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Modification of Fick's Law

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In the presence of long-time memory effects, Fick's law must be modified by replacing the diffusion coefficient by a convolution over time of the velocity autocorrelation function. This leads to a convergent Chapman-Enskog expansion in a fluid provided the proper reference frame is taken in the presence of hydrodynamic motion.

After the discovery that the velocity autocorrelation of a particle in a fluid decays nonexponentially at long times,[1] it was recognized that the coefficients in the Chapman-Enskog expansion diverge.[2] The cause for the divergence of these coefficients, called the Burnett coefficients, is that the distribution for the positions of particles (measured relative to their root-mean-square displacement) as a function of time, does not approach its long-time limit as a Gaussian. The long persistent correlations lead to the non-Gaussian approach and also necessarily introduce nonlocality in time (memory) into the description of transport theory.

Fick's law, consistent with a Markovian random process, implies that the distribution function is Gaussian for all times. The actual non-Markovian nature of the process is here shown by molecular-dynamics simulation to correspond to a random walk, where after each step the particle waits for a time as sampled from a waiting-time distribution[3] before making the next move. The major physical consequence of the validity of this stochastic process is that the higher-order correlations decay sufficiently fast so they can be expressed, as they approach their long-time limit, in terms of the lowest-order one, namely, the velocity autocorrelation function, or, equivalently, the waiting-time distribution.

Fick's law is valid only in the infinite-time limit and only if the distribution is Gaussian in that limit. The latter requirement is by no means assured since in many cases the diffusion coefficient is zero and in at least one known nontrivial case, the two-dimensional fluid,[1] divergent. If we restrict discussion for the present to a well-defined diffusion coefficient, D, that is, an integrable velocity autocorrelation function, the first Burnett coefficient, B, is defined[4] through

$$\frac{\partial f(x,t)}{\partial t}=D\frac{\partial^2 f(x,t)}{\partial x^2}+B\frac{\partial^4 f(x,t)}{\partial x^4}+\dots, \qquad (1)$$

where $f(x,t)$ is the distribution function along the x direction. The coefficients D, B, and further ones can be expressed in terms of infinite-time limits of the rate of growth of successive cumulants of the distribution function.[5] Depending on the exponent of the power-law decay of the velocity autocorrelation function, either B or higher ones can be shown to diverge.[2] The power-law decay at long times, resulting from the long-term correlations, leads to a distribution that is far from Gaussian at finite but long time, as shown in Fig. 1.

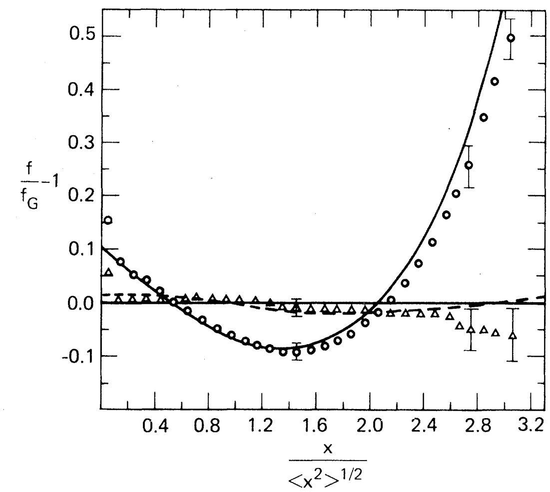

FIG. 1. The distribution for the overlapping-disk Lorentz gas relative to a Gaussian distribution of the same root-mean-square width, $\langle x^2\rangle^{1/2}$, as a function of $x/\langle x^2\rangle^{1/2}$ after 100 mean collision times at a density NR^2/A of 0.20. The molecular-dynamics results are given by the circles and the solid line is the solution of Eq. (2). The difference between these two results is given by the triangles and compared to the correction obtained by treating the B term (replaced numerically by D_4) as a perturbation in Eq. (1). The vertical lines indicate estimated uncertainties.

The physical causes of the memory effects differ in different situations. In fluids persistence has been shown to be due to slowly decaying hydrodynamic fields.[1] In the Lorentz gas, where a particle moves through stationary scatterers, the hydrodynamic effects are absent, and the slow decay is related to the higher-than-random probability of the particle returning to its origin.[6] If we restrict discussion for the moment to the easier to deal with Lorentz gas, the simplest way to modify Fick's law to take memory into account is

$$\frac{\partial f(x,t)}{\partial t}=\int_0^t dt'\varphi_2(t-t')\frac{\partial^2 f(x,t')}{\partial x^2}, \tag{2}$$

where the kernel, φ_2, relates the distribution at time t' to the rate of change of the distribution at time t. The integration over t' sums all the past effects on the distribution up to the present time, t. If φ_2 is short range, that is, there are no long-term memory effects, then the above equation reduces to Fick's law. φ_2 itself is determined by the requirement that the second moment corresponding to the physical situation be reproduced.

Thus,

$$\frac{d\langle x^2(t)\rangle}{dt}=2\int_0^t \varphi_2(t')\,dt', \tag{3}$$

where $\langle x^2(t)\rangle=\int_{-\infty}^{\infty}x^2 f(x,t)dx$, and $\varphi_2(t)$ is identified as the velocity autocorrelation function. Equation (3) is obtained by multiplying Eq. (2) by x^2 and integrating over all space. The right-hand side is integrated by parts.

Given the asymptotic behavior of the velocity autocorrelation function and the value of the diffusion coefficient, Eq. (2) can be solved at long times by expanding the distribution function about the Gaussian limit. The resulting distribution is plotted in Fig. 1 in a way to show the large deviation from Gaussian behavior at long times. Thus, if the distribution is Gaussian or Fick's law applies, the results will lie on the horizontal axis. The deviations of the molecular-dynamics results from Eq. (2), as seen in Fig. 1, are small and are well accounted for by the higher-order correction to Eq. (2),

$$\frac{\partial f(x,t)}{\partial t}=\int_0^t dt'\varphi_2(t-t')\,\frac{\partial^2 f(x,t')}{\partial x^2}+\int_0^t dt'\,\varphi_4(t-t')\,\frac{\partial^4 f(x,t')}{\partial x^4}, \tag{4}$$

where φ_4 is a higher-order memory function, determined by taking the fourth moment of Eq. (4) and integrating over space:

$$\varphi_4(t)=\frac{1}{4\,!}\frac{d^2}{dt^2}\langle x^4(t)\rangle-\frac{d}{dt}\int_0^t dt'\,D(t-t')D(t'), \tag{5}$$

where $D(t)=\int_0^t dt'\,\varphi_2(t')$.

If there are no long-term correlations, the last term in Eq. (5) can be written as a product, and the expression reduces to the conventional Burnett correlation function. For the two-dimensional Lorentz gas the conventional Burnett coefficient diverges,[6] while in the new formulation, the integral of Eq. (5) leads to convergent coefficients, $D_4=\int_0^\infty dt\,\varphi_4(t)$, as given in Table I. If these D_4 coefficients are used to correct the distribution function, the small deviations from Eq. (2) are accounted for, as shown in Fig. 1. As an approximation sufficiently precise for present purposes, the correction due to the D_4 term was calculated as a perturbation about a Gaussian distribution rather than the actual one resulting from the solution of Eq. (2).

It seems physically plausible that the four-point correlation function involved in φ_4 decays at large times sufficiently fast that it can be ex-

TABLE I. The diffusion coefficient, D, and the newly defined Burnett coefficient, D_4, for the overlapping-disk Lorentz gas.

$(N/A)R^2$ [a]	D/D_E [b]	$D_4\Gamma/D_E^2$ [c]	$D_4/D\lambda^2$ [d]
0.318	0.04	0.07	0.7_4
0.200	0.38	0.26	0.26_4
0.143	0.52	0.30	0.22_3
0.050	0.81	0.50	0.23_2
0.020	0.92	0.57	0.23_2

[a] The density of disk scatterers of radius R.
[b] $D_E = 3v^2/8\Gamma$ is the Enskog value of the diffusion coefficient, where v^2 is the square of the particle velocity and Γ is the collision rate. The uncertainty in the results is ± 0.02.
[c] The uncertainly in the results in ± 0.04.
[d] λ is the mean free path. The error in the last figure is indicated by the subscript.

pressed in terms of the two-point correlation function, φ_2. A successful test of this hypothesis is given in Fig. 2, where it is shown that φ_4 decays at long times with the same power law as φ_2, and the proportionality constant is given by $\varphi_4(t) = D_4\varphi_2(t)/D$. If the same argument can be made about all the higher coefficients, as is to be expected, the Chapman-Enskog expansion is replaced by

$$\frac{\partial f(x,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{D_{2n}}{D}\int_0^t dt'\, \varphi_2(t-t')\frac{\partial^{2n} f(x,t')}{\partial x^{2n}}. \quad (6)$$

The stochastic process corresponding to Eq. (6) involves a random walk where between each step the particle is delayed for a time as sampled from a waiting distribution.[7] The delay can be interpreted physically as the time required for the particle to escape from the various nearly trapping regions. The waiting-time distribution, $\psi(t)$, is uniquely determined by the requirement that the second moment of the distribution is reproduced for all time. This leads to

$$\psi(t) = (2/\langle l^2\rangle)\int_0^t dt' D(t-t')[\delta(t') - \psi(t')], \quad (7)$$

where $\langle l^2\rangle$ is the second moment of the step-size distribution. The solution of Eq. (7) leads to negative, and thus physically unacceptable, values for the waiting distribution at intermediate times.[7] It is only at long times that the higher-order correlations are decomposable, the waiting distribution is positive, and Eq. (2) makes sense. In this time regime Eq. (7) leads to divergent Burnett coefficients for the walk. Furthermore, the stochastic model yields expressions for D_{2n} in terms

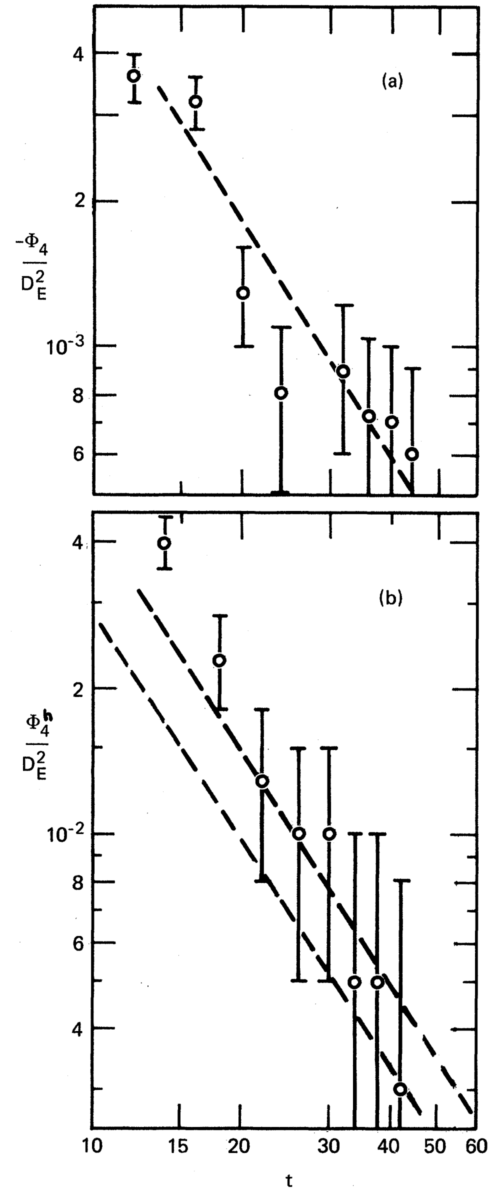

FIG. 2. (a) The Burnett correlation function, φ_4, normalized by D_E^2, for the overlapping-disk Lorentz gas at NR^2/A of 0.20 as a function of mean collision time. The molecular-dynamics results (circles) are compared to the prediction, $\varphi_4(t) = D_4\varphi_2(t)/D$, given by the dashed line. (b) As (a) except for a fluid of spheres (Ref. 8) at $V/V_0 = 3$, and the transformation to φ_{4h}. The upper and lower dashed lines reflect the uncertainty in the values of D_{4h}, D_{2h}, and D'.

of the $(2n)$ moments of the step-size distribution: $D_{2n}/D = 2\langle l^{2n}\rangle/\langle l^2\rangle(2n)!$. The values of D_4 found are consistent with a Gaussian step-size distribution whose second moment, $\langle l^2\rangle$, is the square of the mean free path, λ^2. Thus, a quantitative theory for the Burnett coefficient and the tail of the higher-order correlation functions has been established, for example, $D_4/D = \lambda^2/4$ (see Table I).

The integral of Eq. (5) for three-dimensional fluids, D_4, was found to be divergent. This is because, in a fluid, there are additional long-persisting correlations connected with hydrodynamic flows, particularly the vortex flow, which affect the distribution at long times. In view of this a speculative derivation can be made: In the limit of small fluid velocity, the vorticity obeys a diffusion type of equation, with the diffusion constant replaced by the kinematic viscosity, ν. The combined effect of diffusion and vortex flow leads in the long-time limit to a Gaussian distribution,[1] $p(x,t)$, in a laboratory coordinate system, proportional to $\exp(-x^2/4Dt)\exp(-x^2/4\nu t)$, or a Gaussian with an effective diffusion constant $D' = D\nu/(D+\nu)$. In the framework of relative positions of a particle, by which diffusion coefficients are measured, the motion of the coordinate system due to the hydrodynamic vortex flow must be removed by

$$f(x,t) = \int_{-\infty}^{\infty} dx' p(x-x',t) h(x',t),$$

where $h(x',t)$ is the distribution in the vortex-moving coordinate system and $f(x,t)$ is the distribution resulting from diffusion, equivalent to the one used in the Lorentz gas, but including also the effect of the vortex mode on the relative displacements of particles. D_4 formed from $f(x,t)$ diverges[8] in the fluid because of the vortex-motion–displaced coordinate system and hence D_{4h} must be formed from $h(x,t)$. The second moments of the two distributions differ: $\langle x^2\rangle_h = \langle x^2\rangle - 2D't$, leading to an effective diffusion coefficient in the vortex moving coordinate system of $D_h = D - D'$ and a Burnett correlation function $\varphi_{4h}(t) = \varphi_4(t) - D't\varphi_2(t)$. Subtraction of these terms in the second and fourth moments leads to convergent Burnett coefficients which have the expected asymptotic behavior, that is, $\varphi_{4h}(t) = D_{4h}\varphi_{2h}(t)/D_h$, as shown in Fig. 2, where D_{4h} is the time integral of φ_{4h}. Thus, once the proper coordinate system is used in a fluid, the highest-order correlation function can again be shown to decay fast enough so that, asymptotically, only the second-order correlation function dominates. The distribution can then be obtained again from Eq. (6), which, for a slowly decaying autocorrelation function, replaces the previously divergent Chapman-Enskog expansion.

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