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Boltzmann-Enskog equation analysis of tagged-particle motions with inverse-power-law interactions

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A new method is presented for solving the space-independent Boltzmann-Enskog equation describing the motions of a heavy tagged particle (A) in the medium of light bath particles (B). It is shown how in the case of inverse-power-law repulsive interactions the transport equation can be transformed into a set of partial differential equations which are then solved successively to give the conditional average of an arbitrary physical quantity as a power series in the mass ratio $\Omega^{-1}=m_B/(m_A+m_B)$. The method is explicitly developed to first order in Ω^{-1}, which shows the effects of fluctuations, and in the linear noise approximation the time-dependent distribution function itself is obtained. The velocity autocorrelation function of a tagged particle is evaluated to order Ω^{-2} where one finds corrections to a single exponential decay.

I. INTRODUCTION

Fluctuations in a many-body system can be described by transport equations of which the linearized Boltzmann-Enskog equation is a well-known member.[1,2] In such a description the effects of interparticle collisions are treated in terms of a collision kernel whose explicit form depends on the interaction potential specified for the particles. The complexity of analyzing the transport equation largely depends on the complexity of the kernel.

There has been considerable interest in using transport equations to study equilibrium fluctuations. Time correlation functions describing the dynamical properties of a system in thermal equilibrium can be calculated as certain initial-value solutions.[3] Nonequilibrium fluctuations can be studied even more naturally, since they are given by solutions which are not averaged over an initial equilibrium distribution. In either problem the difficulty of obtaining solutions generally lies in the analysis of the collision kernel, and approximations developed for one type of calculation often are applicable as well to the other.

The use of the linearized Boltzmann-Enskog equation to study equilibrium fluctuations has been carried out most extensively in the case of a hard-sphere interaction.[2,4] With the possible exception of the Maxwell interaction (repulsive force $\propto 1/r^5$), there exists little discussion of direct solutions of the transport equation for continuous potentials. The method of kinetic models has been found to be quite effective in calculating time correlation functions;[5] however, it does not appear to be suitable for the study of nonequilibrium fluctuations.

In this work we consider the Boltzmann-Enskog equation description of the motions of a heavy tagged particle moving in a medium of light bath particles. We develop a method of solving the transport equation in the spatially uniform case for inverse power repulsive interactions between the tagged and bath particles. This method, which involves an expansion in a mass ratio parameter, allows one to investigate the explicit effects of an interaction potential, in contrast to other methods of describing tagged-particle motions, such as the Fokker-Planck or the Langevin equation, which involve phenomenological constants like the friction coefficients.[6]

It is well known that the Boltzmann-Enskog equation, regarded as a special case of a master equation, has two equivalent forms, called the forward and backward forms of the master equation.[7,8] Van Kampen[9] and later Kubo *et al.*[10] have used the forward form to derive a Fokker-Planck equation with time-dependent mean and variance. The backward form has been used to calculate arbitrary conditional averages in powers of a mass ratio parameter.[8,11] This analysis is applicable whenever the transition probability $W(x \to x')$ is only a function of scalar quantities x and x'. In this paper we generalize the method to the case where the transition probability $W(\vec{v} \to \vec{v}')$ is only a function of the tagged-particle speeds v, v' and the angle between $\vec{v}$ and $\vec{v}'$.

In Sec. II we begin with the backward form of the Boltzmann-Enskog equation and derive a system of partial differential equations whose solutions are the coefficients of expansion of an arbitrary conditional average in powers of $m_B/(m_A+m_B)$, where m_A and m_B are the masses of the tagged and bath particles, respectively. The equations can be solved successively with each equation depending on the solution to the preceding equation, and in place of W the equations involve only certain moments of W which are still velocity dependent. In Sec. III the first two members of the system of equations are analyzed. We show that the first equation describes only the macroscopic motion with no fluctuations. The second equation gives a correction to the macroscopic motion, fluctuations are now expressed in terms of a covariance matrix. We also show that in the linear noise approximation the distribution function can be explicitly determined. Section IV presents an analysis of the transition probability where for inverse-power-law repulsive interactions W is shown to have the desired property mentioned above. Another result is that all the moments of W appearing in the system of differential equations can be expressed in terms of confluent hypergeometric functions. In Sec. V we study the velocity autocorrelation function as an example of calculation of equilibrium fluctuations. It is found that the correlation function does not follow a single exponential decay. A number of concluding remarks are given in Sec. VI.

II. METHOD FOR SOLVING THE BOLTZMANN-ENSKOG TRANSPORT EQUATION

We consider a tagged particle, mass m_A and diameter σ_A, moving in the field of bath particles, mass m_B and diameter σ_B. The system is assumed to be spatially uniform. Let $h(\vec{v}t \mid \vec{v}_0)$ be the conditional probability that particle A has velocity $\vec{v}$ at time t given that at $t=0$ its velocity was $\vec{v}_0$. If the density of bath particles B is not too high, then $h(\vec{v}t \mid \vec{v}_0)$ satisfies the Boltzmann-Enskog equation[12,13]

$$\frac{\partial h(\vec{v}t \mid \vec{v}_0)}{\partial t}+P_\Omega(\vec{v})h(\vec{v}t \mid \vec{v}_0) = \int d^3v_1\, W_\Omega(\vec{v}_1 \rightarrow \vec{v})h(\vec{v}_1 t \mid \vec{v}_0) \quad (2.1)$$

with initial condition

$$h(\vec{v}t=0 \mid \vec{v}_0)=\delta(\vec{v}-\vec{v}_0) . \quad (2.2)$$

In (2.1) $W_\Omega(\vec{v}_0 \rightarrow \vec{v}_1)$ is the transition probability per unit time that particle A will change in velocity $\vec{v}_0$ to $\vec{v}_1$ upon collision with particle B, and

$$P_\Omega(\vec{v}_0)=\int d^3v_1\, W_\Omega(\vec{v}_0 \rightarrow \vec{v}_1) \quad (2.3)$$

is the collision frequency. Here W_Ω and P_Ω are space and time independent; the subscript Ω denotes an explicit dependence on the mass ratio (see Sec. IV).

In the terminology of Markov processes,[14,15] (2.1) can be regarded as the forward master equation for the time distribution function $h(\vec{v}t \mid \vec{v}_0)$. It is well known[7,8] that there exists a corresponding backward master equation of the form

$$\frac{\partial h(\vec{v}t \mid \vec{v}_0)}{\partial t}+P_\Omega(\vec{v}_0)h(\vec{v}t \mid \vec{v}_0) = \int d^3v_1\, W_\Omega(\vec{v}_0 \rightarrow \vec{v}_1)h(\vec{v}t \mid \vec{v}_1) . \quad (2.4)$$

Notice that the loss term is written as $P_\Omega(\vec{v}_0)h(\vec{v}t \mid \vec{v}_0)$. One is usually interested in the time-dependent conditional average

$$\chi(\vec{v}_0,t)=\langle f(\vec{v}) \mid \vec{v}_0\rangle_t \equiv \int d^3v\, f(\vec{v})h(\vec{v}t \mid \vec{v}_0) , \quad (2.5)$$

where

$$\chi(\vec{v}_0, t=0)=f(\vec{v}_0) . \quad (2.6)$$

Using (2.4) one can therefore calculate $\chi(\vec{v}_0,t)$ by solving

$$\frac{\partial \chi(\vec{v}_0,t)}{\partial t}+P_\Omega(\vec{v}_0)\chi(\vec{v}_0,t) = \int d^3v_1\, W_\Omega(\vec{v}_0 \rightarrow \vec{v}_1)\chi(\vec{v}_1,t) \quad (2.7)$$

with (2.6) as the initial condition.

Our approach to the solution of (2.7) is to consider the expansion of $\chi(\vec{v}_0,t)$ in powers of the mass ratio

$$\Omega^{-1}=\frac{m_B}{m_A+m_B} . \quad (2.8)$$

We first make use of the fact that for all purely repulsive interaction potentials the transition probability W can be written in the form

$$W_\Omega(\vec{v}_0 \rightarrow \vec{v}_1)=F(\Omega)\Omega^3 W[\vec{v}_0,\Omega(\vec{v}_0-\vec{v}_1)] , \quad (2.9)$$

where on the right-hand side (rhs) of (2.9) the dependence on Ω appears explicitly. This will be shown in Sec. IV where an expression for $F(\Omega)$ is given.

If we now expand $\chi(\vec{v}_1,t)$ in the integrand of (2.7) into a Taylor series about $\vec{v}_1=\vec{v}_0$, the dependence of (2.7) on the parameter Ω then appears explicitly,

$$\frac{\partial \chi(\vec{v}_0,t)}{\partial t}=\sum_{k=1}^{\infty}\frac{F(\Omega)}{\Omega^k}\frac{1}{k!}L^{(k)}\chi(\vec{v}_0,t) , \quad (2.10)$$

where the Ω-independent differential operator $L^{(k)}$ is defined by

$$L^{(k)} \equiv \int d^3y\, W[\vec{v}_0,\vec{y}]\left[\vec{y}\cdot\frac{\partial}{\partial \vec{v}_0}\right]^k . \quad (2.11)$$

It should be noted that the integration with respect to $\vec{y}$ can be carried out analytically if one introduces the jump moments $\alpha_{n,k}(v_0)$ [see (A7)—(A9)]. Equation (2.10) can be simplified further by introducing a new time scale

$$\tau=\frac{F(\Omega)}{\Omega}t \quad (2.12)$$

so that

$$\chi(\vec{v}_0,t)=\tilde{\chi}(\vec{v}_0,\tau) . \quad (2.13)$$

We will henceforth suppress the tilde. With the aid of Eq. (A7) we then obtain instead of (2.10)

$$\frac{\partial \chi(\vec{v}_0,\tau)}{\partial \tau}-\alpha_{1,0}(v_0)\left[\vec{a}\cdot\frac{\partial}{\partial \vec{v}_0}\right]\chi(\vec{v}_0,\tau) = \sum_{k=2}^{\infty}\frac{1}{\Omega^{k-1}}\frac{1}{k!}L^{(k)}\chi(\vec{v}_0,\tau) , \quad (2.14)$$

where $\vec{a}$ is the unit vector of $\vec{v}_0$ and $\alpha_{1,0}(v_0)$ is the jump moment defined in (A5).

The reason for the particular time scaling (2.12) becomes more clear if we interpret (2.14) as follows. The time evolution of an arbitrary conditional average χ (e.g., the mean velocity or the mean energy of a tagged particle) has been separated into two parts, namely, the left-hand side (lhs) of (2.14) which is independent of Ω and contains only first-order derivatives with respect to τ and $\vec{v}_0$, and the rhs of (2.14) which depends on Ω and contains only second- and higher-order derivatives with respect to $\vec{v}_0$.

In the limit $\Omega \rightarrow \infty$ (2.14) reduces to

$$\frac{\partial \chi(\vec{v}_0,\tau)}{\partial \tau}-\alpha_{1,0}(v_0)\left[\vec{a}\cdot\frac{\partial}{\partial \vec{v}_0}\right]\chi(\vec{v}_0,\tau)=0 \quad (2.15)$$

which describes the deterministic motion of the particle since it is a homogeneous first-order partial differential equation (see also Appendix C). For finite values of Ω one has to include the rhs of (2.14) which is responsible for fluctuations (see Sec. III).

In order to solve (2.14) we separate the conditional average $\mathcal{X}$ into a nonfluctuating part $\mathcal{X}_0$ and fluctuating parts $\mathcal{X}_l$ $(l\geq 1)$ and write

$$\mathcal{X}=\mathcal{X}_0+\sum_{l=1}^{\infty}\frac{1}{\Omega^l}\mathcal{X}_l \ . \tag{2.16}$$

Inserting this into (2.14) and collecting terms of the same order in Ω^{-1} we obtain a system of partial differential equations for $\mathcal{X}_l(\vec{v}_0,\tau)$,

$$\frac{\partial \mathcal{X}_0(\vec{v}_0,\tau)}{\partial\tau}-\alpha_{1,0}(v_0)\vec{a}\cdot\frac{\partial \mathcal{X}_0(\vec{v}_0,\tau)}{\partial\vec{v}_0}=0\ , \tag{2.17}$$

$$\frac{\partial \mathcal{X}_l(\vec{v}_0,\tau)}{\partial\tau}-\alpha_{1,0}(v_0)\vec{a}\cdot\frac{\partial \mathcal{X}_l(\vec{v}_0,\tau)}{\partial\vec{v}_0}=H_l(\vec{v}_0,\tau) \tag{2.18}$$

with

$$H_l(\vec{v}_0,\tau)=\sum_{k=2}^{l+1}\frac{1}{k!}L^{(k)}\mathcal{X}_{l+1-k}(\vec{v}_0,\tau),\ \ l\geq 1\ . \tag{2.19}$$

The initial conditions, which are independent of Ω, are

$$\mathcal{X}_0(\vec{v}_0,\tau=0)=f(\vec{v}_0)\ , \tag{2.20}$$

$$\mathcal{X}_l(\vec{v}_0,\tau=0)=0,\ \ l\geq 1\ . \tag{2.21}$$

We see that H_l depends on $\mathcal{X}_k$, $k<l$; therefore, the equations can be solved successively, starting at the lowest order.

To solve the partial differential equations (2.17) and (2.18) we can either use the standard methods of characteristics[16] or more simply apply a theorem which is discussed in detail in Appendix C. In our particular case this theorem can be stated as follows. Let $\vec{\overline{V}}(\vec{v}_0,\tau)$ be a solution of

$$\frac{d\vec{\overline{V}}}{d\tau}=\alpha_{1,0}(\overline{V})\frac{\vec{\overline{V}}}{\overline{V}} \tag{2.22}$$

subject to the initial condition

$$\vec{\overline{V}}(\vec{v}_0,\tau=0)=\vec{v}_0 \tag{2.23}$$

then $\vec{\overline{V}}(\vec{v}_0,\tau)$ also satisfies

$$\frac{\partial\vec{\overline{V}}(\vec{v}_0,\tau)}{\partial\tau}-\alpha_{1,0}(v_0)\left[\vec{a}\cdot\frac{\partial}{\partial\vec{v}_0}\right]\vec{\overline{V}}(\vec{v}_0,\tau)=0\ . \tag{2.24}$$

Comparing (2.24) with (2.17) and (2.18) one can verify that the solutions of these equations subject to the initial conditions (2.20) and (2.21) are given by

$$\mathcal{X}_0(\vec{v}_0,\tau)=f(\vec{\overline{V}}(\vec{v}_0,\tau))\ , \tag{2.25}$$

$$\mathcal{X}_l(\vec{v}_0,\tau)=\int_0^{\tau}ds\,H_l(\vec{\overline{V}}(\vec{v}_0,\tau-s),s),\ \ l\geq 1\ . \tag{2.26}$$

Thus, one can first solve the macroscopic equation (2.22) for $\vec{\overline{V}}(\vec{v}_0,\tau)$ and then obtain $\mathcal{X}_0$ by replacing $\vec{v}_0$ by $\vec{\overline{V}}(\vec{v}_0,\tau)$ in the argument of the known function f. For $\mathcal{X}_l$ one has to evaluate the integral of H_l, as defined in (2.19) with $\vec{v}_0$ replaced by $\vec{\overline{V}}(\vec{v}_0,\tau-s)$.

At this point we already see the significance of the macroscopic equation (2.22). In the limit $\Omega\rightarrow\infty$ the motion of the tagged particle is completely determined by $\mathcal{X}_0$ which only involves the solution of (2.22). Fluctuations which are described by $\mathcal{X}_l$ $(l\geq 1)$ are of order Ω^{-1} (see also Sec. III) and vanish for $\Omega\rightarrow\infty$. We therefore can regard (2.22) as the macroscopic, deterministic equation of the system describing the motion of the tagged particle when fluctuations become negligible. The jump moment $\alpha_{1,0}(v)$ is completely determined by the microscopic binary interaction potential (see Sec. IV and Appendix A) and gives rise to a nonlinear, macroscopic damping. Only in the case for a Maxwell-interaction potential the friction coefficient $\alpha_{1,0}(\overline{V})/\overline{V}$ is a velocity-independent constant and can be calculated with the aid of (4.15) and (4.17).

III. THE LINEAR NOISE APPROXIMATION

In this section we will derive an explicit expression for $\mathcal{X}_1(\vec{v}_0,\tau)$ and show how in the linear noise approximation one can obtain $h(\vec{v}t\mid\vec{v}_0)$ as a Gaussian distribution with time-dependent mean and variance.

We first observe that (2.22) can be simplified on account of $\alpha_{1,0}$ being only a function of the magnitude of $\vec{\overline{V}}$. We can set $\vec{\overline{V}}=\overline{V}\vec{a}$, so it is only necessary to solve

$$\frac{d\overline{V}}{d\tau}=\alpha_{1,0}(\overline{V}) \tag{3.1}$$

with $\overline{V}(\tau=0)=v_0$. Also, (2.24) becomes

$$\frac{d\overline{V}}{d\tau}-\alpha_{1,0}(v_0)\frac{d\overline{V}}{dv_0}=0\ . \tag{3.2}$$

Comparing (3.1) and (3.2) allows us to express the v_0 derivative of $\overline{V}$ in terms of the moment $\alpha_{1,0}$,

$$\frac{d\overline{V}}{dv_0}=\frac{\alpha_{1,0}(\overline{V})}{\alpha_{1,0}(v_0)}\ . \tag{3.3}$$

We will see in the following that such a relation is very useful.

According to the method just developed the evaluation of $\mathcal{X}_0(\vec{v}_0,\tau)$ requires the solution of (3.1) which, in general, can be carried out by quadrature. Once $\overline{V}$ is known, $\mathcal{X}_0$ is obtained from (2.25). Since $\mathcal{X}_0$ is the leading term in the series expression of $\mathcal{X}(\vec{v}_0,\tau)$, we see that in the limit of large mass ratio Ω, $\mathcal{X}(\vec{v}_0,\tau)$ is essentially determined by (3.1) involving only the first moment $\alpha_{1,0}$ of W_Ω. In order to study the motion of the particle for finite Ω we have to include higher-order terms $\mathcal{X}_l$ $(l\geq 1)$ of our series expansion (2.16).

To evaluate $\mathcal{X}_1(\vec{v}_0,\tau)$ using (2.26) we need to find H_1 from (2.19). This gives

$$H_1(\vec{v}_0,\tau)=\tfrac{1}{2}L^{(2)}\chi_0(\vec{v}_0,\tau)$$
$$=\tfrac{1}{2}\int d^3y\, W[\vec{v}_0,\vec{y}]y_iy_j\partial_i\partial_j\chi_0(\vec{v}_0,\tau)\ , \quad (3.4)$$

where we have introduced index notation, $\{y_i\}=\vec{y}$, $\partial_i=\partial/\partial v_{0i}$, and the Einstein summation convention. In the differentiation of χ_0 one has

$$\partial_i\chi_0=\partial_i f(\vec{\bar{V}})=\frac{\partial f}{\partial\vec{\bar{V}}}\frac{\partial\vec{\bar{V}}}{\partial v_{0i}} \quad (3.5)$$

so we can replace the v_0 derivation of $\bar{V}$ by the moments $\alpha_{1,0}$ as given in (3.3). Carrying out the indicated operation in (3.4) we obtain (see Appendix A)

$$H_1(\vec{v}_0,\tau)=\frac{1}{2}\frac{\partial^2 f(\vec{\bar{V}})}{\partial\bar{V}_k\partial\bar{V}_l}\left\{a_ka_l\left[\frac{\alpha_{1,0}^2(\bar{V})}{\alpha_{1,0}^2(v_0)}\beta_{2,1}(v_0)+\frac{1}{3}\left[\frac{\bar{V}}{v_0}\right]^2\beta_{2,2}(v_0)\right]-\tfrac{1}{3}\delta_{kl}\left[\frac{\bar{V}}{v_0}\right]^2\beta_{2,2}(v_0)\right\}$$
$$+\frac{\partial f(\vec{\bar{V}})}{\partial\bar{V}_k}a_k\left[\tfrac{1}{2}\beta_{2,1}(v_0)\frac{\alpha_{1,0}(\bar{V})}{\alpha_{1,0}^2(v_0)}[\alpha'_{1,0}(\bar{V})-\alpha'_{1,0}(v_0)]-\frac{\beta_{2,2}(v_0)}{3v_0}\left[\frac{\alpha_{1,0}(\bar{V})}{\alpha_{1,0}(v_0)}-\frac{\bar{V}}{v_0}\right]\right]\ , \quad (3.6)$$

where the prime denotes derivative with respect to the argument and the various moments are defined in (A5) and (A10).

It can be seen from (3.6) that the τ dependence enters only through the solution $\bar{V}(v_0,\tau)$ to (3.1). This means that we can write $H_1(\vec{v}_0,\tau)\equiv H_1[\vec{\bar{V}},v_0]$ using square brackets if H_1 or any other function is expressed by the independent variable $\vec{\bar{V}}$ and v_0 instead of $\vec{v}_0$ and τ. It is then easy to show that the general expression for χ_1 as given in (2.26) can be replaced by

$$\chi_1(\vec{v}_0,\tau)=\int_{v_0}^{\bar{V}}dy\frac{H_1[\vec{\bar{V}},y]}{\alpha_1(y)} \quad (3.7)$$

which shows that in general χ_1 can be evaluated by quadrature once $\vec{\bar{V}}(\tau)$ is known. Using (3.7) and (3.6) one obtains

$$\chi_1[\vec{\bar{V}},v_0]=\tfrac{1}{2}A_{kl}[\bar{V},v_0]\frac{\partial^2 f(\vec{\bar{V}})}{\partial\bar{V}_k\partial\bar{V}_l}+\phi[\bar{V},v_0]a_k\frac{\partial f(\vec{\bar{V}})}{\partial\bar{V}_k}\ , \quad (3.8)$$

where

$$A_{kl}[\bar{V},v_0]=a_ka_l\sigma_v^2[\bar{V},v_0]-(a_ka_l-\tfrac{1}{3}\delta_{kl})\Gamma[\bar{V},v_0]\ , \quad (3.9)$$

$$\sigma_v^2[\bar{V},v_0]=\int_{v_0}^{\bar{V}}dy\left[\frac{\alpha_{1,0}^2(\bar{V})}{\alpha_{1,0}^3(y)}\beta_{2,1}(y)-\frac{2}{3}\frac{\beta_{2,2}(y)}{\alpha_{1,0}(y)}\left[\frac{\bar{V}}{y}\right]^2\right]\ , \quad (3.10)$$

$$\Gamma[\bar{V},v_0]=-\int_{v_0}^{\bar{V}}dy\left[\frac{\beta_{2,2}(y)}{\alpha_{1,0}(y)}\left[\frac{\bar{V}}{y}\right]^2\right]\ , \quad (3.11)$$

$$\phi[\bar{V},v_0]=\int_{v_0}^{\bar{V}}dy\left[\frac{1}{2}\frac{\alpha_{1,0}(\bar{V})\beta_{2,1}(y)}{\alpha_{1,0}^3(y)}[\alpha'_{1,0}(\bar{V})-\alpha'_{1,0}(y)]-\frac{\beta_{2,2}(y)}{3y\alpha_{1,0}(y)}\left[\frac{\alpha_{1,0}(\bar{V})}{\alpha_{1,0}(y)}-\frac{\bar{V}}{y}\right]\right]\ . \quad (3.12)$$

Notice that in (3.8) the dependence on f is explicit, and the quantities A_{kl} and ϕ only need be evaluated once for a given interaction potential.

Applying the same procedure successively, this method of reduction can be carried out to higher order $\chi_l[\vec{\bar{V}},v_0]$ so that the entire calculation then involves solving (3.1) for $\bar{V}(v_0,\tau)$ and using the explicit expressions for $\chi_k[\vec{\bar{V}},v_0]$ with $k<l$ in order to obtain $\chi_l[\vec{\bar{V}},v_0]$.

We now show that χ_1 is needed to describe fluctuations. Since the average of f is

$$\langle f(\vec{v})\,|\,\vec{v}_0\rangle_\tau\equiv\chi[\vec{\bar{V}},v_0]$$
$$=f(\vec{\bar{V}})+\frac{1}{\Omega}\chi_1[\vec{\bar{V}},v_0]+O\left[\frac{1}{\Omega^2}\right] \quad (3.13)$$

we find the mean square deviation to be

$$\langle f^2(\vec{v})\,|\,\vec{v}_0\rangle_\tau-\langle f(\vec{v})\,|\,\vec{v}_0\rangle_\tau^2$$
$$=\frac{1}{\Omega}\frac{\partial f}{\partial\bar{V}_k}\frac{\partial f}{\partial\bar{V}_l}A_{kl}+O\left[\frac{1}{\Omega^2}\right]\ . \quad (3.14)$$

This shows that fluctuations enter at order Ω^{-1} and they depend on A_{kl}. The trace of A_{kl}, given by σ_v^2, describes the mean square velocity deviation, while ϕ gives a correction to the macroscopic motion $\vec{\bar{V}}(\tau)$ of the tagged particle which has its origin in the nonlinearity of the moment $\alpha_{1,0}$ [see (3.12)].

An interesting property of the covariance matrix A_{kl} can be derived by considering the limit $\tau\to\infty$. From (3.10) and (3.11) we obtain using the explicit expressions for the moments $\alpha_{n,k}$ (see Sec. IV)

$$\lim_{\tau\to\infty}\Gamma(\tau)=\lim_{\tau\to\infty}\sigma_v^2(\tau)=-\frac{\alpha_{0,2}(0)}{2\alpha'_{1,0}(0)}\ . \quad (3.15)$$

Inserting (3.15) into (3.9) we find that the covariance matrix A_{kl} becomes diagonal for long times. It is worthwhile to compare this result with the analysis of Brownian motion based on either the Langevin equation or the Fokker-Planck equation.[6] There one assumes

$\alpha_{1,0}=-\beta V$ and $\alpha_{0,2}=\gamma$ and all other moments vanish. For large Ω these assumptions are equivalent to assuming $v/v_T^B \ll 1$ and expanding the moments $\alpha_{1,0}$ and $\alpha_{0,2}$, cf. (4.15) and (4.17), in a Taylor series in v/v_T^B. In doing this we obtain explicit expressions for β and γ, namely, $\beta=-\alpha'_{1,0}(0)$ and $\gamma=-3(v_T^B)^2\alpha'_{1,0}(0)$.

In either case (3.1), (3.10), and (3.11) give

$$\vec{\vec{V}}=\vec{v}_0 e^{-\beta\tau} , \tag{3.16}$$

$$\sigma_v^2=\frac{\gamma}{2\beta}(1-e^{-2\beta\tau}) , \tag{3.17}$$

and A_{kl} is diagonal for all times,

$$A_{kl}=\frac{\gamma}{6\beta}(1-e^{-2\beta\tau})\delta_{kl} . \tag{3.18}$$

In contrast we have shown here that when the details of interatomic interactions are considered the covariance matrix is diagonal only at long times.

Thus far we have been concerned with a physical property $f(\vec{v})$, averaged over the distribution function $h(\vec{v}t \mid \vec{v}_0)$. We now show that in the linear noise approximation $h(\vec{v}t \mid \vec{v}_0)$ can be determined. We begin by considering the characteristic function defined as the Fourier transform

$$\chi(\vec{n},\vec{v}_0,t)=\int d^3v\, e^{i\vec{n}\cdot\vec{v}}h(\vec{v}t \mid \vec{v}_0) \tag{3.19}$$

with

$$\chi(\vec{n},\vec{v}_0,t=0)=e^{i\vec{n}\cdot\vec{v}_0} . \tag{3.20}$$

One can imagine that this quantity also can be given a power-series expression in Ω^{-1}. However, in view of (3.20) it would be more natural to write[10]

$$\begin{aligned}\chi(\vec{n},\vec{v}_0,t)&=e^{q(\vec{n},\vec{v}_0,t)}\\ &=\exp\left[\sum_{k=0}^{\infty}\frac{1}{\Omega^k}q_k(\vec{n},\vec{v}_0,t)\right] .\end{aligned} \tag{3.21}$$

The coefficients q_k can be found as follows. Divide (2.14) by χ to obtain an equation for $\partial q/\partial t$. Then expanding q in a power series in Ω^{-1} and using the time scaling relation (2.12) we arrive at the same set of equations for q_k as given in (2.17) and (2.18), with the only differences being the functions H_l now replaced by more involved functions H_l^n, and the initial conditions (2.20) and (2.21) replaced by

$$q_0(\vec{n},\vec{v}_0,\tau=0)=i(\vec{n}\cdot\vec{v}_0) , \tag{3.22}$$

$$q_l(\vec{n},\vec{v}_0,\tau=0)=0,\quad l\geq 1 . \tag{3.23}$$

In the linear noise approximation only q_0 and q_1 are retained in (3.21). For H_1^n one has

$$\begin{aligned}H_1^n(\vec{v}_0,\tau)=&\tfrac{1}{4}L^{(2)}q_0^2(\vec{n},\vec{v}_0,\tau)\\ &+\tfrac{1}{2}[1-q_0(\vec{n},\vec{v}_0,\tau)]L^{(2)}q_0(\vec{n},\vec{v}_0,\tau) .\end{aligned} \tag{3.24}$$

To proceed to find q_1 one can follow the procedure outlined in Secs. II and III. However, one can take advantage of the common structure of (3.24) and (3.4), and obtain the effect of operating with the $L^{(2)}$ operator by inspection of (3.8), which holds for any arbitrary function f. With either approach one obtains the same results:

$$q_0(\vec{n},\vec{v}_0,\tau)=i(\vec{n}\cdot\vec{\vec{V}}) , \tag{3.25}$$

$$q_1(\vec{n},\vec{v}_0,\tau)=-\tfrac{1}{2}\vec{n}\underline{A}\vec{n}+i(\vec{a}\cdot\vec{n})\phi , \tag{3.26}$$

where $\vec{\vec{V}}$ is again the solution of the macroscopic equation (3.1), and the covariance matrix $\underline{A}$ and function ϕ have been given previously in (3.9) and (3.12). Inserting these results into (3.21) gives

$$\chi(\vec{n},\vec{v}_0,\tau)=\exp\left[-\frac{1}{2\Omega}\vec{n}\underline{A}\vec{n}+i(\vec{n}\cdot\vec{B})\right] , \tag{3.27}$$

where

$$\vec{B}=\vec{\vec{V}}+\frac{1}{\Omega}\vec{a}\phi \tag{3.28}$$

is the mean velocity of the tagged particle correct to order Ω^{-1}. The inverse transform can be carried out,

$$\begin{aligned}h(\vec{v}\tau \mid \vec{v}_0)=&\left[\frac{\Omega}{2\pi}\right]^{3/2}(\det\underline{A})^{-1/2}\\ &\times\exp\left[-\frac{\Omega}{2}(\vec{v}-\vec{B})A^{-1}(\vec{v}-\vec{B})\right]\end{aligned} \tag{3.29}$$

with

$$A_{kl}^{-1}=\frac{9}{\Gamma}\left[a_k a_l\left[\frac{2\sigma_v^2-\Gamma}{3\sigma_v^2-2\Gamma}\right]-(a_k a_l-\tfrac{1}{3}\delta_{kl})\right] . \tag{3.30}$$

So the distribution function is a multivariate Gaussian in the linear noise approximation.

The corresponding result based on the Langevin equation or Fokker-Planck equation is well known. We have already shown that A_{kl}, and therefore also A_{kl}^{-1}, is diagonal for all times [cf. (3.18)]. If we now relate the constants γ and β to the thermal speed according to the fluctuation-dissipation theorem,

$$\begin{aligned}\lim_{\tau\to\infty}\langle\vec{v}^2 \mid \vec{v}_0\rangle_\tau=&\lim_{\tau\to\infty}\frac{\sigma_v^2(\tau)}{\Omega}\\ =&\frac{\gamma}{2\beta\Omega}=3\frac{k_B T}{m_A}\end{aligned} \tag{3.31}$$

then using (3.16) and (3.18) we find

$$\begin{aligned}h(\vec{v}\tau \mid \vec{v}_0)=&\left[\frac{m_A}{2\pi k_B T(1-e^{-2\beta\tau})}\right]^{3/2}\\ &\times\exp\left[-\frac{m_A(\vec{v}-\vec{v}_0 e^{-\beta\tau})^2}{2k_B T(1-e^{-2\beta\tau})}\right]\end{aligned} \tag{3.32}$$

a result originally derived by Chandrasekhar.[6] Thus (3.29) is a generalization of (3.32) in the sense of taking into account details of interatomic collisions and velocity-dependent friction effects. According to (3.29) the surface of constant probability in the coordinate system fixed on the macroscopic velocity, $\vec{x}=\vec{v}-\vec{B}$, is in general an ellipsoid. One can show using (3.30) that $\vec{a}$ is an eigenvector of $\underline{A}^{-1}$ with eigenvalue $\lambda_1=3(3\sigma_v^2-2\Gamma)^{-1}>0$, and two eigenvectors perpendicular to $\vec{a}$ with degenerate eigenvalues $\lambda_2=\lambda_3=3/\Gamma$. By comparison the surface according to (3.32) is a sphere. One can point out still another generalization. That is, (3.29) is the three-dimensional analog of the Green's-function solution to the one-dimensional Fokker-Planck equation with time-dependent coefficients.[8,14] Finally, we want to mention that averaging (3.32) over the angle $\theta=\cos^{-1}[(\vec{v}_0\cdot\vec{v}_1)/v_0v_1]$ yields the distribution function for the energy relaxation of a heavy particle, a result that is identical to that obtained by Anderson and Shuler[17] using a different derivation. One can perform the same average on (3.29) and thus obtain a more general expression for the distribution function describing energy relaxation.

IV. JUMP MOMENTS FOR $1/r^\nu$ POTENTIALS

In Sec. II we made use of a particular dependence of the transition probability $W_\Omega(\vec{v}_0\to\vec{v}_1)$ on the mass ratio parameter Ω [cf. (2.9)] in order to cast the transport equation into a set of partial differential equations of first order. In this section we will prove that for all purely repulsive $1/r^\nu$ potentials this dependence appears naturally if one chooses Ω^{-1} to be $m_B/(m_A+m_B)$. Furthermore, we will show that all the jump moments $\alpha_{n,k}$ can be expressed in terms of a confluent hypergeometric function.

We first observe that the transition probability can be written in the following way:

$$\int d^3v_0' W_\Omega(\vec{v}_0\to\vec{v}_0')\varphi(\vec{v}_0') = \int n_B\,|\vec{v}_1-\vec{v}_0|\,f_0^B(v_1)\varphi(\vec{v}_0')b\,db\,d\epsilon\,d^3v_1\ , \quad (4.1)$$

where $\varphi(\vec{v})$ is an arbitrary function, b and ϵ denote the collision variables, $(\vec{v}_0,\vec{v}_1)$ are the velocities of the colliding particles before the collision, and primed quantities are the post-collision velocities. Furthermore, n_B is the number density of bath particles B and

$$f_0^B(v)=(\sqrt{\pi}v_T^B)^{-3}\exp\left[-\frac{v^2}{(v_T^B)^2}\right]\ , \quad (4.2)$$

with $(v_T^B)^2=2k_BT/m_B$, is the Maxwell-Boltzmann velocity distribution. In the rhs of (4.1) one calculates the average of φ with the aid of Boltzmann's *Stosszahlenansatz* where $\vec{v}_0'$ has to be expressed in terms of $\vec{v}_0,\vec{v}_1$ and the collision variables (b,ϵ), while in the lhs of (4.1) a variable transformation has been performed so that $\vec{v}_0'$ now serves as an integration variable. Since the explicit expression for $W_\Omega(\vec{v}_0\to\vec{v}_0')$ is rather involved,[13,18] we will proceed with the rhs of (4.1) in calculating the jump moments.

Let us choose for $\varphi(\vec{v}_0')$ in (4.1)

$$\varphi(\vec{v}_0')=[(\vec{v}_0'-\vec{v}_0)\cdot\vec{d}]^n = \frac{1}{\Omega^n}[(\vec{g}-\vec{g}\,')\cdot\vec{d}]^n\ , \quad (4.3)$$

where $\vec{g}=\vec{v}_1-\vec{v}_0$ is the relative velocity and Ω is given in (2.8) and $\vec{d}$ is an arbitrary vector. Equation (4.1) then reads

$$\int d^3v_0' W_\Omega(\vec{v}_0\to\vec{v}_0')[(\vec{v}_0'-\vec{v}_0)\cdot\vec{d}]^n = \frac{1}{\Omega^n}\left[\frac{m_A}{\Omega}\right]^{-2/\nu} n_B\int d^3g\,gG_n^*f_0^B(|\vec{g}+\vec{v}_0|) \quad (4.4)$$

with

$$G_n\equiv\int[(\vec{g}-\vec{g}\,')\cdot\vec{d}]^n b\,db\,d\epsilon = \left[\frac{m_A}{\Omega}\right]^{-2/\nu} G_n^*\ . \quad (4.5)$$

The functions G_n^* do not depend on Ω (see Appendix B). Inserting (2.9) into the lhs of (4.4) and then comparing both sides we can identify $F(\Omega)$ as

$$F(\Omega)=\left[\frac{m_A}{\Omega}\right]^{-2/\nu} n_B \quad (4.6)$$

and

$$\int d^3y\,W[\vec{v}_0,\vec{y}](\vec{y}\cdot\vec{d})^n=\int d^3g\,gG_n^*f_0^B(|\vec{g}+\vec{v}_0|)\ . \quad (4.7)$$

To evaluate (4.7) we introduce the Legendre coefficients of the Maxwell-Boltzmann distribution (see also Appendix A)

$$B_n(v_0,g)\equiv 2\pi g^2\int_{-1}^{1}d\xi\,P_n(\xi)f_0^B(|\vec{g}+\vec{v}_0|) \quad (4.8)$$

with $\xi=(\vec{v}_0\cdot\vec{g})/v_0g$, and the moments

$$\gamma_{n,k}\equiv\int_0^\infty dg\,g^{k+n}B_n(v_0,g)\ . \quad (4.9)$$

Using the expression for G_n^* given in (B14) and the corresponding relation to (A6)

$$\int d^3g\,f_0^B(|\vec{g}+\vec{v}_0|)g^kP_n(\vec{g}\cdot\vec{d}/gd) = \gamma_{n,k-n}(v_0)P_n(\vec{v}_0\cdot\vec{d}/v_0d) \quad (4.10)$$

we find

$$\int d^3g\,gG_n^*f_0^B(|\vec{g}+\vec{v}_0|) = d^n\sum_{k=0}^{n}a_{k,n}\gamma_{k,n-k+\mu}P_k(\vec{v}_0\cdot\vec{d}/v_0d)\ , \quad (4.11)$$

where the index μ depends on the potential index ν through

$$\mu\equiv 1-4/\nu\ . \quad (4.12)$$

Now we want to relate $\gamma_{n,k}$ to the jump moments $\alpha_{n,k}$. Expand $(\vec{y}\cdot\vec{d})^n$ in (4.7) in Legendre polynomials,

$$\left[\frac{\vec{y}\cdot\vec{d}}{yd}\right]^n=\sum_{k=0}^{n}b_{k,n}P_k\left[\frac{\vec{y}\cdot\vec{d}}{yd}\right] \quad (4.13)$$

with $b_{2k,2s+1}=b_{2k+1,2s}=0$. Inserting this into the lhs of (4.7) and using (A6) we obtain

$$\int d^3y\, W[\vec{v}_0,\vec{y}](\vec{y}\cdot\vec{d})^n = d^n \sum_{k=0}^{n} b_{k,n}\alpha_{k,n-k}P_k\left[\frac{\vec{v}_0\cdot\vec{d}}{v_0 d}\right] . \quad (4.14)$$

If we compare (4.14) and (4.11) we find

$$\alpha_{n,k-n}=\frac{a_{n,k}}{b_{n,k}}\gamma_{n,k-n+\mu} . \quad (4.15)$$

It remains to show that all the moments $\gamma_{n,s}$ can be expressed in terms of a confluent hypergeometric function. We begin by noting that

$$B_n(v_0,g)=\frac{2}{v_T^B}(-1)^n\left[\frac{y}{x_0}\right]^{1/2} y \times e^{-(x_0^2+y^2)}I_{n+1/2}(2x_0 y) , \quad (4.16)$$

where $x_0=v_0/v_T^B$, $y=g/v_T^B$, and use has been made of the integral expression[19] of the modified Bessel function $I_{n+1/2}(x)$. Putting this into (4.9) and using an integral formula derived by Kummer[20] we get

$$\gamma_{n,s}(v_0)=(v_T^B)^{n+s}(-1)^n x_0^n\frac{\Gamma(n+\frac{1}{2}(s+3))}{\Gamma(n+\frac{3}{2})} \times {}_1F_1(-\tfrac{1}{2}s,n+\tfrac{3}{2},-x_0^2) , \quad (4.17)$$

where ${}_1F_1(a,b,x)$ is the confluent hypergeometric function. When this is combined with (4.15) we see that all the moments $\alpha_{n,k}(x_0)$ are proportional to $x_0^n[{}_1F_1(-(k+\mu)/2,n+\frac{3}{2},-x_0^2)]$. Note that for evaluating (4.14) we need only the moments $\alpha_{n,k}$ for k even. In this case the $\alpha_{n,k}$ moments for a Maxwell potential ($\mu=0$) reduce to a polynomial in x_0, while for a hard-sphere potential ($\mu=1$) they can be expressed in the form $\sum A_n x_0^n e^{-x_0^2}+\sum B_n x_0^n \mathrm{erf}(x_0)$. For all other cases ($0<\mu<1$) integral representations and recurrence relations[19,20] can be used to evaluate the confluent hypergeometric function.

V. EQUILIBRIUM FLUCTUATIONS

In Sec. II we have developed a method of calculating an arbitrary conditional average $X(\vec{v}_0,\tau)$ in powers of Ω^{-1}. The method is applicable to time correlation functions which describe the various fluctuations occurring in an equilibrium system. Such a quantity could be the autocorrelation function $\langle X(\vec{v}_0,\tau=0)X(\vec{v}_0,\tau)\rangle_{\mathrm{eq}}$, where the brackets $\langle\ \rangle_{\mathrm{eq}}$ denote an average over the equilibrium distribution function of (2.1), the Maxwell-Boltzmann distribution $f_0^A(\vec{v}_0)$. In this section we will confine our discussion to the calculation of the velocity autocorrelation function. This is a central quantity in any study of diffusion processes; it also appears in the determination of the intermediate scattering function $F_s(Q,t)$ for neutron and laser scattering within the Gaussian approximation.

We choose the initial condition (2.6) to be $f(\vec{v}_0)=\vec{v}_0$ and define

$$\vec{\phi}(\vec{v}_0,\tau)\equiv\langle\vec{v}\mid\vec{v}_0\rangle_\tau \quad (5.1)$$

as the time-dependent velocity of the tagged particle. Replacing in our general expression (3.13) the function $f(\vec{v})$ by $\vec{v}$ we immediately obtain for the Ω expansion of $\vec{\phi}$ up to order Ω^{-1}

$$\vec{\phi}(\vec{v}_0,\tau)=\sum_{l=0}^{\infty}\frac{1}{\Omega^l}\vec{\phi}_l(\vec{v}_0,\tau) =\vec{a}\left[\bar{V}+\frac{1}{\Omega}\phi[\bar{V},v_0]\right]+O\left[\frac{1}{\Omega^2}\right] , \quad (5.2)$$

where again $\vec{a}$ is the unit vector of $\vec{v}_0$, $\bar{V}$ is the solution of (3.1), and ϕ is given in (3.12). In order to calculate the velocity autocorrelation function (VAF) $\langle\vec{\phi}(\vec{v}_0,\tau)\vec{\phi}(\vec{v}_0,0)\rangle_{\mathrm{eq}}$ we have to keep in mind that the equilibrium distribution of (2.1) is given by

$$f_{\mathrm{eq}}(v)=\frac{1}{\pi^{3/2}}\frac{(\Omega-1)^{3/2}}{(v_T^B)^3}\exp\left[-\left[\frac{v}{v_T^B}\right]^2(\Omega-1)\right] \quad (5.3)$$

and contains the parameter Ω explicitly. For arriving at a systematic expansion of the VAF in powers of Ω^{-1} we therefore have to expand in (5.2) $\bar{V}$ and $\phi[\bar{V},v_0]$ in a Taylor series in v_0, performing the average $\langle v_0^k\rangle_{\mathrm{eq}}$ and then collecting terms in Ω^{-k}. Since this procedure is somewhat tedious we want to sketch a more direct method which is in particular suited for calculating equilibrium correlation functions. We write for $\vec{\phi}_l(\vec{v}_0,\tau)$, the solutions of (2.17)—(2.21) for the initial condition $f(\vec{v})=\vec{v}$, the following ansatz:

$$\vec{\phi}_l(\vec{v}_0,\tau)=\vec{a}\phi_l(v_0,\tau) =\vec{a}\sum_{n=0}^{\infty}A_{l,2n+1}(\tau)\frac{v_0^{2n+1}}{(2n+1)!} . \quad (5.4)$$

Inserting (5.4) into (2.17) and (2.18) and comparing equal powers in v_0 yields ordinary differential equations for $A_{l,2n+1}(\tau)$ which can be solved successively.

It should be noted that the Taylor expansion for the jump moments $\alpha_{n,k}$ can be found with the aid of (4.15) and (4.17). Since for all $r^{-\nu}$ potentials $\alpha_{n,k}(v_0)$ is even (odd) if n is even (odd) one can prove that $\phi_l(v_0,\tau)$ is always an odd function of v_0 which justifies the ansatz (5.4). Once the functions $A_{l,2n+1}(\tau)$ are determined it is straightforward to obtain the VAF. We obtain for the normalized VAF after some minor manipulations

$$\psi(\tau)\equiv\langle\vec{\phi}(\vec{v}_0,\tau)\vec{\phi}(\vec{v}_0,0)\rangle_{\mathrm{eq}}/\langle v_0^2\rangle_{\mathrm{eq}} =\sum_{n=0}^{\infty}\frac{1}{\Omega^n}B_n(\tau) , \quad (5.5)$$

where the Ω-independent coefficients $B_n(\tau)$ are given by

$$B_n(\tau)=\frac{1}{3}\sum_{s=0}^{n}(v_T^B)^{2s}\frac{(2s+3)}{4^s s!} \times\sum_{l=0}^{n-s}\begin{bmatrix} n-l-1\\ n-s-l\end{bmatrix}A_{l,2s+1}(\tau) . \quad (5.6)$$

Since the detailed calculations for $A_{l,2s+1}$ are rather involved and do not provide further insight, we only present the result for $\psi(\tau)$ up to order Ω^{-2},

$$\psi(z)=e^{-z}\left\{1-\frac{\mu z}{2\Omega}+\frac{1}{\Omega^2}\left[\frac{\mu^2}{40}(e^{-2z}-1)-\frac{\mu z}{4}\left[\frac{3\mu}{10}+1\right]+\frac{\mu^2 z^2}{8}\right]\right\}+O\left[\frac{1}{\Omega^3}\right], \quad (5.7)$$

where $\mu\equiv 1-4/\nu$ and z is a scaled time variable,

$$z=\frac{2\sqrt{2}}{3}\left[\frac{m_B}{m_A}\right]\left[\frac{m_A}{m_A+m_B}\right]^{1-2/\nu}\Omega_{A,B}^{*(1,1)}t/t_E\ . \quad (5.8)$$

Here $\Omega_{A,B}^{*(1,1)}$ is the Ω integral[13]

$$\Omega_{A,B}^{*(1,1)}=\left[\frac{\nu}{k_B T}\right]^{2/\nu}A_1(\nu)\Gamma(3-2/\nu) \quad (5.9)$$

and t_E is the Enskog collision time

$$t_E^{-1}=2\sqrt{2\pi}n_B\sigma_{AB}^2 v_T^B\ . \quad (5.10)$$

Equation (5.7) has been obtained from the Boltzmann-Enskog equation without any approximation. It shows that to order Ω^{-3} the velocity autocorrelation function has the same structure for all repulsive inverse power-law potentials, the specific properties of the potential enter explicitly through the index μ and implicitly through the scaled time variable z. We can compare (5.7) with a commonly used[21] single exponential decay of $\psi(z)$,

$$\psi^{\exp}(z)=\exp[-z(1-1/\Omega)^{-\mu/2}]$$
$$=e^{-z}\left\{1-\frac{\mu z}{2\Omega}+\frac{1}{\Omega^2}\left[\frac{\mu^2 z^2}{8}-\frac{\mu z}{4}\left[\frac{\mu}{2}+1\right]\right]\right\}+O\left[\frac{1}{\Omega^3}\right]. \quad (5.11)$$

The deviation of $\psi^{\exp}$ from the exact result is therefore

$$\psi(z)-\psi^{\exp}(z)=\frac{\mu^2}{40\Omega^2}e^{-z}(e^{-2z}-1+2z)+O\left[\frac{1}{\Omega^3}\right]. \quad (5.12)$$

While the absolute error may be small, the relative error is seen to increase linearly with z for long times. This holds for all repulsive inverse-power potentials except for the Maxwell interaction ($\mu=0$) where the single exponential decay agrees with (5.7).

In order to have a feeling for the convergence of our Ω expansion, we next calculate the diffusion coefficient D_{AB} through the Green-Kubo relation,

$$D_{AB}=\tfrac{1}{3}\langle v_0^2\rangle_{\rm eq}\int_0^\infty dt\,\psi(z)$$
$$=[D_{AB}]^{\rm I}\phi(\mu,\Omega^{-1})\ , \quad (5.13)$$

where $[D_{AB}]^{\rm I}$ is the first Chapman-Enskog approximation corresponding to the use of (5.11),

TABLE I. Comparison of diffusion coefficient ratios $D_{AB}/[D_{AB}]^{\rm I}$ for various mass ratios.

m_A/m_B	Numerical results (Ref. 22)	Ω expansion Eq. (5.15)
1000	1.000 000 033	1.000 000 033
100	1.000 003 316	1.000 003 345
10	1.000 316 138	1.000 341 167
1	1.018 953 785	1.028 251 117

$$[D_{AB}]^{\rm I}=\frac{3}{8n_B\sigma_{AB}^2}\frac{v_T^B}{\sqrt{2\pi}}\frac{1}{\Omega_{A,B}^{*(1,1)}}\left[\frac{m_A+m_B}{2m_A}\right]^{1/2} \quad (5.14)$$

and ϕ is a correction,

$$\phi(\mu,\Omega^{-1})=\left[1-\frac{1}{\Omega}\right]^{-\mu/2}\left[1-\frac{\mu}{2\Omega}+\frac{1}{\Omega^2}\left[\frac{19}{120}\mu^2-\frac{\mu}{4}\right]+O\left[\frac{1}{\Omega^3}\right]\right]. \quad (5.15)$$

For the special case of a hard-sphere gas ($\mu=1$) we have solved the Boltzmann-Hilbert integral equation numerically[22] and calculated the ratio $D_{AB}/[D_{AB}]^{\rm I}$ for a set of mass ratios m_A/m_B. These results are compared with the values obtained from (5.15) in Table I. One sees that even for a mass ratio $m_A/m_B\sim 1$ the Ω expansion is within 1% of the numerical solutions.

VI. DISCUSSION

We have presented a method for solving the Boltzmann-Enskog equation describing tagged-particle motions where the conditional average $\chi(\vec{v}_0,t)$ is evaluated as a power series in the mass ratio parameter $\Omega^{-1}=m_B/(m_A+m_B)$. The method is worked out in detail for inverse-power-law repulsive interactions between the tagged particle (m_A) and a bath particle (m_B), but more generally it is applicable to any master equation in which the transition probability $W(\vec{x}\to\vec{x}\,')$ depends only on the magnitudes of $\vec{x}$ and $\vec{x}\,'$, and the angle between them, where the stochastic variables $\vec{x}$ and $\vec{x}\,'$ need not be velocities. This latter property, in the case of transport in velocity space, should hold for any central force scattering in the absence of an external field. In the present study, it was used explicitly in Appendix A to show that the tensorial character of the moments of W appears only through unit vectors $\vec{a}$ [cf. (A7)] and that the jump moments $\alpha_{n,k}$ are functions only of v_0. This has the important consequence that all the differential equations (2.17) and (2.18) can now be integrated by quadrature, as indicated in Sec. III [cf. (3.7)].

Our explicit results are restricted to inverse-power-law potentials because we are only able to show that in this case one can have the property (2.9) which is, of course, essential for transforming the master equation (2.7) to the system of differential equations (2.17) and (2.18). In Appendix B, where we want to determine explicitly the mass dependence of the quantity $Q_{AB}^{(l)}$, this is possible for inverse-power-law potentials [see (B8)]; otherwise, one would have to resort to additional assumptions.[13]

Using the present method, both equilibrium and nonequilibrium fluctuations can be studied. In the linear noise approximation we find that a multivariate Gaussian distribution function (3.29) is obtained which differs from the Fokker-Planck or Langevin-equation approach in two respects. First, the covariance matrix A_{kl} takes into account the effects of an actual collision process by virtue of its dependence on the first and second moments of the transition probability. Second, (3.29) gives an ellipsoid for the surface of constant probability. Although no explicit calculations have been carried out thus far, we anticipate that results such as σ^2 and Γ, (3.10) and (3.11), will show significant dependence on the interaction potential index ν and the initial velocity $\vec{v}_0$. Also, we believe that nonequilibrium fluctuations can give more insight into interatomic interactions than equilibrium fluctuations. In the case of the velocity autocorrelation, our result to order Ω^{-2}, (5.7), shows only a weak dependence on the potential index ν.

In the case of the Fokker-Planck equation, the width of the time-dependent distribution $h(\vec{v},t\mid\vec{v}_0)$ is a monotonically increasing function. In our result (3.29) one can transform to a set of principal axes and consider the growth of $h(\vec{v}t\mid\vec{v}_0)$ along a particular direction. We expect, on the basis of explicit calculations in the one-dimensional case,[23] that the width of the distribution can have a nonmonotonic behavior, a more rapid increase with time initially followed by a slower decrease to the equilibrium value. This behavior depends on the value of $\vec{v}_0$. When $\vec{v}_0=0$, the result reduces to the Fokker-Planck description. For $\vec{v}_0$ exceeding the thermal speed of the bath particles, the width can have maximum values much greater than the equilibrium value.[23]

The Boltzmann-Enskog equation we have analyzed is the spatially uniform version of the transport equation. The analysis can be extended to include spatial dependence provided there are no external fields acting on the system. This means that we can study the van Hove density fluctuation or the intermediate scattering function $F_s(q,t)$ in the manner described here.

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APPENDIX A

Here we want to define the jump moments $\alpha_{n,k}(v_0)$ which appear in Sec. II. The transition probability is first expanded in spherical harmonics

$$W[\vec{v}_0,\vec{y}]=\frac{1}{y^2}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}W_l[v_0,y]Y_l^m(\Omega_{\vec{v}_0})Y_l^{m*}(\Omega_{\vec{y}}) \tag{A1}$$

with

$$W_l[v_0,y]=2\pi y^2\int_{-1}^{1}d\xi\,P_l(\xi)W[\vec{v}_0,\vec{y}]\ , \tag{A2}$$

$$P_l(\xi)=\frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_l^m(\Omega_{\vec{y}})Y_l^{m*}(\Omega_{\vec{v}_0})\ , \tag{A3}$$

and $\xi=(\vec{v}_0\cdot\vec{y})/v_0y$. Using orthogonality of the spherical harmonics we obtain

$$\int d^3y\,W[\vec{v}_0,\vec{y}]P_n\left[\frac{\vec{d}\cdot\vec{y}}{dy}\right]=P_n\left[\frac{\vec{d}\cdot\vec{v}_0}{dv_0}\right]\int_0^{\infty}dy\,W_n[v_0,y]\ , \tag{A4}$$

where $\vec{d}$ denotes an arbitrary vector. Now define

$$\alpha_{n,k}(v_0)=\int_0^{\infty}dy\,W_n[v_0,y]y^{k+n}\ . \tag{A5}$$

Then instead of (A4) one has

$$\int d^3y\,W[\vec{v}_0,\vec{y}]y^kP_n\left[\frac{\vec{d}\cdot\vec{y}}{dy}\right]=\alpha_{n,k-n}(v_0)P_n\left[\frac{\vec{v}_0\cdot\vec{d}}{v_0d}\right]\ . \tag{A6}$$

Since any power of $\mu=(\vec{d}\cdot\vec{y})/dy$ can be expressed as a linear combination of Legendre polynomials $P_n(\mu)$, we can relate any integral of the form

$$\int d^3y\,W[\vec{v}_0,\vec{y}](\vec{y}\cdot\vec{d})^n$$

to the jump moments. In particular, the first three moments are

$$\int d^3y\,W[\vec{v}_0,\vec{y}]y_i=a_i\alpha_{1,0}(v_0)\ , \tag{A7}$$

$$\int d^3y\,W[\vec{v}_0,\vec{y}]y_iy_k=a_ia_k\alpha_{2,0}(v_0)-\tfrac{1}{3}[\alpha_{2,0}(v_0)-\alpha_{0,2}(v_0)]\delta_{i,k}\ , \tag{A8}$$

$$\int d^3y\,W[\vec{v}_0,\vec{y}]y_iy_ky_l=a_ia_ka_l\alpha_{3,0}(v_0)-\tfrac{1}{5}[\alpha_{3,0}(v_0)-\alpha_{1,2}(v_0)]\times(\delta_{i,k}a_l+\delta_{i,l}a_k+\delta_{k,l}a_i)\ , \tag{A9}$$

where we have introduced index notation and $\vec{a}=\vec{v}_0/v_0$.

In the derivation of (3.6) we have introduced the moments $\beta_{2,1}$ and $\beta_{2,2}$ which are defined by

$$\beta_{2,1}(v_0)=\tfrac{2}{3}\alpha_{2,0}(v_0)+\tfrac{1}{3}\alpha_{0,2}(v_0)\ ,$$
$$\beta_{2,2}(v_0)=\alpha_{2,0}(v_0)-\alpha_{0,2}(v_0)\ . \tag{A10}$$

APPENDIX B

We will evaluate the function

$$G_n=\int b\,db\,d\epsilon[(\vec{g}-\vec{g}\,')\cdot\vec{d}]^n \tag{B1}$$

defined in (4.5). Let us introduce an orthonormal reference frame with the unit vectors $\vec{e}_x$, $\vec{e}_y$, $\vec{e}_z$, where $\vec{e}_z$ lies in the direction of $\vec{g}$,

$$\vec{g}=g\vec{e}_z \ , \tag{B2}$$

$$\vec{g}\,'=g(\vec{e}_x\sin\chi\cos\epsilon+\vec{e}_y\sin\chi\sin\epsilon+\vec{e}_z\cos\chi)\ , \tag{B3}$$

and χ and ϵ denote the polar and azimuthal angles of $\vec{g}\,'$. Notice that for potential scattering $|\vec{g}|=|\vec{g}\,'|=g$. The quantity $[(\vec{g}-\vec{g}\,')\cdot\vec{d}]^n$ is now expanded in a binomial series

$$G_n=\int b\,db\,d\epsilon g^n\sum_{k=0}^{n}\begin{bmatrix}n\\k\end{bmatrix}(-1)^k\sin^k\chi(1-\cos\chi)^{n-k}\,d_z^{n-k}(d_x\cos\epsilon+d_y\sin\epsilon)^k\ . \tag{B4}$$

With the aid of the formula

$$\int_0^{2\pi}d\epsilon(d_x\cos\epsilon+d_y\sin\epsilon)^n=\begin{cases}\dfrac{2\pi}{2^{2k}}\dfrac{(2k)!}{(k!)^2}(d_x^2+d_y^2)^k, & n=2k\\ 0, & n=2k+1\end{cases} \tag{B5}$$

we can perform the ϵ integration to obtain

$$G_n=2\pi(gd)^n\sum_{k=0}^{[n/2]}\frac{1}{2^{2k}}\begin{bmatrix}n\\2k\end{bmatrix}\begin{bmatrix}2k\\k\end{bmatrix}\left[\frac{\vec{g}\cdot\vec{d}}{gd}\right]^{n-2k}\left[1-\left[\frac{\vec{g}\cdot\vec{d}}{gd}\right]^2\right]^k\int b\,db(1+\cos\chi)^k(1-\cos\chi)^{n-k}\ , \tag{B6}$$

where $[n/2]=n/2$ for n even and $(n-1)/2$ for n odd. Since $(1+\cos\chi)^k(1-\cos\chi)^{n-k}$, for $n>k$, always can be written as a polynomial in $1-\cos^l\chi$, $l=1,\ldots,n$, we can express G_n in terms of the functions

$$Q_{AB}^{(l)}\equiv 2\pi\int_0^\infty b\,db(1-\cos^l\chi)\ . \tag{B7}$$

For a repulsive potential $1/r^\nu$ one has[13]

$$Q_{AB}^{(l)}=\left[\frac{m_Am_B}{m_A+m_B}\right]^{-2/\nu}\left[\frac{1}{g}\right]^{4/\nu}Q_{AB}^{*(l)} \tag{B8}$$

with

$$Q_{AB}^{*(l)}=2\pi\sigma_{AB}^2\left[\frac{1}{2\nu}\right]^{-2/\nu}A_l(\nu)\ , \tag{B9}$$

where $A_l(\nu)$ are pure numbers. In (B8) the mass dependence of $Q_{AB}^{(l)}$ appears explicitly, one can write

$$G_n=\left[\frac{m_Am_B}{m_A+m_B}\right]^{-2/\nu}G_n^*\ , \tag{B10}$$

where G_n^*, now mass independent, can be determined uniquely using (B6)—(B9). In particular, one has

$$G_1^*=(gd)\left[\frac{1}{g}\right]^{4/\nu}P_1(\xi_g)Q_{AB}^{*(1)}\ , \tag{B11}$$

$$G_2^*=(gd)^2\left[\frac{1}{g}\right]^{4/\nu}[\tfrac{2}{3}P_0(\xi_g)Q_{AB}^{*(1)}+\tfrac{1}{3}P_2(\xi_g)(4Q_{AB}^{*(1)}-3Q_{AB}^{*(2)})]\ , \tag{B12}$$

$$G_3^*=(gd)^3\left[\frac{1}{g}\right]^{4/\nu}[\tfrac{6}{5}P_1(\xi_g)(2Q_{AB}^{*(1)}-Q_{AB}^{*(2)})+\tfrac{1}{5}P_3(\xi_g)(3Q_{AB}^{*(1)}-9Q_{AB}^{*(2)}+5Q_{AB}^{*(3)})]\ , \tag{B13}$$

where $\xi_g=(\vec{g}\cdot\vec{d})/gd$. Note that according to (B6) and (B10) the general structure of G_n^* is given by

$$G_n^*=(gd)^n\left[\frac{1}{g}\right]^{4/\nu}\sum_{k=0}^{n}a_{k,n}P_k(\xi_g) \tag{B14}$$

with $a_{2k+1,2s}=a_{2k,2s+1}=0$ and the coefficients $a_{k,n}$ are linear combinations of $Q_{AB}^{*(l)}$.

APPENDIX C

There exists a basic equivalence between the initial-value solution to a first-order ordinary differential equation and the solution to a corresponding partial differential equation. Since this property seems not to be widely recognized, we give here a detailed proof and consider its implications concerning the Liouville equation.

Lemma I. Let $\vec{\varphi}(t\,|\,\vec{x}_0,t_0)$ be the solution to the differential equation

$$\frac{d\vec{x}}{dt}=\vec{f}(\vec{x},t) \tag{C1}$$

subject to the initial condition

$$\vec{\varphi}(t_0\,|\,\vec{x}_0,t_0)=\vec{x}_0\ . \tag{C2}$$

Then $\vec{\varphi}(t\,|\,\vec{x}_0,t_0)$ also satisfies

$$\frac{\partial\vec{\varphi}(t\,|\,\vec{x}_0,t_0)}{\partial t_0}+\sum_k f_k(\vec{x}_0,t_0)\frac{\partial\vec{\varphi}(t\,|\,\vec{x}_0,t_0)}{\partial x_{0k}}=0 \tag{C3}$$

and

$$\frac{\partial\vec{\varphi}(t\,|\,\vec{x}_0,t_0)}{\partial t}-\sum_k f_k(\vec{x}_0,t)\frac{\partial\vec{\varphi}(t\,|\,\vec{x}_0,t_0)}{\partial x_{0k}}=0\ , \tag{C4}$$

where a subscript k denotes a vector component.

Proof. We first note that (C1) has a unique solution once the initial value is chosen. This means that two functions, $\vec{\varphi}_1(t \mid \vec{x}_1,t_1)$ and $\vec{\varphi}_2(t \mid \vec{x}_2,t_2)$, which satisfy (C1) will be identical for all t if they are identical at any one instant, say $t=t_1$. For the solution to (C1) subject to (C2) we can write

$$\vec{\varphi}(t \mid \vec{x}_0,t_0)\equiv\vec{\varphi}(t \mid \vec{\varphi}(t_1 \mid \vec{x}_0,t_0),t_1) \quad \text{(C5)}$$

which is just an identity at $t=t_1$. Notice that since the lhs of (C5) is independent of t_1, it must be true also for the rhs. Therefore, the total derivative of $\vec{\varphi}(t \mid \vec{a},t_1)$ with respect to t_1 must vanish, or

$$\frac{\partial\vec{\varphi}(t \mid \vec{a},t_1)}{\partial t_1}+\sum_k \frac{\partial\vec{\varphi}(t \mid \vec{a},t_1)}{\partial a_k}\frac{\partial a_k}{\partial t_1}=0 \quad \text{(C6)}$$

with $\vec{a}\equiv\vec{\varphi}(t_1 \mid \vec{x}_0,t_0)$. Making use of (C1) we have

$$\frac{\partial \vec{a}}{\partial t_1}=\frac{d\vec{\varphi}(t_1 \mid \vec{x}_0,t_0)}{dt_1}=\vec{f}(\vec{a},t_1) \quad \text{(C7)}$$

and so (C6) becomes

$$\frac{\partial\vec{\varphi}(t \mid \vec{a},t_1)}{\partial t_1}+\sum_k f_k(\vec{a},t_1)\frac{\partial\vec{\varphi}(t \mid \vec{a},t_1)}{\partial a_k}=0 \ . \quad \text{(C8)}$$

Since (C5) holds for any t_0 we can set $t_0=t_1$ in $\vec{a}$, which means $\vec{a}$ then becomes $\vec{x}_0$. Now (C8) is an equation in the variable t_1 with no dependence on t_0 anywhere. If we furthermore write t_0 in place of t_1 everywhere, this equation becomes identical to (C3).

To show the equivalence between (C3) and (C4) we introduce the time-dependent operator

$$L(t)=-i\sum_k f_k(\vec{x}_0,t)\frac{\partial}{\partial x_{0k}} = -i\,\vec{f}(\vec{x}_0,t)\cdot\vec{\nabla}_0 \quad \text{(C9)}$$

and rewrite (C3) in the form

$$\frac{\partial\vec{\varphi}(t \mid \vec{x}_0,t_0)}{\partial t_0}=-iL(t)\vec{\varphi}(t \mid \vec{x}_0,t_0) \quad \text{(C10)}$$

with the formal solution

$$\vec{\varphi}(t \mid \vec{x}_0,t_0)=\exp\left[i\int_{t_0}^{t} d\tau L(\tau)\right]\vec{x}_0 \ . \quad \text{(C11)}$$

Differentiating (C11) with respect to t gives (C4). With the aid of lemma I we can now prove the following.

Lemma II. Let $\vec{\varphi}(t \mid \vec{x}_0,t_0)$ again denote the solution of (C1) subject to (C2). Then the solution of the partial differential equation

$$\frac{\partial\phi(\vec{x}_0,t)}{\partial t}-\sum_k f_k(\vec{x}_0,t)\frac{\partial\phi(\vec{x}_0,t)}{\partial x_{0k}}=0 \quad \text{(C12)}$$

subject to the initial condition

$$\phi(\vec{x}_0,t=t_0)=A(\vec{x}_0) \ , \quad \text{(C13)}$$

where A is an arbitrary function, is given by

$$\phi(\vec{x}_0,t)=A(\vec{\varphi}(t \mid \vec{x}_0,t_0)) \ . \quad \text{(C14)}$$

Proof. According to (C2) we see that (C14) satisfies (C13). Substituting (C14) into (C12) and using the fact that $\vec{\varphi}(t \mid \vec{x}_0,t_0)$ satisfies (C4), we see that (C14) is indeed a solution of (C12).

A useful property of the operator $L(t)$ can be established by comparing the formal solution of (C12)

$$\phi(\vec{x}_0,t)=\exp\left[i\int_{t_0}^{t} d\tau L(\tau)\right]A(\vec{x}_0) \quad \text{(C15)}$$

with (C14). One obtains the relation

$$\exp\left[i\int_{t_0}^{t} d\tau L(\tau)\right]A(\vec{x}_0) = A\left[\exp\left[i\int_{t_0}^{t} d\tau L(\tau)\right]\vec{x}_0\right] \ , \quad \text{(C16)}$$

where use is made of (C11). This shows that the action of the operator $\exp[i\int_{t_0}^{t} d\tau L(\tau)]$ on an arbitrary function $A(\vec{x}_0)$ is given by its action on the argument $\vec{x}_0$.

We suppose that an N-particle system can be described by (C1) and we are interested in calculating the time-dependent average of a physical property $A(\vec{x}_0)$,

$$\langle A(t)\rangle_{t_0}=\int d\vec{x}_0\rho(\vec{x}_0)A(\vec{\varphi}(t \mid \vec{x}_0,t_0)) \ , \quad \text{(C17)}$$

where $\vec{\varphi}$ is the solution of (C1) and $\rho(\vec{x}_0)$ denotes a given probability density. Using (C16) we get

$$\langle A(t)\rangle_{t_0} = \int d\vec{x}_0\rho(\vec{x}_0)\left[\exp\left[i\int_{t_0}^{t} d\tau L(\tau)\right]A(\vec{x}_0)\right] = \sum_{n=0}^{\infty}\frac{1}{n!}\int d\vec{x}_0\rho(\vec{x}_0)\left[i\int_{t_0}^{t} d\tau L(\tau)\right]^n A(\vec{x}_0) \ . \quad \text{(C18)}$$

Integrating by parts and assuming the surface integrals vanish, one finds

$$\langle A(t)\rangle_{t_0}=\int d\vec{x}_0 A(\vec{x}_0)\exp\left[i\int_{t_0}^{t} d\tau \tilde{L}(\tau)\right]\rho(\vec{x}_0) \ , \quad \text{(C19)}$$

where

$$\tilde{L}=i\vec{\nabla}_0\cdot\vec{f}(\vec{x}_0,t) \ . \quad \text{(C20)}$$

Equation (C19) shows that the time-dependent average can be expressed as an integral over a time-dependent probability density $\rho(\vec{x}_0,t)$

$$\langle A(t)\rangle_{t_0}=\int d\vec{x}_0 A(\vec{x}_0)\rho(\vec{x}_0,t) \quad \text{(C21)}$$

which is the solution of the "generalized" Liouville equation

$$\frac{\partial\rho(\vec{x}_0,t)}{\partial t}=i\tilde{L}(t)\rho(\vec{x}_0,t) \quad \text{(C22)}$$

with initial condition $\rho(\vec{x}_0,t_0)=\rho(\vec{x}_0)$. For a Hamiltonian system one can readily show that $\vec{\nabla}_0\cdot\vec{f}(\vec{x}_0,t)=0$ and so

$$\tilde{L}(t)=-L(t) \ . \quad \text{(C23)}$$

Common derivations of the Liouville equation make use of the Hamiltonian equations of motion and therefore arrive only at (C23), whereas (C22) describes the probability density also for non-Hamiltonian systems, including, for example, dissipative forces.

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