt{\pi}}\left(\frac{m}{kT}\right)^{5/2}\int_0^\infty dv\, v^2 e^{-\beta m v^2/4}\int d\vec{r}R_{sc}(\vec{r},v)[\vec{v}\cdot\vec{\nabla}_r e^{-\beta V(r)}(\vec{v}\cdot\vec{v}')+z e^{-\beta V(r)}\vec{v}\cdot(\vec{v}'-\vec{v})], \quad (3.17)$$

$$\tilde{M}^{bs}_{1,1}(z)=-z\frac{n}{24\sqrt{\pi}}\left(\frac{m}{kT}\right)^{5/2}\int_0^\infty dv\, v^2 e^{-\beta m v^2/4}\int d\vec{r}R_{bs}(\vec{r},v)e^{-\beta V(r)}\vec{v}\cdot(\vec{v}'-\vec{v}), \quad (3.18)$$

where the functions $R_{sc}(\vec{r},v)$ and $R_{bs}(\vec{r},v)$ are defined by Eqs. (3.7) and (3.8).

The bound-state part and the second term of the scattering part can be further simplified by performing an integration by parts over the time

$$\vec{v}'\equiv z\int_0^\infty dt\, e^{-zt}e^{-\bar{L}(12)t}\vec{v}=\vec{v}+\int_0^\infty dt\, e^{-zt}\frac{d\vec{v}(-t)}{dt}, \quad (3.19)$$

where

$$\vec{v}(-t)\equiv e^{-\bar{L}(12)t}\vec{v}.$$

Substituting in Eqs. (3.17) and (3.18), these become

$$\tilde{M}^{sc}_{1,1}(z)=\frac{-n}{24\sqrt{\pi}}\left(\frac{m}{kT}\right)^{5/2}\int_0^\infty dv\, v^2 e^{-\beta m v^2/4}\int d\vec{r}R_{sc}(\vec{r},v)\{\vec{v}\cdot\vec{\nabla}_r e^{-\beta V(r)}\vec{v}\cdot[\vec{v}+\vec{v}''(z)]+z e^{-\beta V(r)}\vec{v}\cdot\vec{v}''(z)\}, \quad (3.20)$$

$$\tilde{M}^{bs}_{1,1}(z)=-z\frac{n}{24\sqrt{\pi}}\left(\frac{m}{kT}\right)^{5/2}\int_0^\infty dv\, v^2 e^{-\beta m v^2/4}\int d\vec{r}R_{bs}(\vec{r},v)e^{-\beta V(r)}\vec{v}\cdot\vec{v}''(z), \quad (3.21)$$

with

$$\vec{v}''(z)\equiv\int_0^\infty dt\, e^{-zt}\frac{d\vec{v}(-t)}{dt}. \quad (3.22)$$

Let $\vec{F}(r)\equiv f(r)\hat{r}$ be the relative force of the pair. From the equation of motion,

$$\frac{m}{2}\frac{d\vec{v}(t)}{dt}=\vec{F}(r(t)),$$

Eq. (3.22) can be rewritten

$$\vec{v}\cdot\vec{v}''(z)=\frac{-2v}{m}\int_0^\infty dt\, e^{-zt}f(r(-t))\cos\theta(-t), \quad (3.23)$$

where $\theta(t)$ is the scattering angle, whose time evolution is formally given by the solution of the equation

$$\theta(t)=\theta+\sqrt{m}\,vb\int_r^{r(t)}\frac{dr'}{r'^2[E-V'(r')]^{1/2}}, \quad (3.24)$$

and $r(t)$ can be obtained by inverting the equation

$$t=\int_r^{r(t)}\frac{dr'}{\{4[E-V'(r')]/m\}^{1/2}}. \quad (3.25)$$

Inserting Eqs. (3.23), (3.24), and (3.25) in the expression for $\tilde{M}_{1,1}(z)$, it appears that the calculation of the collision integral requires knowledge of the trajectory of the scattered pair at all times. However, the symmetry of the problem allows a great simplification to be introduced for the calculation of the bound-states part of $\tilde{M}_{1,1}(z)$. For any central potential with two turning points the orbit of a bound pair is symmetric with respect to the apsidal radii. The time integral in Eq. (3.23) can thus be reduced to an integration over the transit time $T(\vec{r},v)$ between two successive turning points,

$$[\vec{v}\cdot\vec{v}'']_{bs} = \frac{-2v}{m}\sum_{p=1}^{\infty}\int_{T_{p-1}(\vec{r},v)}^{T_p(\vec{r},v)} dt\, e^{-zt} f(r(-t))\cos\theta(-t) \tag{3.26}$$

or, since T_p is independent of the section of trajectory considered, i.e., $T_p(\vec{r},v)=pT(\vec{r},v)$,

$$(\vec{v}\cdot\vec{v}'')_{bs} = \frac{-2v}{m}\sum_{p=1}^{\infty} e^{-(p-1)zT(\vec{r},v)}\int_0^{T(\vec{r},v)} dt\, f(r(-t))\cos[\theta(-t)-(p-1)\theta_0], \tag{3.27}$$

where θ_0 is the change in angle between the two turning points. In Eq. (3.27) use has been made of the properties

$$r(-t-pT)=r(-t),$$

$$\theta(-t-pT)=\theta(-t)-p\theta_0 .$$

The bound-state part of $\tilde{M}_{1,1}(z)$ can then be written

$$\tilde{M}_{1,1}^{bs} = +z\frac{n}{12m\sqrt{\pi}}\left(\frac{m}{kT}\right)^{5/2}\int_0^{\infty} dv\, v^3 e^{-\beta m v^2/4}\int d\vec{r}\, R_{bs}(\vec{r},v)e^{-\beta V(r)} \times\sum_{p=1}^{\infty} e^{-(p-1)zT(\vec{r},v)}\int_0^{T(\vec{r},v)} dt\, e^{-zt} f(r(-t))\cos[\theta(-t)-(p-1)\theta_0]. \tag{3.28}$$

The series may be summed for $\mathrm{Re}z>0$ to give

$$\tilde{M}_{11}^{bs} = +\frac{n}{12m\sqrt{\pi}}\left(\frac{m}{kT}\right)^{5/2}\int_0^{\infty} dv\, v^3 e^{-\beta m v^2/4}\int d\vec{r}\, e^{-\beta V(r)}\frac{G(\vec{r},v;z)}{1-2e^{-zT}\cos\theta_0+e^{-2zT}}, \tag{3.29}$$

where

$$G(\vec{r},v;z)=R_{bs}(\vec{r},v)\int_0^{T(\vec{r},v)} dt\, f(r(-t))\{\cos\theta(-t)-e^{-zT(\vec{r},v)}\cos[\theta(-t)+\theta_0]\}. \tag{3.30}$$

The bound-state contribution to $\tilde{M}_{1,1}(z)$ is therefore seen to exist for $\mathrm{Re}z>0$. To show that it vanishes in the Boltzmann limit $z\to 0$ is somewhat more difficult. The integrand of Eq. (3.29) has poles at

$$z=\frac{1}{T}\cosh^{-1}(\cos\theta_0). \tag{3.31}$$

Consequently, for trajectories such that $\cos\theta_0\neq 1$, the integrand is finite and vanishes as $z\to 0$. However, the limit is clearly not uniform in $\vec{r}$ and v because for those trajectories such that $\cos\theta_0=1$ the integrand is finite and nonzero at $z=0$. Since the Boltzmann limit requires that all bound-state contributions vanish for sufficiently long times ($z\to 0$), it may be expected that the trajectories with $\cos\theta_0=1$ are of vanishingly small measure with respect to all possible trajectories. The difficulties associated with the long time or small-z limits for the bound-state contribution may be traced to the quasiperiodic motion of a bound pair. In contrast to the scattering part, any limiting behavior can only result from a phase averaging over the allowed initial conditions. Consequently, the velocity and relative coordinate integrals in Eq. (3.29) should be performed before the limit $z\to 0$ is taken. In the next section this problem is discussed in more detail for the square-well potential. In that case the series corresponding to Eq. (3.28) is transformed to the time representation. The series is then shown to converge uniformly with respect to time and to vanish term-by-term as $t\to\infty$. This is sufficient also to conclude $\tilde{M}_{1,1}^{bs}(z)\to 0$ as $z\to 0$.

The finite-collision-time effects also occur for the scattering contribution to $\tilde{M}_{1,1}$. In that case, however, the velocity $\vec{v}'$ of Eq. (3.15) approaches a limiting value for $z\leq v/\sigma$, or about one mean collision time

$$\lim_{z\to 0}\vec{v}'(z)=\lim_{t\to\infty} e^{-\bar{L}t}\vec{v}. \tag{3.32}$$

Since this limit exists for scattering states, the second term in Eq. (3.17) vanishes for $z\to 0$. Substitution of (3.32) in the first term of (3.17) and transformation to a surface integral shows that

$\tilde{M}^{sc}_{1,1}(z=0)$ is simply proportional to the collision integral $\Omega_{1,1}$ obtained from the Boltzmann equation.

The finite collision-time effects are associated with the z dependence of $\tilde{M}_{1,1}(z)$. It is somewhat easier to indicate such effects for the corresponding time-dependent collision integral

$$M_{1,1}(t) \equiv \int \frac{dz}{2\pi i} e^{zt} \tilde{M}_{1,1}(z) , \qquad (3.33)$$

where, for a continuous potential, $M_{1,1}(t)$ is nonsingular at $t \to 0$.

The time dependence of $M_{1,1}(t)$ arises from the change in the collision rate during the passage through the well, for both bound and scattering states. For the scattering states, the final scattered velocities are attained in a time of the order of $\sigma/v \sim \sigma(m/kT)^{1/2}$. As noted in the introduction, the situation is more complicated for the bound-states contribution because the times T_p in Eq. (3.23) are of the order $n\sigma/v$ and no obvious time scale or limiting behavior is indicated. Qualitatively it may be expected that the scattering contribution to $M_{1,1}(t)$ should decrease from some maximum value and vanish for $t > \sigma/v$. The area under this curve would then be proportional to the Boltzmann $\Omega_{1,1}$ integral. For the bound-state part of $M_{1,1}(t)$, it may be expected that the function should oscillate at a frequency associated with the mean time between turning points and attenuate to zero due to phase averaging over trajectories. The area under the curve for the bound states must be zero for the Boltzmann limit to be valid. This general picture is verified in detail in the next section for the square-well potential.

IV. SQUARE-WELL POTENTIAL

Determination of matrix elements of the collision operator in the binary-collision approximation is straightforward in principle because only two-particle dynamics are involved. In practice, the evaluation can be difficult for a general potential, but is considerably simplified for the special case of a square-well potential,

$$V(r) = \begin{cases} \infty, & r < \sigma \\ -\epsilon, & \sigma < r < R\sigma \\ 0, & R\sigma < r \end{cases} . \qquad (4.1)$$

The force is therefore zero everywhere except at the surfaces on which the potential is discontinuous. The radial integration in Eq. (2.17) may therefore be restricted to the infinitesimal volume elements between the spheres $R\sigma - \delta < r < R\sigma + \delta$ and $\sigma - \delta < r < \sigma + \delta$, where δ is an arbitrarily small positive constant. The second term in Eq. (2.17) is then vanishingly small; the first term may be transformed to surface integrals with the result (only the matrix element $\tilde{M}_{1,1}$ will be considered in this section)

$$\tilde{M}_{1,1}(z) = -\frac{n\sigma^2}{24\sqrt{\pi}} \left(\frac{m}{kT}\right)^{5/2} \int_0^\infty dv\, v^2 e^{-mv^2/4kT} \int d\Omega (\hat{\sigma} \cdot \vec{v}) [R^2 (\vec{v} \cdot \vec{v}')_{R\sigma^+} + e^{1/T^*} (\vec{v} \cdot \vec{v}')_{\sigma^+} - R^2 e^{1/T^*} (\vec{v} \cdot \vec{v}')_{R\sigma^-}] , \qquad (4.2)$$

where $T^* \equiv kT/\epsilon$. The notation $(\vec{v} \cdot \vec{v}')_r$ indicates the relative scattered velocity for initial relative coordinate r. Consequently, the collision integral for the square well is expressed in terms of collisions initiating at $R\sigma^+$, $R\sigma^-$, and σ^+. The first term in the square brackets refers to relative distances such that the particles are initially free and consequently have no bound states. The other two terms at σ^+ and $R\sigma^-$ refer to particles initially within the region of interaction and can be either bound or free. The particles will be free if the radial kinetic energy exceeds the potential energy, i.e., $\frac{1}{4}m(\hat{\sigma} \cdot \vec{v})^2 > \epsilon$, and will be bound if $\frac{1}{4}m(\hat{\sigma} \cdot \vec{v})^2 < \epsilon$ ($\hat{\sigma} \cdot \vec{v}$ has to be calculated at $R\sigma^-$). With this distinction, the memory function can again be written as the sum of a bound-state and a scattering-state contribution.

The scattering part can then be separated into the sum of three terms, referring to scattered pairs originating at $R\sigma^+$, $R\sigma^-$, and σ^+, respectively. As noted above, the matrix element $\tilde{M}_{1,1}(z)$ is expected to be proportional to the collision integral $\Omega_{1,1}$, studied for the Boltzmann equation, in the limit $z \to 0$. To suggest this relationship a generalized dimensionless collision integral is defined by

$$\Omega^*(z) \equiv \tilde{M}_{1,1}(z) / [\tilde{M}_{1,1}]_{HS} , \qquad (4.3)$$

where $[\tilde{M}_{1,1}]_{HS} = \frac{8}{3} n\sigma^2 (kT\pi/m)^{1/2}$ is the corresponding matrix element for the hard-sphere potential. The contributions to $\Omega^*(z)$ corresponding to different initial conditions are identified as

$$\Omega^*(z) = \Omega^*_{R\sigma^+}(z) + \Omega^*_{R\sigma^-}(z) + \Omega^*_{\sigma^+}(z) + \Omega^*_{bs}(z) , \qquad (4.4)$$

where

$$\Omega^*_{R\sigma^+}(z) = [I_1(z) + I_2(z)] , \qquad (4.5)$$

$$\Omega^*_{\sigma^+}(z) = e^{1/T^*} [I_3(z) + I_4(z)] , \qquad (4.6)$$

$$\Omega^*_{R\sigma^-}(z) = e^{1/T^*} [I_5(z) + I_6(z)] , \qquad (4.7)$$

$$\Omega^*_{bs}(z) = e^{1/T^*}[I_7(z)+I_8(z)]\,. \tag{4.8}$$

The explicit expression of the integrals from I_1 to I_8 and the details of the calculation are given in Appendix B.

The two-body dynamics are entirely contained in the expression (3.7) for $\vec{v}'$. The simplifications associated with the step potential are twofold. First, as illustrated in (4.2) the force is nonzero only at $r=\sigma$ and $r=R\sigma$ so that initial data are required only at these two surfaces. The second important property is that the relative velocity is constant along each section of trajectory corresponding to $T_{p-1} \le t \le T_p$, so that Eq. (3.7) becomes

$$\vec{v}' = z\sum_{p=1}^{\infty}\int_{T_{p-1}}^{T_p} dt\, e^{-zT}\vec{v}_p = -\sum_{p=1}^{\infty}\left(e^{-zT_p}-e^{-zT_{p-1}}\right)\vec{v}_p\,, \tag{4.9}$$

where T_p is the time of the pth velocity change and $\vec{v}_p$ is the value of the relative velocity during the interval $(T_p - T_{p-1})$. For scattering events the maximum number of velocity changes possible is three and the series in (4.9) is finite. The types of scattering for particles separated by $R\sigma^+$, $R\sigma^-$, and σ^+ are illustrated in Figs. 1 and 2. For bound states, arbitrarily many partial collisions can occur and the series in (4.9) has an infinite number of nonvanishing terms. For the square-well potential (and all discontinuous potentials) there is a contribution to $\bar{\Omega}(t)$ associated with initial instantaneous momentum change, leading to a delta function in time. The form of $\bar{\Omega}(t)$ is therefore

$$\bar{\Omega}(t) = \bar{\Omega}_0\delta(t) + \bar{\Omega}_1(t)\,, \tag{4.10}$$

where $\bar{\Omega}_1(t)$ is nonsingular and vanishes as $t\to 0$. In the hard-sphere limit $\bar{\Omega}_1 = 0$ and $\bar{\Omega}_0 = 1$, reflecting the fact that the interaction time is zero. In the case of the square-well potential it is found (see below) that the bound-states contribution vanishes for times long compared to the collision time. It follows from the results of Appendix B that only the integrals $I_1(z=0)$ and $I_2(z=0)$ contribute in this limit and that the result is just the Boltzmann collision integral $\Omega_{1,1}$ normalized to the hard-sphere result. In the opposite limit of short times $\bar{\Omega}_0$ contributes

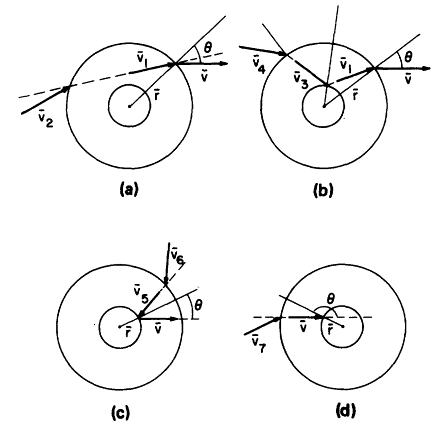

FIG. 1. Square-well trajectories for particles starting at $R\sigma^+$ (a) and (b) and starting at σ^+ (c) and (d), with $m(\hat{\sigma}\cdot\vec{v})/4 > \epsilon$.

$$\lim_{t\to 0}\bar{\Omega}(t) \to \bar{\Omega}_0\delta(t)\,, \tag{4.11}$$

where $\bar{\Omega}_0$ may also be identified as $\mathrm{Re}[\Omega^*(z\to\infty)]$. All eight integrals, I_1–I_8, contribute in this limit, leading to the result

$$\bar{\Omega}_0 = 1 + R^2\Xi(T^*)\,, \tag{4.12}$$

$$\Xi(T^*) \equiv e^{1/T^*} - \frac{1}{2T^*} - \int_0^\infty dx\, e^{-x}x^{1/2}\left(x+\frac{1}{T^*}\right)^{1/2}. \tag{4.13}$$

The first term in Eq. (4.12) is the hard-sphere result and is regained in the high-temperature limit where $\Xi(T^*)$ vanishes. (It may be interesting to note that the short-time limit (4.12) agrees with the low-density limit of the Davis-Rice-Sengers model for square-well transport, which is based on an assumption that only partial collisions are important.[14])

Before describing the transition between these two limits, the convergence of the contribution from the infinite sum of partial collisions for bound states must be established. In the time representation, the bound-state contribution to $\bar{\Omega}(t)$ in Eq. (4.10) is given by (see Appendix B)

$$[\bar{\Omega}(t)]_{bs} = (\bar{\Omega}_0)_{bs}\delta(t) + e^{1/T^*}\sum_{n=1}^{\infty}A_n(t)\,, \tag{4.14}$$

where $A_n(t)$ is defined by

$$A_n(t) \equiv \int_0^\infty dy\, y^5 e^{-y^2}\int_0^R dx\, x[R_1(x,y)C_n(x,y)\delta(t-nT_3(x,y)) + R_2(x,y)D_n(x,y)\delta(t-nT_4(x,y))]\,. \tag{4.15}$$

Here $R_1(x,y)$ and $R_2(x,y)$ are restrictions on the domain of integration, the coefficients $C_n(x,y)$ and $D_n(x,y)$ are the differences between the scattering angle after the nth partial collision for the positive and negative hemispheres, and T_3 and T_4 are the times between partial collisions for the trajector-

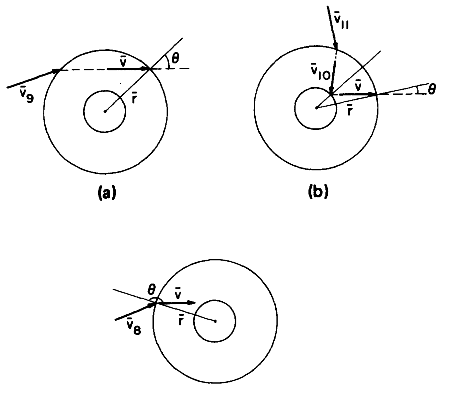

FIG. 2. Same as Fig. 1 for particles starting at $R\sigma^-$ with $m(\hat{\sigma}\cdot\vec{v})/4>\epsilon$.

ies shown in Fig. 3. The detailed forms of these functions are given in Appendix B. It is straightforward to show that for fixed n the coefficients $A_n(t)$ go to zero for large t. However, to conclude that the entire bound-state contribution is finite and vanishes in this limit it is necessary to prove that the series in Eq. (4.14) is uniformly convergent. To simplify the discussion only the least favorable case for convergence is described here, namely that of a very deep well ($\epsilon\to\infty$) and well-width large compared to the core ($\sigma\to 0$, $R\sigma=1$). In this limit $R_1(x,y)\to 1$ and Eq. (3.24) has the limiting form

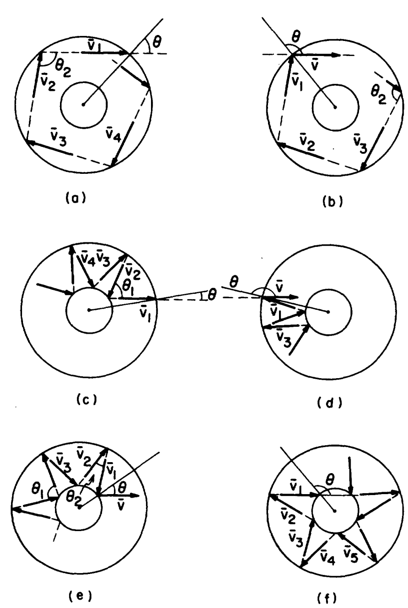

FIG. 3. Bound-state square-well trajectories, $m(\sigma\cdot\vec{v})^2/4<\epsilon$, for particles starting at $R\sigma^-$ (a)–(d) and at σ^+ (e) and (f).

$$A_n(t)\to a_n(t)\,, \tag{4.16}$$

$$a_n(t)\equiv 4(-1)^n\int_0^\infty dy\, y^5 e^{-y^2}\int_0^1 dx\, x(1+\cos\theta)\cos n\theta \times\delta\left(t-\frac{n}{y}(1-x^2)^{1/2}\right), \tag{4.17}$$

where $\cos[\theta(x)]=1-2x^2$. The x integration may be performed to give

$$a_n(t)=2\frac{(-1)^n}{n}\alpha^7\int_0^1 dz\, z^3 e^{-\alpha^2 z}(1+\cos\theta)\cos n\theta\,,$$

where now $\cos[\theta(z)]=2z-1$ and $\alpha=n/t$. A change of variable to integrate over θ leads to consideration of the series

$$\sum_{n=1}^{\infty}a_n(t)=\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\int_0^{n\pi}d\theta(\cos\theta)G\left(\alpha,\frac{\theta}{n}\right), \tag{4.18}$$

with

$$G\left(\alpha,\frac{\theta}{n}\right)=\frac{\alpha^7}{8}e^{-\alpha^2(1+\cos\theta/n)/2}\left(1+\cos\frac{\theta}{n}\right)^4\sin\left(\frac{\theta}{n}\right). \tag{4.19}$$

In order to determine an upper bound for the general term of the series in Eq. (4.18), it is convenient to write it in the form

$$a_n(t)=\frac{(-1)^n}{n^2}\sum_{p=0}^{n-1}\int_0^{\pi}d\theta\cos(\theta+p\pi)G\left[\alpha,\left(\frac{\theta}{n}+\frac{p\pi}{n}\right)\right]. \tag{4.20}$$

Considering separately the case corresponding to p even and p odd, Eq. (4.20) can be rearranged in the convenient form

$$a_n(t)=\frac{(-1)^n}{n^2}\int_0^{(n-1)\pi}d\theta\cos\theta \times\left[G\left(\alpha,\frac{\theta}{n}\right)-G\left(\alpha,\frac{\theta}{n}+\frac{\pi}{n}\right)\right], \tag{4.21}$$

for $n>1$, and

$$a_1(t)=-\int_0^{\pi}d\theta(\cos\theta)G(\alpha,\theta)\,,$$

for $n=1$. The integrand in $a_n(t)$ for $n>1$ is thus written as the difference between the function $G(\alpha,\theta/n)$ evaluated at two points separated by π/n. For large n, π/n becomes arbitrarily small and

$$G\left(\alpha,\frac{\theta}{n}\right)-G\left(\alpha,\frac{\theta}{n}+\frac{\pi}{n}\right)\underset{n\gg1}{\longrightarrow}-\frac{\pi}{n}G'\left(\alpha,\frac{\theta}{n}\right),$$

where G' indicates the derivative of G: $G'(\alpha,\theta)\equiv(\partial G/\partial\theta)_\alpha$. It is easily shown that the magnitude of G' is bounded by a constant independent of α,

$$|G'(\alpha,\theta)|\le K\,,\quad 0\le\theta\le n\pi\,.$$

An upper limit for the general term of the series is thus immediately found:

$$|a_n(t)| \leq \frac{\pi}{n^3}\int_0^{(n-1)\pi} d\theta\,|\cos\theta|\,G'\!\left(\alpha,\frac{\theta}{n}\right)$$
$$\leq \pi^2\left(\frac{1}{n^2}-\frac{1}{n^3}\right)\max\left|G'\!\left(\alpha,\frac{\theta}{n}\right)\right|$$

or

$$|a_n(t)| \leq K\pi^2/n^2\,. \tag{4.22}$$

From Eq. (4.22) the series converges at least as $1/n^2$, and the convergence is uniform in time.

The bound-state contribution $\Omega^*_{bs}(z)$ in Eq. (4.4) may be obtained from the Laplace transform of Eq. (4.14). For $\mathrm{Im}z > 0$ the series may be summed to a closed form. For the limit ($\epsilon\to\infty$, $\sigma\to 0$, $R\sigma$ = finite) considered here the result is (see Appendix B for the general case)

$$\Omega^*_{bs}(z)\to 2\int_0^\infty dy\,y^5 e^{-y^2}\int_0^1 dx\,x\,\frac{(1+\cos\theta)(1-e^{-2zT})}{D(x,y;z)}\,, \tag{4.23}$$

where $D(x,y;z)$ is defined by

$$D(x,y;z)\equiv 1+2e^{-zT}\cos\theta+e^{-2zT} \tag{4.24}$$

and T is obtained from Eq. (B30) for $R=1$. Analytic continuation of $\Omega^*_{bs}(z)$ to $z=i\omega$ shows that the integrand has a countably infinite number of poles at $\omega=[\theta-(2n+1)\pi]/T$ (n = positive or negative integer). The uniform convergence of (4.14) and vanishing of $[\bar{\Omega}(t)]_{bs}$ for large t, however, assures that $\Omega^*_{bs}(z)$ is analytic for $z=i\omega$ and the integral

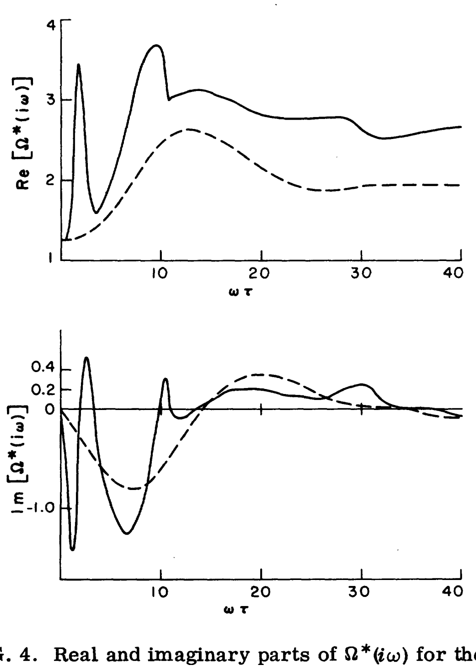

FIG. 4. Real and imaginary parts of $\Omega^*(i\omega)$ for the scattering contribution only (- - -), and for both scattering and bound-state contributions (——); $T^*=1.5$.

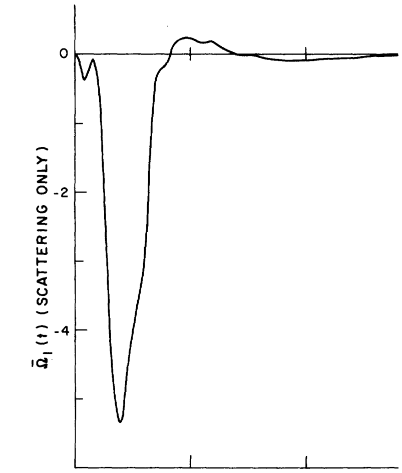

FIG. 5. Contribution to $\bar{\Omega}_1(t)$ from scattering parts only; $T^*=1.5$.

representation for the velocity-autocorrelation function, Eq. (3.5), is well defined.

To illustrate the approach of the collision integral to the Boltzmann limit at $t\gg\tau$ in the general case of finite ϵ and σ, the integrals $I_1(z)-I_8(z)$ defined in Eqs. (4.4)–(4.8) have been evaluated numerically for $z=i\omega$ and $R=1.5$. Figure 4 shows the real and imaginary parts of $\Omega^*(z)$ at $T^*=1.5$ and compares the total collision integral with the corresponding result for scattering states alone. The bound-state contribution is significant for $\omega \neq 0$ and is entirely responsible for the two resonances at $\omega\tau\sim 2$ and $\omega\tau\sim 9.5$. The corresponding time-dependent contributions to the function $\bar{\Omega}_1(t)$ is shown in Figs. 5–8. As expected, both bound-state and scattering contributions present a significant structure at short times, and approach the Boltzmann (scattering only) limit for $t>\tau$. The effect of the bound states on the short-time behavior of the velocity-autocorrelation function is shown in Fig. 9 in terms of its derivative at $n^*=0.01$ and several values of T^*. At high

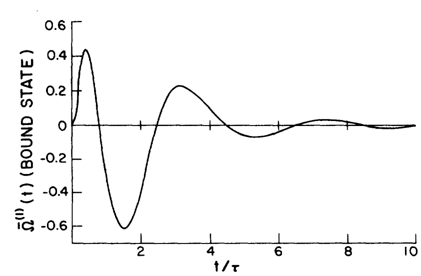

FIG. 6. Contribution to $\bar{\Omega}_1(t)$ from bound-state trajectories not hitting the core (coefficient of e^{1/T^*} not included); $T^*=1.5$.

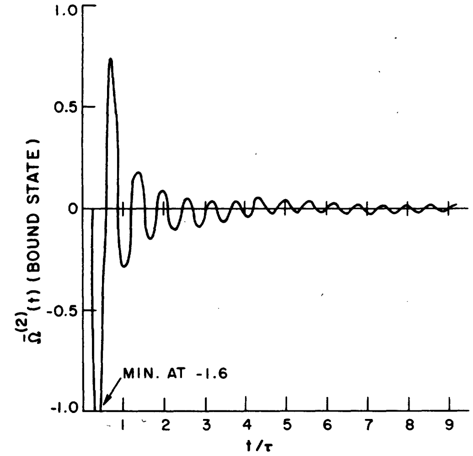

FIG. 7. Same as Fig. 6 for trajectories hitting the core.

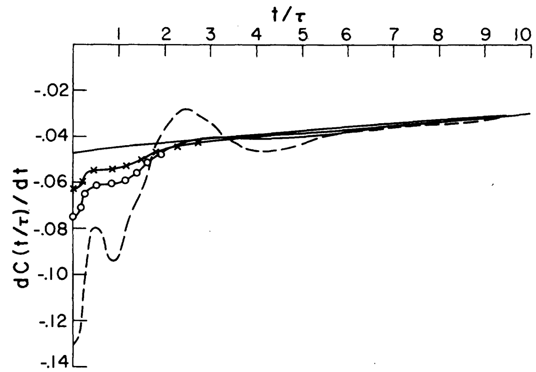

FIG. 9. Derivative of the velocity autocorrelation function at $T^*=1.5$ (- - -), $T^*=3.0$ (o-o), $T^*=4.5$ (**), and $T^*=\infty$ (—); all at $n^*=0.01$ and time in units of $\tau = \sigma/v$.

temperatures the single exponential decay characteristic of hard spheres is obtained. As the temperature is lowered both the finite collision time for scattering and the dynamics for bound pairs gives additional structure at short times. The relative contributions from finite collision times and bound states at low temperatures are illustrated in Fig. 10. The change in slope obtained when only scattering contributions are included is due to incomplete scattering events. Also shown in Fig. 10 for comparison are the molecular dynamics results of Michels and Trappeniers. Certainly all of the qualitative features agree; further comment on the quantitative agreement is given in the next section.

V. CONCLUSION

The presence of an attractive part in the intermolecular potential has been shown to affect considerably the short-time behavior of velocity-correlation functions, even at low density. In a kinetic theory approach, space-independent time-correlation functions in a gas have been expressed in terms of specific matrix elements of the binary-collision operator, $\tilde{M}(z)$, as defined in Eqs. (2.17) and (2.18). The attempt to calculate such collision integrals for potentials with an attractive part immediately poses a technical problem at low density. In a binary-collision approximation such potentials allow for the existence of isolated bound pairs with infinite interaction times. The problem of the existence of the bound-state contribution to $\tilde{M}(z)$ and of its convergence to the Boltzmann (scattering only) limit for times long compared to the collision time has been considered in detail. More exactly, the bound-state part of the collision operator has been written as a series of contributions from sections of trajectories between two turning points [Eqs. (3.28) and (4.14)]. The series has been shown to converge uniformly to zero at $t\to\infty$ for the square-well potential. Explicit calculations have been performed for the velocity-autocorrelation function for the

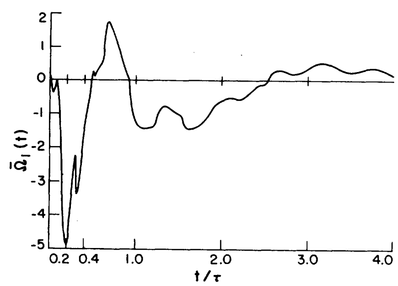

FIG. 8. $\Omega_1(t)$ at $T^*=1.5$ (scattering and bound-state contributions).

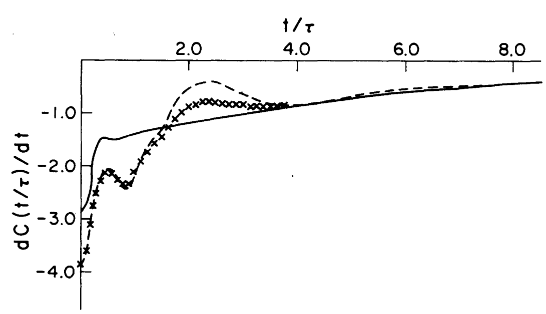

FIG. 10. Same as Fig. 9 for $T^*=1.5$ and $n^*=0.03$ (- - -), scattering part only (—), and molecular dynamics (xxx).

square-well potential. Figure 10 shows that the presence of bound pairs and the effects associated with the finite duration of binary collisions are responsible for the considerable deviation from the single exponential decay calculated for a hard-sphere gas. The agreement with molecular dynamics simulation here is not entirely quantitative and the difference can be shown to be due to finite density corrections. When collisions of a given pair with other atoms are taken into account through a collisional damping mechanism,[9] quantitative agreement with molecular dynamics is obtained (Fig. 2 in Ref. 9). Even at the low densities considered here such corrections may be important at low temperature, since the rate of collisional damping is proportional to $n^* e^{1/T^*}$.

It can then be concluded that the details of the potential model and the binary dynamics, which do not influence transport coefficients in a low-density gas, nevertheless strongly affect the time dependence of velocity correlations. Furthermore, knowledge of the exact dynamics of collisions appears to be important in interpreting other properties of low-density fluids, such as collision-induced light scattering, and some cases of pressure braodening and frequency shifts of rotational or vibrational Raman lines of diatomic molecules perturbed by rare gases.[5] All the calculations here have been limited to the case of square-well potential because of the considerable simplification of the problem. In the general case of continuous potentials the equation of motion of an isolated pair of particles in a central force field has to be integrated numerically. However, the structure of the collision operator is analogous to the one obtained in the discontinuous case, and the result can then be expected to be qualitatively similar. This expectation is also supported by molecular-dynamics results for a Lennard-Jones gas.[6]

Finally, at higher density the inclusion of an attractive part in the potential has a strong influence also on transport coefficients. This is confirmed by both analytic[8] and molecular dynamics calculations[6] of the coefficient of self-diffusion at moderate density for square-well potential. Similar effects are found for the viscosity, again determined through molecular dynamics simulation,[15] both below and above the critical density.

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APPENDIX A: KINETIC EQUATION IN THE BINARY-COLLISION APPROXIMATION

It is convenient to introduce a notation such that the self-correlation and total correlation functions may be treated on the same basis. To do so, define the permutation operator P_{1i} which interchanges the particle lables 1 and i:

$$P_{1i}A(1,i)=A(i,1)\,. \tag{A1}$$

Also let λ be a parameter with the value 1 for total correlation functions and 0 for self-correlation functions. Then both hierarchies of functions $\{\psi_A^{(T)}\}$ and $\{\psi_a^{(s)}\}$ may be represented as

$$\begin{aligned} n^l\phi^{(l)}(1,\ldots,l;t) &= \sum_{N\geq l}\frac{N!}{(N-l)!}\int dx_{l+1}\cdots dx_N\rho \\ &\quad\times e^{-Lt}\left(1+\lambda\sum_{i=2}^{N}P_{1i}\right)a(1) \\ &\equiv U(1,\ldots,l;t)a(1)\,. \end{aligned} \tag{A2}$$

Here the l-particle operator $U(1,\ldots,l;t)$ has been defined formally as the operator that maps $a(1)$ into $\phi^{(l)}(1,\ldots,l;t)$. It is readily verified that these operators are linear. The $\{\phi^{(l)}\}$ satisfy the BBGKY hierarchy of equations, the first of which is

$$\left(\frac{\partial}{\partial t}+\vec{v}_1\cdot\vec{\nabla}_1\right)\phi^{(1)}(1;t)=n\int dx_2\theta_{12}\phi^{(2)}(12;t)\,, \tag{A3}$$

where θ_{12} is defined in terms of the potential $V(\vec{r}_1-\vec{r}_2)$ by

$$\theta_{12}=\frac{1}{m}[\vec{\nabla}_{r_1}V(\vec{r}_1-\vec{r}_2)]\cdot(\vec{\nabla}_{v_1}-\vec{\nabla}_{v_2})\,. \tag{A4}$$

Here it has been assumed that the interaction among particles can be represented by a pairwise additive continuous potential. The final form of the kinetic equation obtained here will nevertheless be such that it applies for both continuous and discontinuous potentials.

The Laplace transforms of Eqs. (A2) and (A3) are

$$n^l\tilde{\phi}^{(l)}(1,\ldots,l;z)=\tilde{U}(1,\ldots,l;z)a(1)\,, \tag{A5}$$

$$(z+\vec{v}_1\cdot\vec{\nabla}_1)\tilde{\phi}^{(1)}(1;z)=\phi^{(1)}(1;0)+n\int dx_2\theta_{12}\tilde{\phi}^{(2)}(12;z)\,. \tag{A6}$$

A closed equation for $\tilde{\phi}^{(1)}(1,z)$ may now be obtained by eliminating a (1) in Eq. (A5) for the cases $l=1$ and 2 to give $\tilde{\phi}^{(2)}$ in terms of $\tilde{\phi}^{(1)}$,

$$n\tilde{\phi}^{(2)}(1,2;z)=\tilde{U}(12;z)\tilde{U}^{-1}(1;z)\tilde{\phi}^{(1)}(1;z)\,. \tag{A7}$$

This assumes that $\tilde{U}(1;z)$ is invertible; in the low-density limit considered here this assumption is verified explicitly. Substitution of (A7) in (A6) and inversion of the transform leads to the desired formal kinetic equation,

$$\left(\frac{\partial}{\partial t}+\vec{v}_1\cdot\vec{\nabla}_1\right)\phi^{(1)}(1;t)=\int_0^t d\tau\, C(t-\tau)\phi^{(1)}(1;\tau)\,, \tag{A8}$$

where the "collision operator" $C(t)$ is given by

$$C(t)\equiv\int\frac{dz}{2\pi i}\tilde{C}(z)e^{zt}\,, \tag{A9}$$

$$\tilde{C}(z)\equiv\int dx_2\theta_{12}\tilde{U}(12;z)\tilde{U}^{-1}(1;z)\,. \tag{A10}$$

[The right-hand side of (A9) is a Bromwich integral with contour parallel to the imaginary z axis and $\mathrm{Re}z>0$.]

The binary-collision approximation results from determination of $\tilde{U}(12;z)\tilde{U}^{-1}(1;z)$ to lowest order in a formal density expansion. This expansion in density is generated by a cluster expansion for $\tilde{U}(12;z)$ and $\tilde{U}(1;z)$. The results to lowest order are

$$\tilde{U}(1;z)\to[z+L(1)]^{-1}f_0(1)\,, \tag{A11}$$

$$\tilde{U}(12;z)\to[z+L(12)]^{-1}f_0(1)f_0(2)e^{-\beta V(12)}(1+\lambda P_{12})\,. \tag{A12}$$

Here $L(1)$ and $L(12)$ are the Liouville operators for a single-particle and two-particle system, respectively,

$$L(1)=\vec{v}_1\cdot\vec{\nabla}_1\,, \tag{A13}$$

$$L(12)=L(1)+L(2)-\theta_{12}\,, \tag{A14}$$

and $f_0(1)$ is the Maxwell-Boltzmann distribution. The binary-collision approximation to the collision operator is therefore given by (A9) with

$$\tilde{C}(z)\to\int dx_2\theta_{12}[z+L(12)]^{-1}\times f(12)(1+\lambda P_{12})f_0^{-1}(1)[z+L(1)] \tag{A15}$$

and $f_0(12)=f_0(1)f_0(2)e^{-\beta V(r)}$. Use of the identity

$$\theta_{12}[z+L(12)]^{-1}=[z+L_0(12)][z+L(12)]^{-1}-1 \tag{A16}$$

allows this to be written as

$$\tilde{C}(z)=\int_0^\infty dt\,e^{-zt}\int dx_2[z+L_0(12)](e^{-L(12)t}-e^{-L_0(12)t})\times f_0(12)[z+L_0(12)](1+\lambda P_{12})f_0^{-1}(1)\,. \tag{A17}$$

Here $L_0(12)\equiv L(1)+L(2)$.

For simplicity the following is restricted to the case for space-independent correlation functions. Then $\phi^{(1)}$ is a function only of the velocity and time, and $\tilde{C}(z)$ becomes

$$\tilde{C}(z)=z\int_0^\infty dt\,e^{-zt}\int dx_2[z+L_0(12)](e^{-L(12)t}-e^{-L_0(12)t})\times f_0(12)(1+\lambda P_{12})f_0^{-1}(1)\,. \tag{A18}$$

To further analyze the collision operator define $y(1;t)$ by

$$n\phi^{(1)}(1;t)=f_0(1)y(1;t)\,. \tag{A19}$$

The kinetic equation then takes the form

$$\frac{\partial y(1;t)}{\partial t}=-\int_0^t d\tau\,M(t-\tau)y(1;\tau)\,, \tag{A20}$$

$$M(t)\equiv\int\frac{dz}{2\pi i}e^{zt}\tilde{M}(z)\,, \tag{A21}$$

$$\tilde{M}(z)=-z\int_0^\infty dt\,e^{-zt}f_0^{-1}(1)\times\int dx_2[z+L_0(12)](e^{-L(12)t}-e^{-L_0(12)t})\times f_0(12)(1+\lambda P_{12})\,. \tag{A22}$$

APPENDIX B: CALCULATION OF $\Omega^*(z)$ FOR THE SQUARE-WELL POTENTIAL

The details of the calculation of $\Omega^*(z)$, defined by Eq. (4.3) are given here. For convenience the scattering and bound-state parts are considered separately.

A. Scattering states

The scattering states contribution to $\Omega^*(z)$ may be obtained by restricting the integration in Eq. (4.2) to $\frac{1}{4}m(\hat{\sigma}\cdot\vec{v})>\epsilon$,

$$\Omega_s^*(z)=-\frac{1}{64\pi}\left(\frac{m}{kT}\right)^3\int_0^\infty dv\,v^2e^{-mv^2/4kT}\int d\Omega(\hat{\sigma}\cdot\vec{v})\theta[\tfrac{1}{4}m(\hat{\sigma}\cdot\vec{v})^2-\epsilon]\times[R^2(\vec{v}\cdot\vec{v}')_{R\sigma^+}+e^{1/T^*}(\vec{v}\cdot\vec{v}')_{\sigma^+}-R^2e^{1/T^*}(\vec{v}\cdot\vec{v}')_{R\sigma^-}]\,, \tag{B1}$$

where $\theta(x)$ is the Heaviside step function. The integrand consists of three contributions corresponding to particles initially separated by distances $R\sigma^+$, $R\sigma^-$, and σ^+. Accordingly $\Omega_s^*(z)$ will be written as the sum of such contributions,

$$\Omega_s^*(z)\equiv\Omega_{R\sigma^+}^*(z)+\Omega_{\sigma^+}^*(z)+\Omega_{R\sigma^-}^*(z)\,. \tag{B2}$$

The solid angle integration may be performed by writing it as the sum of integrals for $(\hat{\sigma}\cdot\vec{v})>0$ and $(\hat{\sigma}\cdot\vec{v})<0$. Let $\vec{v}_+'(\vec{v}_-')$ denote the scattered relative velocity originating on the positive (negative) hemisphere. Then with the change of variables $\theta \to \theta+\pi$, $\phi \to \phi+\pi$ in the integral for $(\hat{\sigma}\cdot\vec{v})<0$, each of the terms in Eq. (B2) can be written in the form

$$\Omega_r^*(z) = -\frac{1}{64\pi}\left(\frac{m}{kT}\right)^3 g(r)\int_0^\infty dv\, v^2 e^{-mv^2/4kT}\int_{(\hat{\sigma}\cdot\vec{v})>0} d\Omega(\hat{\sigma}\cdot\vec{v})\theta[\tfrac{1}{4}m(\hat{\sigma}\cdot\vec{v})^2-\epsilon](\vec{v}\cdot\vec{v}_+'-\vec{v}\cdot\vec{v}_-')_r\,, \tag{B3}$$

where r denotes the separation distance $(R\sigma^+,\, R\sigma^-,\, \sigma^+)$ and $g(r)$ is the low-density pair correlation function $[g(R\sigma^-)=g(\sigma^+)=e^{1/T^*},\, g(R\sigma^+)=1]$. Furthermore, the scattering is isotropic about the vector $\vec{v}$, so that the integrand is independent of ϕ. Introducing the reduced velocity $y=v(m/4kT)^{1/2}$ and the reduced impact parameter $x=b/\sigma$, Eq. (B3) becomes

$$\Omega_r^*(z) = 2g(r)\int_0^\infty dy\, y^5 e^{-y^2}\int_0^R dx\, x\,\theta\left[y^2\left(1-\frac{x^2}{R^2}\right)^{1/2}-\frac{1}{T^*}\right]\left(\frac{\vec{v}\cdot\vec{v}_+'}{v^2}-\frac{\vec{v}\cdot\vec{v}_-'}{v^2}\right)_r. \tag{B4}$$

Here $T^*\equiv kT/\epsilon$ is the dimensionless temperature. It remains to calculate $\vec{v}_+'$ and $\vec{v}_-'$ from Eq. (4.9) for the three relative separations $R\sigma^+$, $R\sigma^-$, and σ^+. The time integral in Eq. (4.9) can be performed in the square-well case because the velocity is piecewise constant and only changes (discontinuously) at the edges of the well. The relative velocity of the scattering pair can be calculated for all times from consideration of the two-body conservation laws and the geometry of the well. The transit times, $T_i(x,y)$, between partial collisions depends on the initial velocity and impact parameter.

1. Particles starting at $R\sigma^+$

For $(\hat{\sigma}\cdot\vec{v})<0$ the particles are initially free and remain free for all times; consequently, $\vec{v}_-'=\vec{v}$. For $(\hat{\sigma}\cdot\vec{v})>0$ two types of scattering events are possible, as indicated in Figs. 1(a) and 1(b). These are characterized by a critical reduced impact parameter a defined by

$$a \equiv (1+1/y^2T^*)^{1/2}. \tag{B5}$$

For $x>a$ the trajectory is that of Fig. 1(a) and determination of $\vec{v}_+'$ gives

$$(\vec{v}\cdot\vec{v}_+')_{R\sigma^+,x>a} = (1-e^{-\epsilon T_1})\vec{v}\cdot\vec{v}_1 + e^{-\epsilon T_1}\vec{v}\cdot\vec{v}_2. \tag{B6}$$

For $x<a$ the trajectory is that shown in Fig. 1(b) and

$$(\vec{v}\cdot\vec{v}_+')_{R\sigma^+,x<a} = (1-e^{-\epsilon T_2})\vec{v}\cdot\vec{v}_1 + (e^{-\epsilon T_2}-e^{-2\epsilon T_2})\vec{v}\cdot\vec{v}_3 + e^{-2\epsilon T_2}\vec{v}\cdot\vec{v}_4. \tag{B7}$$

The scattered velocities for each partial collision are

$$\vec{v}_1 = \vec{v}+\hat{\sigma}v\beta\,, \tag{B8}$$

$$\vec{v}_2 = \vec{v}\left[1-\frac{2\beta}{a}\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}\right]+2\hat{\sigma}v\beta\left[1-\frac{\beta}{a}\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}\right], \tag{B9}$$

$$\vec{v}_3 = \vec{v}\left[\frac{2x^2}{a^2}-1+2R\left(1-\frac{x^2}{a^2}\right)^{1/2}\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}\right] + \hat{\sigma}v\left[\beta\left(\frac{2x^2}{a^2}-1\right)+2R\beta\left(1-\frac{x^2}{a^2}\right)^{1/2}\left(1-\frac{x^2}{R^2a^2}\right)^{1/2} - 2Ra\left(1-\frac{x^2}{a^2}\right)^{1/2}\right], \tag{B10}$$

$$\vec{v}_4 = \hat{\sigma}v\beta+\vec{v}_3\left[1-\frac{\beta}{a}\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}+\frac{\beta}{Ra}\left(1-\frac{x^2}{a^2}\right)^{1/2}\right] - \vec{v}_1\frac{\beta}{a}\left[\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}-\frac{1}{R}\left(1-\frac{x^2}{a^2}\right)^{1/2}\right]. \tag{B11}$$

Here β is defined by

$$\beta \equiv a\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}-\left(1-\frac{x^2}{R^2}\right)^{1/2}, \tag{B12}$$

and the interaction times T_1 and T_2 are

$$T_1(x,y) \equiv \frac{R}{ay}\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}, \tag{B13}$$

$$T_2(x,y) \equiv \frac{1}{2ay}\left[R\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}-\left(1-\frac{x^2}{a^2}\right)^{1/2}\right]. \tag{B14}$$

2. Particles starting at σ^+

The scattering events for particles initially separated by $r=\sigma$ are shown in Figs. 1(c) and 1(d). For $(\hat{\sigma}\cdot\vec{v})>0$ calculation of $\vec{v}_+'$ gives

$$(\vec{v}\cdot\vec{v}_+')_{\sigma^+} = (1-e^{-\epsilon T_3})\vec{v}\cdot\vec{v}_5 + e^{-\epsilon T_3}\vec{v}\cdot\vec{v}_6\,, \tag{B15}$$

and for $(\hat{\sigma}\cdot\vec{v})<0$ calculation of $\vec{v}_+'$ gives

$$(\vec{v}\cdot\vec{v}_-')_{\sigma^+} = (1-e^{-\epsilon T_3})v^2 + e^{-\epsilon T_3}\vec{v}\cdot\vec{v}_7\,. \tag{B16}$$

The scattered velocities are

$$\vec{v}_5 = \vec{v}-\hat{\sigma}2v(1-x^2)^{1/2}\,, \tag{B17}$$

$$\vec{v}_6=\vec{v}\left[\frac{x^2}{R^2}+\alpha\left(1-\frac{x^2}{R^2\alpha^2}\right)^{1/2}\left(1-\frac{x^2}{R^2}\right)^{1/2}-\frac{\beta'}{R}(1-x^2)^{1/2}\right]$$
$$-\hat{\sigma}v\left[\frac{\beta'}{R}(2x^2-1)+\frac{2x^2}{R^2}(1-x^2)^{1/2}\right.$$
$$\left.+2\alpha\left(1-\frac{x^2}{R^2\alpha^2}\right)^{1/2}\left(1-\frac{x^2}{R^2}\right)^{1/2}(1-x^2)^{1/2}\right], \tag{B18}$$

$$\vec{v}_7=\vec{v}\left[1+\beta'\left(1-\frac{x^2}{R^2}\right)^{1/2}-\frac{\beta'}{R}(1-x^2)^{1/2}\right]+\hat{\sigma}v\frac{\beta'}{R}, \tag{B19}$$

with

$$\beta'=\alpha\left(1-\frac{x^2}{R^2\alpha^2}\right)^{1/2}-\left(1-\frac{x^2}{R^2}\right)^{1/2}, \tag{B20}$$

$$\alpha=(2-a^2)^{1/2}=(1-1/y^2T^*)^{1/2}. \tag{B21}$$

The interaction time is

$$T_3(x,y)=\frac{1}{2y}[(R^2-x^2)^{1/2}-(1-x^2)^{1/2}]. \tag{B22}$$

3. *Particles starting at $R\sigma^+$*

The scattering for $(\hat{\sigma}\cdot\vec{v})<0$ is shown in Fig. 2(c), giving

$$(\vec{v}\cdot\vec{v}'_-)_{R\sigma^-}=\vec{v}\cdot\vec{v}_8. \tag{B23}$$

For $(\hat{\sigma}\cdot\vec{v})>0$ there are two types of collision sequences. For $x>\alpha$ [defined by Eq. (B21)] there is no contact at the core [Fig. 2(a)] with the result

$$(\vec{v}\cdot\vec{v}'_+)_{R\sigma^-,x>\alpha}=(1-e^{-\epsilon T_4})v^2+e^{-\epsilon T_4}\vec{v}\cdot\vec{v}_9. \tag{B24}$$

For impact parameters $x<\alpha$ there is contact at the core [Fig. 2(b)] so that

$$(\vec{v}\cdot\vec{v}')_{R\sigma^-,x<\alpha}=(1-e^{-\epsilon T_4})v^2+(e^{-\epsilon T_4}-e^{-2\epsilon T_4})\vec{v}\cdot\vec{v}_{10}$$
$$+e^{-2\epsilon T_4}\vec{v}\cdot\vec{v}_{11}. \tag{B25}$$

The scattered velocities are

$$\vec{v}_8=\vec{v}+\hat{\sigma}v\beta', \tag{B26}$$

$$\vec{v}_9=\vec{v}\left[1+2\beta'\left(1-\frac{x^2}{R^2}\right)^{1/2}\right]-\hat{\sigma}v\beta', \tag{B27}$$

$$\vec{v}_{10}=\vec{v}[2x^2-1+2(1-x^2)^{1/2}(R^2-x^2)^{1/2}]$$
$$-\hat{\sigma}2vR(1-x^2)^{1/2}, \tag{B28}$$

$$\vec{v}_{11}=\vec{v}\left\{-\frac{2\beta'}{R}x^2(1-x^2)^{1/2}+\beta'(2x^2-1)\left(1-\frac{x^2}{R^2}\right)^{1/2}\right.$$
$$+[2(R^2-x^2)^{1/2}(1-x^2)^{1/2}$$
$$\left.+(2x^2-1)]\left[\frac{x^2}{R^2}+\alpha\left(1-\frac{x^2}{R^2\alpha^2}\right)^{1/2}\left(1-\frac{x^2}{R^2}\right)^{1/2}\right]\right\}$$
$$-\hat{\sigma}v\left\{\beta'(2x^2-1)+2R(1-x^2)^{1/2}\right.$$
$$\left.\times\left[\frac{x^2}{R^2}+\alpha\left(1-\frac{x^2}{R^2\alpha^2}\right)^{1/2}\left(1-\frac{x^2}{R^2}\right)^{1/2}\right]\right\}, \tag{B29}$$

and the interaction time is

$$T_4(x,y)=\frac{R}{y}\left(1-\frac{x^2}{R^2}\right)^{1/2}. \tag{B30}$$

A summary of the results for various scattering angles is

$$\frac{\vec{v}_1\cdot\vec{v}}{v^2}=a\left[\frac{x^2}{R^2a}+\left(1-\frac{x^2}{R^2a^2}\right)^{1/2}\left(1-\frac{x^2}{R^2}\right)^{1/2}\right]\equiv aF_1(x,y),$$

$$\frac{\vec{v}_2\cdot\vec{v}}{v^2}=2F_1^2-1,$$

$$\frac{\vec{v}_3\cdot\vec{v}}{v^2}=a[-F_1F_2+(1-F_1^2)^{1/2}(1-F_2^2)^{1/2}],$$
$$F_2(x,y)=1-2\frac{x^2}{a^2}$$

$$\frac{\vec{v}_4\cdot\vec{v}}{v^2}=2F_1(1-F_1^2)^{1/2}(1-F_2^2)^{1/2}-F_2(2F_1^2-1)\equiv F_3(x,y),$$

$$\frac{\vec{v}_5\cdot\vec{v}}{v^2}=\frac{\vec{v}_{10}\cdot\vec{v}}{v^2}=2x^2-1\equiv F_4(x,y),$$

$$\frac{\vec{v}_7\cdot\vec{v}}{v^2}=\frac{\vec{v}_8\cdot\vec{v}}{v^2}=\frac{\vec{v}_9\cdot\vec{v}}{v^2}$$
$$=\alpha\left[\frac{x^2}{R^2\alpha^2}+\left(1-\frac{x^2}{R^2\alpha^2}\right)^{1/2}\left(1-\frac{x^2}{R^2}\right)^{1/2}\right]$$
$$\equiv\alpha F_5(x,y),$$

$$\frac{\vec{v}_6\cdot\vec{v}}{v^2}=\frac{\vec{v}_{11}\cdot\vec{v}}{v^2}=\alpha[F_4F_5+(1-F_4^2)^{1/2}(1-F_5^2)^{1/2}]. \tag{B31}$$

Finally, the integrals defined in Eqs. (3.12), (3.13), and (3.14) are

$$I_1(z)=2\int_0^\gamma dy\,y^5e^{-y^2}\int_0^R dx\,x\,A(x,y), \tag{B32}$$

$$I_2(z)=2\int_\gamma^\infty dy\,y^5e^{-y^2}\left(\int_0^a dx\,x\,A(x,y)\right.$$
$$\left.+\int_a^R dx\,x\,B(x,y)\right), \tag{B33}$$

$$I_3(z)=2\int_{1/\sqrt{T^*}}^{R\gamma} dy\,y^5e^{-y^2}\int_0^{R\alpha} dx\,xC(x,y), \tag{B34}$$

$$I_4(z)=2\int_{R\gamma}^\infty dy\,y^5e^{-y^2}\int_0^1 dx\,xC(x,y), \tag{B35}$$

$$I_5(z)=2\int_{1/\sqrt{T^*}}^{R\gamma} dy\,y^5e^{-y^2}\int_0^{R\alpha} dx\,xD(x,y), \tag{B36}$$

$$I_6(z)=2\int_{R\gamma}^\infty dy\,y^5e^{-y^2}\left(\int_0^1 dx\,xD(x,y)\right.$$
$$\left.+\int_1^{R\alpha} dx\,xE(x,y)\right), \tag{B37}$$

with

$$\gamma=[T^*(R^2-1)]^{-1/2},$$

and

$$A(x,y)=1-a(1-e^{-\epsilon T_2})F_1-a(e^{-\epsilon T_2}-e^{-2\epsilon T_2})$$
$$\times[-F_1F_2+(1-F_1^2)^{1/2}(1-F_2^2)^{1/2}]-e^{-2\epsilon T_2}F_3,$$

$$B(x,y)=1-(1-e^{-\epsilon T_1})\alpha F_1-e^{-\epsilon T_1}(2F_1^2-1),$$

$$C(x,y)=(1-F_4)(1-e^{-\epsilon T_3})+\alpha e^{-\epsilon T_3}[F_5(1-F_4)-(1-F_4^2)^{1/2}(1-F_5^2)^{1/2}],$$

$$D(x,y)=1-e^{-\epsilon T_3}+(e^{-\epsilon T_3}-e^{-2\epsilon T_3})F_4-\alpha F_5+e^{-2\epsilon T_3}\alpha[F_4F_5+(1-F_4^2)^{1/2}(1-F_5^2)^{1/2}],$$

$$E(x,y)=(1-e^{-\epsilon T_4})(1-\alpha F_5). \qquad \text{(B38)}$$

B. Bound states

The bound-states contribution to $\Omega^*(z)$ may be obtained by restricting the integration in Eq. (4.2) to $\frac{1}{4}m(\hat{\sigma}\cdot\vec{v})^2<\epsilon$. Only particles initially inside the well can be bounded. Then, in terms of reduced velocity and impact parameter:

$$\Omega_{bs}^*(z)=-2\int_0^\infty dy\,y^5e^{-y^2}\int_0^R dx\,x\,\theta\left[\frac{1}{T^*}-y^2\left(1-\frac{x^2}{R^2}\right)^{1/2}\right]e^{1/T^*}\left[\left(\frac{\vec{v}\cdot\vec{v}_+}{v^2}-\frac{\vec{v}\cdot\vec{v}'_-}{v^2}\right)_{\sigma^+}-\left(\frac{\vec{v}\cdot\vec{v}_+}{v^2}-\frac{\vec{v}\cdot\vec{v}_-}{v^2}\right)_{R\sigma^-}\right], \qquad \text{(B39)}$$

where the scattered velocity is given from Eqs. (3.7) and (4.9). For bound states the series in Eq. (4.9) has an infinite number of terms. Each relative velocity $\vec{v}_p$ can be expressed in terms of the scattering angles at the inner and outer edge of the well. From consideration of the conservation laws and of the geometry of Fig. 3,

$$\cos\theta_1=1-2x^2,\qquad \cos\theta_2=1-2x^2/R^2. \qquad \text{(B40)}$$

$(\pi+\theta_1)$ is the scattering angle for each partial collision at the core and $(\pi-\theta_2)$ is the scattering angle for each partial collision at the outer edge of the well.

1. *Particles starting at* $R\sigma^-$

Two types of orbits are possible, as indicated in Fig. 3. For critical impact parameter $x>1$, the trajectory of the bound pair does not hit the core [see Figs. 3(a) and 3(b)]. The time T_4 between two scattering events is given by

$$T_4(x,y)=\frac{1}{y}(R^2-x^2)^{1/2}. \qquad \text{(B41)}$$

Indicating with $\vec{v}_p$ the scattered relative velocity during the time interval $(p-1)T_4\le t\le pT_4$, the scattering angle is

$$\vec{v}\cdot\vec{v}_p=\begin{cases}v^2\cos[(p-1)(\pi-\theta_2)], & \text{for } (\hat{\sigma}\cdot\vec{v})>0\\ v^2\cos[p(\pi-\theta_2)], & \text{for } (\hat{\sigma}\cdot\vec{v})<0\end{cases}$$

and

$$\left(\frac{\vec{v}\cdot\vec{v}'}{v^2}\right)_{R\sigma^-,\,x>1}=(1+\cos\theta_2)+\sum_{p=1}^{\infty}(-1)^pe^{-\epsilon pT_4}C_p(x,y), \qquad \text{(B42)}$$

with

$$C_p(x,y)=2(1+\cos\theta_2)\cos p\theta_2. \qquad \text{(B43)}$$

Writing the cosine in exponential form the series in Eq. (B42) can be summed and

$$\left(\frac{\vec{v}\cdot\vec{v}'}{v^2}\right)_{R\sigma^-,\,x>1}=\frac{(1-e^{-2\epsilon T_4})(1+\cos\theta_2)}{D_1(x,y;z)}\equiv H(x,y), \qquad \text{(B44)}$$

where $D_1(x,y;z)$ is defined by

$$D_1(x,y;z)=1+2e^{-\epsilon T_4}\cos\theta_2+e^{-2\epsilon T_4}. \qquad \text{(B45)}$$

For critical impact parameter $x<1$ the trajectory is shown in Figs. 3(c) and 3(d); for $(\hat{\sigma}\cdot\vec{v})>0$:

$$\vec{v}\cdot\vec{v}_p=\begin{cases}v^2\cos\left(\frac{p}{2}(\pi+\theta_1)+\frac{p-2}{2}(\pi-\theta_2)\right), & p \text{ even}\\ v^2\cos\left(\frac{p-1}{2}(\pi+\theta_1)+\frac{p-1}{2}(\pi-\theta_2)\right), & p \text{ odd}\end{cases}$$

and for $(\hat{\sigma}\cdot\vec{v})<0$:

$$\vec{v}\cdot\vec{v}_p=\begin{cases}v^2\cos\left(\frac{p}{2}(\pi-\theta_2)+\frac{p}{2}(\pi+\theta_1)\right), & p \text{ even}\\ v^2\cos\left(\frac{p-1}{2}(\pi+\theta_1)+\frac{p+1}{2}(\pi-\theta_2)\right), & p \text{ odd}.\end{cases}$$

Rearranging the summation in Eq. (B42), the scattering angle can be written

$$\left(\frac{\vec{v}\cdot\vec{v}'}{v^2}\right)_{R\sigma^-,\,x<1}=(1+\cos\theta_2)+2\sum_{p=1}^{\infty}e^{-2p\epsilon T_3}\cos[p(\theta_1-\theta_2)](1+\cos\theta_2)-\sum_{p=1}^{\infty}e^{-(2p+1)\epsilon T_3}A_p(\theta_1,\theta_2), \qquad \text{(B46)}$$

with

$$A_p(\theta_1,\theta_2)=\cos[p(\theta_1-\theta_2)]+\cos[(p+1)(\theta_1-\theta_2)]+\cos[p(\theta_1-\theta_2)+\theta_1]+\cos[p(\theta_1-\theta_2)-\theta_2]. \qquad \text{(B47)}$$

The transit time T_3 is again calculated from the geometry of Fig. 3:

$$T_3(x,y)=\frac{1}{2y}[(R^2-x^2)^{1/2}-(1-x^2)^{1/2}]. \qquad \text{(B48)}$$

As before, the series in Eq. (B46) can be summed by writing the trigonometric functions in exponential form, leading to

$$\left(\frac{\vec{v}\cdot\vec{v}'}{v^2}\right)_{R\sigma^-,\,x<1}=\frac{(1-e^{-zT_3})}{D_2(x,y;z)}\{(1+e^{-3zT_3})(1+\cos\theta_2)-e^{-zT_3}(1+e^{-zT_3})[\cos(\theta_1-\theta_2)+\cos\theta_1]\}\equiv G_2(x,y)\,, \tag{B49}$$

with

$$D_2(x,y;z)=1-2e^{-2zT_3}\cos(\theta_1-\theta_2)+e^{-4zT_3}\,. \tag{B50}$$

2. Particles starting at σ^+

It appears immediately from Fig. 3 that the orbit of particles starting at $r=\sigma^+$ is directly related to the orbit of particles starting at $r=R\sigma^-$ and impact parameter $x<1$. The former can be obtained from the latter by adding a time interval T_3 for $(\hat{\sigma}\cdot\vec{v})>0$ and subtracting the same time interval for $(\hat{\sigma}\cdot\vec{v})<0$. Then, for $(\hat{\sigma}\cdot\vec{v})>0$,

$$\vec{v}\cdot\vec{v}_p=\begin{cases} v^2\cos\left(\frac{p+1}{2}(\pi+\theta_1)+\frac{p+1}{2}(\pi-\theta_2)\right), & p \text{ even}\\ v^2\cos\left(\frac{p-1}{2}(\pi+\theta_1)+\frac{p-1}{2}(\pi-\theta_2)\right), & p \text{ odd}\end{cases}$$

and, for $(\hat{\sigma}\cdot\vec{v})<0$,

$$\vec{v}\cdot\vec{v}_p=\begin{cases} v^2\cos\left(\frac{p-2}{2}(\pi+\theta_1)+\frac{p}{2}(\pi-\theta_2)\right), & p \text{ even}\\ v^2\cos\left(\frac{p-1}{2}(\pi+\theta_1)+\frac{p-1}{2}(\pi-\theta_2)\right), & p \text{ odd}\,.\end{cases}$$

Then

$$\left(\frac{\vec{v}\cdot\vec{v}'}{v^2}\right)_{\sigma^+}=-(1+\cos\theta_1)-2\sum_{p=1}^{\infty}e^{-2pzT_3}\cos p(\theta_1-\theta_2)(1+\cos\theta_1)+\sum_{p=1}^{\infty}e^{-(2p+1)zT_3}A_p(\theta_1,\theta_2)\,. \tag{B51}$$

Again, the series in Eq. (B50) can be summed and

$$\left(\frac{\vec{v}\cdot\vec{v}'}{v^2}\right)_{\sigma^+}=-\frac{(1-e^{-zT_3})}{D_2(x,y;z)}\{(1+e^{-zT_3})(1+\cos\theta_1)-e^{-zT_3}(1+e^{-zT_3})[\cos(\theta_1-\theta_2)+\cos\theta_2]\}\equiv G_1(x,y)\,. \tag{B52}$$

Finally the integrals I_7 and I_8, defined in Eq. (4.8) are

$$I_7(z)=2\int_0^{1/\sqrt{T^*}}dy\,y^5e^{-y^2}\int_0^1 dx\,xG_2(x,y)+2\int_{1/\sqrt{T^*}}^{R\gamma}dy\,y^5e^{-y^2}\int_{R\alpha}^1 dx\,xG_2(x,y)+2\int_0^{R\gamma}dy\,y^5e^{-y^2}\int_1^R dx\,xH(x,y)+2\int_{R\gamma}^{\infty}dy\,y^5e^{-y^2}\int_{R\alpha}^R dx\,xH(x,y)\,, \tag{B53}$$

$$I_8(z)=2\int_0^{1/\sqrt{T^*}}dy\,y^5e^{-y^2}\int_0^1 dx\,xG_1(x,y)+2\int_{1/\sqrt{T^*}}^{R\gamma}dy\,y^5e^{-y^2}\int_{R\alpha}^1 dx\,xG(x,y)\,, \tag{B54}$$

where the functions $G_1(x,y)$, $G_2(x,y)$ and $H(x,y)$ have been defined in Eqs. (B52), (B49), and (B44), respectively.

At the low-density limit considered here, it is more convenient both for numerical calculations and for the discussion of the existence of the bound-state part of the collision operator, to consider the time representation of Ω^*_{bs},

$$\bar{\Omega}_{bs}(t)=\int\frac{dz}{2\pi i}e^{zt}\Omega^*_{bs}(z)\,. \tag{B55}$$

Indicating with $\bar{\Omega}^{(1)}(t)$ the contribution from particles which do not hit the core (i.e., particles starting at $R\sigma^-$, with $x>1$), with $\bar{\Omega}^{(2)}(t)$ the contribution from particles hitting the core (particles starting at σ^+ and particles starting at $R\sigma^-$, with $x<1$), and performing the z integration in Eq. (B55):

$$\bar{\Omega}^{(1)}(t)=\bar{\Omega}_0^{(1)}\delta(t)+\bar{\Omega}^{(1)}(t)\,, \tag{B56}$$

$$\bar{\Omega}^{(2)}(t)=\bar{\Omega}_0^{(2)}\delta(t)+\bar{\Omega}^{(2)}(t)\,, \tag{B57}$$

with

$$\bar{\Omega}_0^{(1)}=2e^{1/T^*}\int_0^{R\gamma}dy\,y^5e^{-y^2}\int_1^R dx\,x(1+\cos\theta_2)+2e^{1/T^*}\int_{R\gamma}^{\infty}dy\,y^5e^{-y^2}\int_{R\alpha}^R dx\,x(1+\cos\theta_2)\,, \tag{B58}$$

$$\bar{\Omega}_0^{(2)}=2e^{1/T^*}\int_0^{1/\sqrt{T^*}}dy\,y^5e^{-y^2}\int_0^1 dx\,x(2+\cos\theta_1+\cos\theta_2)+2e^{1/T^*}\int_{1/\sqrt{T^*}}^{R}dy\,y^5e^{-y^2}\int_R^1 dx\,x(2+\cos\theta_1+\cos\theta_2)\,, \tag{B59}$$

and

$$\bar{\Omega}_1^{(1)}(t) = 4e^{1/T^*} \sum_{p=1}^{\infty} (-1)^p \Big(\int_0^{R\gamma} dy\, y^5 e^{-y^2} \int_1^R dx\, x\, \delta(t - pT_4) \cos(p\theta_2)(1+\cos\theta_2) + \int_R^{\infty} dy\, y^5 e^{-y^2} \int_{R\alpha}^R dx\, x\, \delta(t-pT_4) \cos(p\theta_2)(1+\cos\theta_2) \Big), \tag{B60}$$

$$\bar{\Omega}_1^{(2)}(t) = 4e^{1/T^*} \sum_{p=1}^{\infty} \Big[\int_0^{1/\sqrt{T^*}} dy\, y^5 e^{-y^2} \int_0^1 dx\, x\, \delta(t-pT_3) \cos\Big(\frac{p}{2}(\theta_1-\theta_2)\Big) S_p(x) + \int_{1/\sqrt{T^*}}^{R\gamma} dy\, y^5 e^{-y^2} \int_{R\alpha}^1 dx\, x\, \delta(t-pT_3) \cos\Big(\frac{p}{2}(\theta_1-\theta_2)\Big) S_p(x) \Big], \tag{B61}$$

where

$$S_p(x) = \begin{cases} 2+\cos\theta_1+\cos\theta_2, & p \text{ even} \\ -4\cos\frac{\theta_1}{2}\cos\frac{\theta_2}{2}, & p \text{ odd}. \end{cases} \tag{B62}$$

At this point it appears convenient to interchange the order of integration in Eqs. (B60) and (B61) and perform the y integration with the result

$$\bar{\Omega}_1^{(1)}(t) = 4\frac{e^{1/T^*}}{t} \sum_{p=1} (-1)^p \int_1^R dx\, x(1+\cos\theta_2)\cos(p\theta_2)\Big(\frac{pb(x)}{t}\Big)^6 \exp\Big[-\Big(\frac{pb(x)}{t}\Big)^2\Big] \times \Big[\theta\Big(R\gamma - \frac{pb(x)}{t}\Big) + \theta\Big(\frac{pb(x)}{t} - R\gamma\Big)\theta(x - R\alpha'(x))\Big], \tag{B63}$$

$$\bar{\Omega}_1^{(2)}(t) = 4\frac{e^{1/T^*}}{t} \sum_{p=1} \int_0^1 dx\, x S_p(x) \cos\Big(\frac{p}{2}(\theta_1-\theta_2)\Big)\Big(\frac{p}{t}a(x)\Big)^6 \exp\Big[-\Big(\frac{p}{t}a(x)\Big)^2\Big] \times \Big[\theta\Big(\frac{1}{\sqrt{T^*}} - \frac{p}{t}a(x)\Big) + \theta\Big(\frac{p}{t}a(x) - \frac{1}{\sqrt{T^*}}\Big)\theta\Big(R\gamma - \frac{p}{t}a(x)\Big)\theta(x - R\alpha''(x))\Big], \tag{B64}$$

where

$$b(x) = (R^2 - x^2)^{1/2},$$
$$a(x) = \tfrac{1}{2}[(R^2-x^2)^{1/2} - (1-x^2)^{1/2}],$$
$$\alpha'(x) = [1 - t^2/p^2T^*b^2(x)]^{1/2},$$
$$\alpha''(x) = [1 - t^2/p^2T^*a^2(x)]^{1/2}.$$

APPENDIX C: COMPARISON WITH KIRKWOOD

The role of bound states and finite collision times in the derivation of the Boltzmann equation was first discussed by Kirkwood.[7] For completeness and comparison, Kirkwood's arguments are indicated here, as applied to the velocity-autocorrelation function. In contrast to the memory-function formulation used in Appendix A, it is more convenient to define the time-local equation for the velocity-autocorrelation function,

$$\frac{\partial}{\partial t}F(t) = I(t)F(t), \tag{C1}$$

which defines $I(t)$. The binary-collision approximation for $I(t)$ may be obtained from a corresponding kinetic equation analogous to Eq. (A8). The details will not be given but the result is (for continuous potentials)

$$I(t) = \frac{\partial}{\partial t}[A_{sc}(t) + A_{bs}(t)], \tag{C2}$$

$$A_{sc}(t) \equiv \frac{n}{24\sqrt{\pi}}\Big(\frac{m}{KT}\Big)^{5/2} \int_0^{\infty} dv\, v^2 e^{-\beta m v^2/4} \times \int d\vec{r}\, e^{-\beta V(r)} \times R_{sc}(\vec{r}, v)\vec{v}\cdot[\vec{v}(t) - \vec{v}], \tag{C3}$$

$$\vec{v}(t) \equiv e^{-\bar{L}(12)t}\vec{v}. \tag{C4}$$

The function $A_{bs}(t)$ is the same as (C3) with R_{sc} replaced by R_{bs}. The latter two functions identify the scattering and bound-state contributions, respectively, and are defined in Eqs. (3.7) and (3.8).

Kirkwood's analysis is somewhat different in that he considers time-averaged functions. In the present context, the time-averaged correlation function is defined by

$$\bar{F}(t) \equiv \frac{1}{T}\int_0^T ds\, F(t+s), \tag{C5}$$

and the low-density equation corresponding to (C1) is

$$\frac{\partial \overline{F}}{\partial t}(t) = \overline{I}(t)\overline{F}(t) . \tag{C6}$$

Here, $\overline{I}(t)$ is the time average of Eq. (C2),

$$\overline{I}(t) = \frac{1}{T}\{[A_{sc}(t+T) - A_{sc}(t)] + [A_{bs}(t+T) - A_{bs}(t)]\} . \tag{C7}$$

As indicated by Kirkwood, $A_{sc}(t)$ grows asymptotically as $A_{sc}(t) \to I_\infty t$, whereas $A_{bs}(t)$ remains bounded for large t. Here I_∞ denotes the Boltzmann limit for $\overline{I}(t)$. Consequently,

$$\overline{I}(t) \to I_\infty + O(1/t) \tag{C8}$$

and the time-averaged correlation function is determined from Boltzmann form, if the time interval T of the averaging process is chosen sufficiently large for terms of order $1/T$ to be negligible.

It does not follow from Kirkwood's result for $\overline{F}(t)$ that the correlation function itself, $F(t)$, has a Boltzmann limit. To illustrate this consider the hypothetical case

$$A_{sc}(t) \to I_\infty t ,$$

$$A_{bs}(t) \to \sin\omega t .$$

Then Kirkwood's result, (C8), still holds and $\overline{F}(t)$ has a Boltzmann limit, but

$$I(t) \to I_\infty + \omega\cos\omega t$$

and the Boltzmann limit for $F(t)$ would not result. To establish the Boltzmann limit for $F(t)$ it is necessary to prove a somewhat stronger property of the bound-state contribution than its boundedness, as used by Kirkwood; namely, that its amplitude is sufficiently damped in time. The analysis of Sec. III indicates this is true for a class of continuous potentials, while that of Sec. IV confirms it in detail for the square-well potential.

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