Fokker-Planck and Langevin equations for arbitrary slip velocities

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An expression for the Fokker-Planck equation governing the velocity distribution function of particles or heavy molecules immersed in a host light gas valid for arbitrary mean velocities of the heavy component is given. This expression generalizes previous results which were limited to small differences between the mean velocities of the heavy and light components compared with the thermal velocity of the light gas. The derivation assumes a Maxwellian velocity distribution function for the light gas, elastic heavy-light collisions, and makes use of integrals computed by Riesco-Chueca, Fernández-Feria, and Fernández de la Mora in Ref. 1. The stochastic Langevin equation associated with this Fokker-Planck collision operator is also obtained. More in general, we derive the Langevin equation corresponding to the general form of the Fokker-Planck collision operator, and particularize it to the present case.

I. INTRODUCTION

As is well known, the Fokker-Planck kinetic equation governing the velocity distribution function of particles or heavy molecules diluted in a host light gas can be derived from two different points of view.¹⁻¹⁰ The more traditional one is based on the theory of stochastic processes and the Langevin equation, 2-5 while the other approach makes use of the Boltzmann equation for the heavy component and expands the cross-collision integrals in powers of the small mass ratio.^{1,6-10} Based on this second procedure, we give in Sec. II an expression for the Fokker-Planck equation not restricted to small differences between the mean velocities of the heavy and light components compared to the thermal velocity of the light gas, but assuming a Maxwellian velocity distribution function for the light gas. In order to connect this kinetically derived Fokker-Planck equation with the stochastic approach, the corresponding stochastic Langevin equation is derived in Sec. III.

II. THE FOKKER-PLANCK EQUATION FOR ARBITRARY SLIP VELOCITIES

The cross-collision integral appearing in the Boltzmann equation corresponding to the heavy component (denoted by the subscript p) of a binary mixture whose constituents have very different molecular masses can be simplified to a Fokker-Planck form,⁶⁻¹⁰ after an expansion in the ratio of molecular weights $M \equiv m/m_p \ll 1$. This expansion is based on the small recoil velocity of the heavy molecule or particle upon collision with a much lighter molecule: From the momentum conservation it follows that, for elastic collisions,

$$\mathbf{u}_p - \mathbf{u}'_p = -\frac{m}{m + m_p} \Delta \mathbf{g} , \qquad (1)$$

where \mathbf{u}'_p and \mathbf{u}_p are the molecular velocities of the heavy component before and after the collision with a light molecule and $\Delta \mathbf{g} = \mathbf{g}' - \mathbf{g}$, $\mathbf{g} = \mathbf{u}_p - \mathbf{u}$, $\mathbf{g}' = \mathbf{u}'_p - \mathbf{u}'$. To first order in the mass ratio M, the cross-collision integral may be written as⁹

$$J = \nabla_{\mathbf{u}_p} \cdot \{ \mathbf{B}(f; \mathbf{u}_p) f_p + \frac{1}{2} \nabla_{\mathbf{u}_p} \cdot [\mathbf{\Pi}(f; \mathbf{u}_p) f_p] \} + \cdots ,$$
(2)

where f and f_p are the velocity distribution functions of the light and heavy components. $-m_p \mathbf{B}$ and $m_p^2 \Pi$ represent, respectively, the rate of momentum and energy tensor transfer from the carrier gas to a particle moving with a given velocity \mathbf{u}_p ; for elastic collisions \mathbf{B} and Π can be expressed as [see Eq. (1)]

$$\mathbf{B}(f;\mathbf{u}_p) \equiv \frac{m}{m+m_p} \int d^3 u \int d\Omega \,\sigma(g,\theta) g \Delta \mathbf{g} f(\mathbf{u})$$
$$= \frac{m}{m+m_p} \int d^3 g \,g g \mathcal{Q}^{(1)}(g) f(\mathbf{u}_p - \mathbf{g}) , \qquad (3)$$

$$\Pi(f;\mathbf{u}_p) \equiv \left[\frac{m}{m+m_p}\right]^2 \int d^3 u \int d\Omega \,\sigma(g,\theta) g \Delta g \Delta g f(\mathbf{u})$$
$$= \left[\frac{m}{m+m_p}\right]^2 \int d^3 g \,g[\frac{1}{2}(g^2\mathbf{I}-3gg)Q^{(2)}(g)$$
$$+ 2ggQ^{(1)}(g)]$$

$$\times f(\mathbf{u}_p - \mathbf{g})$$
 . (4)

In the above expressions,

$$Q^{(i)}(g) \equiv 2\pi \int_0^{\pi} d\theta (1 - \cos^i \theta) \sigma(g, \theta) \sin \theta , \qquad (5)$$

 σ is the differential scattering cross section for heavylight collisions, $d\Omega = \sin\theta \, d\theta \, d\phi$, and (g, θ, ϕ) are the

spherical coordinates of g' in a reference frame in which g is along the polar axis.

In this section we shall give a general expression for the cross-collision operator (2) not restricted to small values of the slip velocity parameter v, defined as

$$v \equiv \frac{|\mathbf{U}_p - \mathbf{U}|}{(2kT/m)^{1/2}}$$
, (6)

where U and U_p are the mean velocities of the light and heavy components, T is the temperature of the light gas, and k is Boltzmann's constant. The assumption $v \ll 1$ [more precisely, $v = O(M^{1/2})$] has been used, to our knowledge, in all previous works on the subject (Refs. 6-10). Notice that the assumption $u_p/u = O(M^{1/2})$ used in Refs. 6-8 is equivalent to $v = O(M^{1/2})$, since a frame in which U=0 was used, and since $c_p/c = O(M^{1/2})$, where $c \equiv u - U$ and $c_p \equiv u_p - U_p$ are the thermal velocities of the light and heavy components [more accurately, $c_p/c = O((mT_p/m_pT)^{1/2})$, but we assume that $T_p/T = O(1)$]. To compute the integrals (3) and (4) one needs to specify the light-gas distribution function f. In Refs. 6-8 f was taken to be a Maxwellian distribution,

$$f(\mathbf{u}) = f_0(\mathbf{u}) \equiv n \left[\frac{m}{2\pi kT} \right]^{3/2} \exp\left[-\frac{m |\mathbf{u} - \mathbf{U}|^2}{2kT} \right],$$
(7)

where *n* is the number density of the light gas. More general expressions for *f* were used in Refs. 9 and 10. In particular, Ref. 9 used the first order of the Chapman-Enskog expansion for *f* (considering the light gas as a pure gas), while in Ref. 10 the effect of the heavy species on the light-gas distribution function *f* was taken into account to first order in the Knudsen number of the light gas. Here we shall assume that *f* is the Maxwellian distribution (7) but arbitrary values of *v* will be allowed in the evaluation of (3) and (4). The assumption (7) will restrict our results (as in previous works) to situations in which the light gas is in near-equilibrium conditions (i.e., $Kn \ll 1$, where Kn is the Knudsen number of the light gas, defined as the ratio between the frequency of light-light collisions and a characteristic frequency of the sys-

tem). However, this assumption is appropriate in most practical situations and, moreover, it does not constrain the heavy-gas distribution function since, as shown in Ref. 10, the Boltzmann equation of the light gas is kinetically uncoupled from the kinetic equation of the heavy gas. The distribution function of the light gas used in Refs. 9 and 10 contains additional terms proportional to Kn, but the assumption $v \ll 1$ is used.

When f is given by Eq. (7), the integrals (3) and (4) have been computed in Ref. 1 for arbitrary values of v. In that reference the transfer of momentum and energy between species, involving integrals of $f_p \mathbf{B}$ and $f_p \Pi$ in \mathbf{c}_p space, were evaluated by expansion of $\mathbf{B}(f_0;\mathbf{u}_p)$ and $\Pi(f_0;\mathbf{u}_p)$ in powers of c_p/c around $\mathbf{B}(f_0,\mathbf{U}_p)$ and $\Pi(f_0;\mathbf{U}_p)$. However, since no integration of \mathbf{B} and Π are required here, these expansions need not be made, so that the parameter v appearing in the expression for \mathbf{B} and Π given in Ref. 1 must be substituted here by

$$\delta \equiv \frac{|\mathbf{u}_p - \mathbf{U}|}{(2kT/m)^{1/2}} . \tag{8}$$

[Notice that \mathbf{u}_p enters into the integrals (3) and (4) as a parameter, so that the substitution of \mathbf{u}_p by \mathbf{U}_p , and therefore of δ by v, does not change at all the form of these integrals.] Using a Lennard-Jones potential to describe the interaction between light and heavy components,

$$\phi(r) = 4\epsilon \left[\left[\frac{\sigma}{r} \right]^{12} - \left[\frac{\sigma}{r} \right]^6 \right], \qquad (9)$$

one obtains^{1,11}

$$\mathbf{B} = \mathbf{v}_B \, \frac{\mathbf{u}_p - \mathbf{U}}{\tau} \, , \tag{10}$$

$$\boldsymbol{\Pi} = \boldsymbol{\Pi}_1 + \boldsymbol{\Pi}_2 , \qquad (11a)$$

$$\Pi_1 = \frac{2kT}{\tau m_p} [\nu_B (\mathbf{I} - \mathbf{e}_{\delta} \mathbf{e}_{\delta}) + \nu_{\Pi 1} \mathbf{e}_{\delta} \mathbf{e}_{\delta}] , \qquad (11b)$$

$$\Pi_2 = \frac{2kT}{\tau m_p} \delta^2 G v_{\Pi 2} (\mathbf{I} - 3\mathbf{e}_{\delta} \mathbf{e}_{\delta}) , \qquad (11c)$$

where I is the unit tensor, \mathbf{e}_{δ} is the unit vector along the direction of $\mathbf{u}_{p} - \mathbf{U}$,

$$v_{B} = \frac{3}{2\delta\Omega^{(1,1)}(T^{*})} \int_{0}^{\infty} dx \, x^{4} \exp[-(x^{2} + \delta^{2})] Q^{(1)}(xT^{*1/2}) \left[\frac{\cosh\alpha}{\alpha} - \frac{\sinh\alpha}{\alpha^{2}}\right], \quad (12a)$$

$$v_{\Pi 2} = \frac{5}{4\delta\Omega^{(2,2)}(T^*)} \int_0^\infty dx \, x^5 \exp[-(x^2 + \delta^2)] Q^{(2)*}(xT^{*1/2}) \left[\frac{\sinh\alpha}{\alpha} - \frac{3\cosh\alpha}{\alpha^2} + \frac{3\sinh\alpha}{\alpha^3}\right], \quad (12b)$$

$$v_{\Pi 1} = v_B \left[1 + 2\delta^2 + \delta \frac{\partial \ln v_B}{\partial \delta} \right], \quad T^* = \frac{kTm_p}{\epsilon(m+m_p)}, \quad \alpha = 2x\delta, \quad \tau = \frac{3m_p}{16n\sigma^2 \Omega^{(1,1)*}(T^*)} \left[\frac{2}{\epsilon\pi mT^*} \right]^{1/2}, \quad (12c)$$

$$G = \frac{2\Omega^{(2,2)^*}(T^*)}{5\Omega^{(1,1)^*}(T^*)}, \quad \Omega^{(i,j)^*}(T^*) = \frac{2}{(j+1)!} \int_0^\infty dx \ x^{2j+3} \exp(-x^2) Q^{(i)^*}(xT^{*1/2}) \ . \tag{12d}$$

The dimensionless quantities $Q^{(i)}^*$ are related to the integrals defined by Eq. (5) through Eq. (8.2-7) of Ref. 12. On the other hand, the characteristic collision time τ between heavy and light components is related to the first approximation of the binary diffusion coefficient D via (e.g., Ref. 9)

$$\tau = \frac{m_p D}{kT} \frac{(n+n_p)}{n}$$

where n_p is the number density of the heavy gas.

Then, for arbitrary values of v, the Fokker-Planck equation which results from neglecting the self-collision term in the kinetic equation for the heavy component may be written as

$$\frac{\partial f_{p}}{\partial t} + \mathbf{u}_{p} \cdot \nabla f_{p}$$

$$= \tau^{-1} \nabla_{u_{p}} \cdot \left[(\mathbf{u}_{p} - \mathbf{U}) v_{B} f_{p} + \frac{kT}{m_{p}} \nabla_{u_{p}} \cdot f_{p} [v_{B} (\mathbf{I} - \mathbf{e}_{\delta} \mathbf{e}_{\delta}) + v_{\Pi I} \mathbf{e}_{\delta} \mathbf{e}_{\delta} + \delta^{2} G v_{\Pi 2} (\mathbf{I} - 3 \mathbf{e}_{\delta} \mathbf{e}_{\delta})] \right].$$
(13)

In the particular limit where $\delta \ll 1$, the ν coefficients approach unity and the above equation reduces to the standard form of the Fokker-Planck equation.^{7,8} In effect, the integral expressions (12) can be expanded to show that for $\delta \ll 1$ and $T^* \gg 1$, $\nu_B = 1 + \frac{2}{15}\delta^2 - \frac{4}{315}\delta^4 + \cdots$, $\nu_{\Pi 2} = 1 + \frac{2}{21}\delta^2 - \frac{4}{567}\delta^4 \cdots$, while for $\delta \ll 1$ and $T^* \ll 1$, $\nu_B = 1 + \frac{1}{15}\delta^2 - \frac{1}{126}\delta^4 \cdots$, $\nu_{\Pi 2} = 1 + \frac{1}{21}\delta^2 - \frac{5}{1134}\delta^4 \cdots$. It must be noticed that, in the limit $\nu \ll 1$, $\delta^2 = \nu^2 + O(M, \nu M^{1/2})$, so that the above expansions show the equivalence between Eq. (13) and the standard form of the Fokker-Planck equation for small slip velocity ($\nu \ll 1$). Fitting expressions for the ν coefficients covering the full range of values of δ in the high- and low-temperature limits are^{1,11}

$$\begin{split} \nu_{B} &= (1+0.4596\delta^{2})^{1/3}, \quad 1 \ll T^{*} \text{ or } 1 \ll \delta T^{*1/2} \\ \nu_{B} &= (1+0.4760\delta^{2})^{1/6}, \quad 1 \gg T^{*} \text{ or } 1 \gg \delta T^{*1/2} , \\ \nu_{\Pi 2} &= (1+0.312\delta^{2})^{1/3}, \quad 1 \ll T^{*} \text{ or } 1 \ll \delta T^{*1/2} \\ \nu_{\Pi 2} &= (1+0.322\delta^{2})^{1/6}, \quad 1 \ll T^{*} \text{ or } 1 \ll \delta T^{*1/2} . \end{split}$$
(14b)

More general interpolated formulas are given in Ref. 1 for arbitrary values of T^* and v. Although Eqs. (14a) and (14b) for the v coefficients are computed for a Lennard-Jones potential, expressions (12a)-(12c) are general (for elastic collisions) and can be particularized to any potential of interaction. The limit $T^* >> 1$ is relevant in most far-from-equilibrium physical situations (shock waves, impingement of a flow in a plate, etc.). The opposite limit is more uncommon; it can, however, be used to describe the final stages of the expansion of a jet into a vacuum. The Fokker-Planck equation given in Eq. (13) thus provides a broad description of the kinetics of far-from-equilibrium disparate-mass mixtures under conditions of considerable practical interest.

III. LANGEVIN EQUATION

In the stochastic treatment of the Brownian motion of particles or heavy molecules, the Fokker-Planck equation governing the velocity distribution function of these particles is obtained from the stochastic Langevin equation, applying the theory of Markov processes.^{2,3} In this section we shall proceed inversely: Given the Fokker-Planck equation (13), which has been derived from the kinetic Boltzmann equation, we shall obtain the Langevin equation governing the motion of the individual particles or heavy molecules whose distribution function satisfies that equation. More in general, we will derive the Langevin equation associated with arbitrary momentum and energy transfer functions $\mathbf{B}(f;\mathbf{u}_n)$ and $\Pi(f;\mathbf{u}_n)$ appearing in the Fokker-Planck collision operator (2), of which the right-hand side of Eq. (13) is a particular case [when the distribution function of the light gas is the Maxwellian (7)].

Let us write the equation of motion of the individual particles (Langevin equation) as

$$\frac{d\mathbf{u}_p}{dt} = \mathbf{F}(\mathbf{u}_p; \mathbf{r}, t) + \mathbf{A}(\mathbf{r}, t) , \qquad (15)$$

where the total acceleration of the particles due to collisions with the light molecules has been divided in two terms: a mean acceleration **F**, and a fluctuating or stochastic acceleration **A**, which by definition has zero mean. As in Eq. (13), the heavy component is assumed so diluted that heavy-heavy collisions can be neglected. In addition, we have assumed that there are no external forces [the inclusion of external forces in both Eq. (13) and Eq. (15) is a straightforward matter]. For an interval of time Δt long compared to the period of fluctuation of the acceleration **A** but short compared to the intervals during which the mean acceleration **F** changes appreciably, we can write Eq. (15) as

$$\Delta \mathbf{u}_p = \mathbf{F} \,\Delta t + \Gamma \,\,, \tag{16}$$

where

$$\Gamma(\mathbf{r},t;\Delta t) \equiv \int_{t}^{t+\Delta t} \mathbf{A}(\mathbf{r},t) dt \quad .$$
(17)

Using the theory of Markov processes, it can be shown (e.g., Ref. 3) that, neglecting terms $O(\Delta t)$ and $O(\Delta u_p^3/\Delta t)$, the Fokker-Planck equation governing the velocity distribution function of the heavy component is

$$\frac{\partial f_{p}}{\partial t} + \mathbf{u}_{p} \cdot \nabla f_{p} = -\nabla_{\mathbf{u}_{p}} \cdot \left[\frac{\langle \Delta \mathbf{u}_{p} \rangle}{\Delta t} f_{p} \right] \\ + \frac{1}{2} \nabla_{\mathbf{u}_{p}} : \left[\frac{\langle \Delta \mathbf{u}_{p} \Delta \mathbf{u}_{p} \rangle}{\Delta t} f_{p} \right], \quad (18)$$

where $\langle \Delta \mathbf{u}_p \rangle / \Delta t$ and $\langle \Delta \mathbf{u}_p \Delta \mathbf{u}_p \rangle / \Delta t$ are, respectively, the average time rate of change of $\Delta \mathbf{u}_p$ and $\Delta \mathbf{u}_p \Delta \mathbf{u}_p$. Since Γ has zero mean, from Eq. (16)

$$\langle \Delta \mathbf{u}_p \rangle = \mathbf{F} \, \Delta t \,, \tag{19a}$$

$$\langle \Delta \mathbf{u}_p \ \Delta \mathbf{u}_p \rangle = \mathbf{F} \mathbf{F} (\Delta t)^2 + \langle \Gamma \Gamma \rangle , \qquad (19b)$$

so that identifying the right-hand side of Eq. (18) with the Fokker-Planck collision operator (2) one obtains

$$\mathbf{F} = -\mathbf{B} , \qquad (20a)$$

$$\langle \Gamma \Gamma \rangle = \Delta t \Pi$$
, (20b)

where higher-order terms in Δt have been neglected in Eq. (20b). [Clearly, the relations between $\langle \Delta \mathbf{u}_p \rangle$ and $\langle \Delta \mathbf{u}_p \Delta \mathbf{u}_p \rangle$ and the collision integrals **B** and **II** could have been obtained directly from the definitions (3) and (4); see, e.g., Ref. 13.] Therefore, in the particular case in which the distribution function of the light gas is the Maxwellian (7), the Langevin Eq. (15) becomes

$$\frac{d\mathbf{u}_p}{dt} = -\frac{v_B}{\tau}(\mathbf{u}_p - \mathbf{U}) + \mathbf{A} , \qquad (21)$$

where $\langle \Gamma \Gamma \rangle = \Delta t \Pi$, with Π given by Eqs. (11). Further, it can be shown that, under the assumption that the interval of time Δt is long compared to the periods

of fluctuations of the stochastic acceleration **A** (in other words, if the number N of light molecules that collide with the particle or heavy molecule during Δt is a large number), the probability distribution function of Γ is the Gaussian

$$P(\Gamma) = \frac{\exp\left[\frac{\Gamma_i \Gamma_k}{2 \Delta t \Pi_{ik}}\right]}{(2\pi)^{3/2} (\Delta t \det \Pi)^{1/2}} , \qquad (22)$$

where repeated subscripts are summed. In effect, writing

$$m_p \Delta \mathbf{u}_p = \sum_{i=1}^{N} \mathbf{p}_i \quad , \tag{23}$$

where \mathbf{p}_i is the momentum interchanged by a single heavy-light collision, and assuming that the \mathbf{p}_i are independent random variables, for N large one can apply the central limit theorem (see, e.g., Ref. 14; we assume that the probability distribution functions of the variables \mathbf{p}_i are well behaved so that this theorem applies) to obtain the probability distribution function of $m_p \Delta \mathbf{u}_p$ as

$$P(m_{p} \Delta \mathbf{u}_{p}) = \frac{1}{(2\pi)^{3/2} \left[-\det \sum_{i} \langle \mathbf{p}_{i} \mathbf{p}_{i} \rangle\right]^{1/2}} \exp \left[-\frac{1}{2} \frac{\left[m_{p} \Delta u_{pk} - \sum_{i} \langle p_{ik} \rangle\right] \left[m_{p} \Delta u_{pl} - \sum_{i} \langle p_{il} \rangle\right]}{\sum_{i} \langle p_{ik} p_{il} \rangle}\right] + O(1/N) . \quad (24)$$

In this expression $\langle \mathbf{p}_i \rangle$ and $\langle \mathbf{p}_i \mathbf{p}_i \rangle$ are the first two moments of the probability function of \mathbf{p}_i . Thus $\sum_{i=1}^{N} \langle \mathbf{p}_i \rangle$ and $\sum_{i=1}^{N} \langle \mathbf{p}_i \mathbf{p}_i \rangle$ are, respectively, the average total momentum and the average total tensor **pp** delivered by the light molecules to a particle or heavy molecule with velocity \mathbf{u}_p during Δt . From Eqs. (3) and (4) we have

$$\sum_{i=1}^{N} \langle \mathbf{p}_i \rangle = -m_p \mathbf{B} \,\Delta t \quad , \tag{25}$$

$$\sum_{i=1}^{N} \langle \mathbf{p}_{i} \mathbf{p}_{i} \rangle = m_{p}^{2} \Pi \Delta t \quad .$$
(26)

Therefore, substituting Eqs. (16), (25), and (26) into Eq. (24), and making use of the fact that the probability distribution function of Γ has zero mean, one readily gets $\mathbf{F} = -\mathbf{B}$ [Eq. (20a)] and the Gaussian distribution (22) for $P(\Gamma)$ [with errors O(1/N)].

The Langevin equation derived above [Eq. (15) with Eqs. (20a) and (22)] contains previous results on the subject. For instance, when the distribution function of the light gas is the Maxwellian (7) and, in addition, the slip velocity parameter v is small, in first approximation in v we have $\mathbf{B} = (\mathbf{u}_p - \mathbf{U})/\tau$ and $\mathbf{\Pi} = (2kT/\tau m_p)\mathbf{I}$, so that

$$\frac{d\mathbf{u}_p}{dt} = -\frac{1}{\tau}(\mathbf{u}_p - \mathbf{U}) + \mathbf{A}(\mathbf{r}, t)$$
(27a)

and

$$P(\Gamma) = \frac{\exp\left[-\frac{\Gamma^2}{4kT\,\Delta t\,/m_p\tau}\right]}{(4\pi kT\,\Delta t\,/m_p\tau)^{3/2}}$$
(27b)

(Ref. 2, pp. 22-24; in this reference the host gas is at rest, U=0). In the case in which the first approximation of the Chapman-Enskog expansion of the velocity distribution function for the light gas is used and $v \ll 1$, $\mathbf{B} = (\mathbf{u}_p - \mathbf{U} - D\alpha_T \nabla \ln T)/\tau$ and $\Pi = (2kT/\tau m_p)\mathbf{I}$ (see Ref. 9; α_T is the thermal diffusion factor and it has been assumed that the heavy component is very dilute). Then

$$\frac{d\mathbf{u}_p}{dt} = -\frac{1}{\tau} (\mathbf{u}_p - \mathbf{U} - \alpha_T D \nabla \ln T) + \mathbf{A} , \qquad (28)$$

with the probability distribution function of Γ given by Eq. (27b). The Langevin equation and the distribution of Γ given in Ref. 5 for this same case of a "Chapman-Enskog host gas" and $v \ll 1$ contain additional terms proportional to the stress tensor of the light gas. However, these terms are O(vKn), where Kn is the Knudsen number of the light gas, so that they ought not to be taken into account in a first-order theory in both Kn and v. Finally, in the case considered in this note, where the distribution function of the light gas is Maxwellian but arbitrary slip velocities are allowed, the Langevin equation is given by Eq. (21), and the distribution of Γ is the Gaussian (22) with the tensor **II** given by Eqs. (11).

It is interesting to estimate the range of intervals of time Δt for which the stochastic difference Eq. (16) [with Eqs. (20a) and (22)] is valid in terms of the parameters of the problem. To this end we know that, in order for the Gaussian distribution (22) to hold, $(\Delta t)^{-1}$ must be small compared to the frequency ω_{lp} of heavy-light collisions $[\omega_{lp} \sim n(kT/m)^{1/2}\sigma_p^2]$, where σ_p is the diameter of the

particle or heavy molecule] and Δt must be small compared to the time in which **B** changes appreciably. Thus Δt must be small compared to (i) the time τ in which the properties of the heavy component change by collisions with the light molecules $[\tau \sim (M\omega_{lp})^{-1}]$, since on the order of M^{-1} light-heavy collisions are required to change \mathbf{u}_p by an amount of the same order as itself] and to (ii) a characteristic macroscopic time t_c [in terms of the lightgas Knudsen number, $t_c^{-1} \sim nKn(kT/m)^{1/2}\sigma^2$, where σ is the diameter of a light molecule]. Therefore,

$$1 \ll \Delta t \omega_{lp} \ll M^{-1} ,$$

$$1 \ll \Delta t \omega_{lp} \ll K n^{-1} \left[\frac{\sigma_p}{\sigma} \right]^2 .$$

In the case of a monatomic heavy molecule, the last condition becomes

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 $1 \ll \Delta t \omega_{lp} \ll K n^{-1} M^{-1/2}$,

since, based on the fact that the experimental viscosities of the noble gases are roughly mass independent (see, e.g., Ref. 10), $(\sigma / \sigma_p)^2 \sim M^{1/2}$. All the above conditions for Δt can, in principle, be fulfilled because, by hypothesis, $M \ll 1$, $Kn \ll 1$, and $\sigma / \sigma_p \ll 1$.

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