

Comment on "Kinetic theory of single-particle motion in a fluid"

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The reason Mehaffey and Cukier did not obtain the hydrodynamic Stokes-Einstein relation for the diffusion coefficient of a large particle from kinetic theory is that they did not carry their calculation far enough. When the terms in the repeated-ring sum are evaluated more completely and then summed, the proper hydrodynamic Stokes-Einstein form is obtained. This procedure does not affect Mehaffey and Cukier's results for the long time behavior of the velocity-autocorrelation function. Some inconsistent approximations in Mehaffey and Cukier's ring sum are also discussed here.

In a recent Physical Review Letter and article,¹ Mehaffey and Cukier consider the Brownian motion of a tagged sphere of arbitrary size immersed in a gas of hard spheres. In particular, these authors compute the diffusion coefficient D^B of the tagged particle taking into account the so-called ring and repeated-ring events, which are certain correlated sequences of binary collisions in the system. Among the results reported by Mehaffey and Cukier are the following:

(i) In what Mehaffey and Cukier call the ring approximation, the diffusion coefficient has the form

$$D^B = D_E^B (1 - a)^{-1}, \quad (1)$$

where D_E^B is the diffusion coefficient as given by the Enskog theory for hard spheres, in which rings and repeated rings are not taken into account. The quantity a depends on the gas density, the radius and mass of the gas particles, and the radius and mass of the tagged particle. As the radius of the tagged particle increases, a also increases, and D^B , given by Eq. (1), passes through an infinite value and then becomes negative for sufficiently large values of the tagged particle radius. This unphysical behavior of D^B , given by Eq. (1), is then used to motivate the inclusion of the repeated-ring events in calculating D^B .

(ii) If the repeated-ring events are also taken into account, and if the radius of the tagged sphere is much larger than both the radius and the mean free path of the gas particles, then D^B has a Stokes-Einstein form

$$D^B = k_B T / 5\pi\eta_E R_B. \quad (2)$$

Here k_B is Boltzmann's constant, T is the temperature of the gas, η_E is the Enskog theory value for the shear viscosity of the gas, and R_B is the radius of the tagged sphere. Equation (2) is surprising

since one would have expected from purely hydrodynamic arguments that if the tagged sphere is very large, and if the gas molecules make specular collisions with the tagged sphere, then D^B should

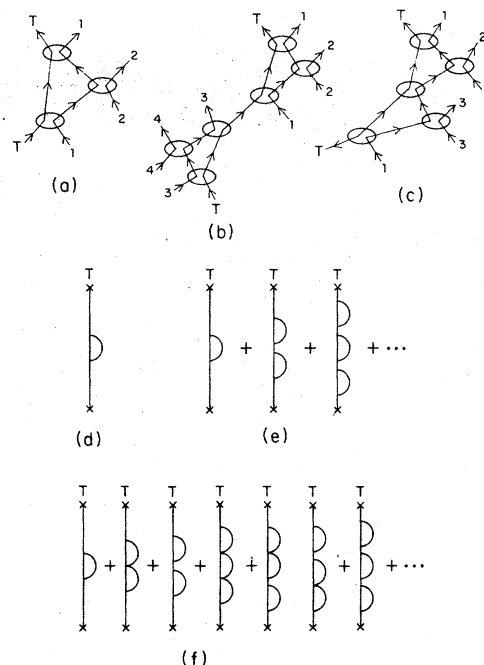


FIG. 1. Ring, iterated-ring, and repeated-ring events. (a) Represents a typical three-body ring event. The particle labeled T is the tagged particle; particles 1 and 2 are gas particles. (b) Typical iterated-or disconnected-ring event. (c) Typical repeated-ring event. (d) Schematic representation of the sum of all ring events, where we use the representation of de Schepper *et al.* in Ref. 2. (e) Schematic representation of the sum of the ring and iterated-ring events. (f) Schematic representation of the sum of the ring, repeated-ring, and iterated-ring terms.

have exactly the Stokes-Einstein form

$$D^B = k_B T / 4\pi\eta_B R_B \quad (3)$$

with a 4 in the denominator and not a 5.

With regard to what Mehaffey and Cukier call the ring approximation to D^B given by Eq. (1), we point out that Eq. (1) is not based on the ring events alone but rather on the ring events plus a set of events called "iterated" or "disconnected" ring events. These events have been mentioned before in the literature,² and the difference between the ring, iterated ring, and repeated-ring events is illustrated in Fig. 1. In calculations of time-correlation functions such as that carried out by Mehaffey and Cukier it is inconsistent to include the contributions from the iterated-ring events without simultaneously including the contributions from the repeated-ring events since both sets of terms are of the same order of magnitude in the relevant physical parameters. In fact, in calculations of the long time tails of time-correlation functions, the iterated-ring and repeated-ring contributions exactly cancel each other.²

To be more specific, Mehaffey and Cukier derive an expression for D^B in what they call the ring approximation which has the form¹

$$D^B = \lim_{z \rightarrow i0^+} \frac{ik_B T}{m_B} [z + i\lambda_E - R_1(z)]^{-1}. \quad (4)$$

Here, z is a Laplace transform variable, k_B is Boltzmann's constant, T the absolute temperature, m_B the mass of the tagged particle, λ_E is a quantity which is related to the Enskog theory diffusion coefficient D_E^B by $D_E^B = (k_B T / m_B) \lambda_E^{-1}$, and $R_1(z)$ is what Mehaffey and Cukier call the ring memory function. Instead of representing the sum of the ring events as Mehaffey and Cukier claim, Eq. (4) represents contributions to the diffusion coefficient from three types of terms: (a) the Enskog theory term, (b) the ring term, and (c) the iterated-ring terms. The Enskog term and the ring term are obtained from Eq. (4) by expanding the quantity in the square brackets in powers of $R_1(z)$, and keeping only the zeroth and first powers of $R_1(z)$, respectively. The second and higher powers of $R_1(z)$ in this expansion correspond to the contribution to D^B from iterated-ring events, and it is inconsistent to include these terms in the calculation of D^B without including the repeated-ring events also. Thus a calculation of D^B where only the Enskog terms and the ring terms are taken into account leads to³

$$D_R^B = D_E^B + \lim_{z \rightarrow i0^+} \frac{ik_B T}{m_B} \frac{1}{z + i\lambda_E} R_1(z) \frac{1}{z + i\lambda_E}. \quad (5)$$

Equation (5) is a useful expression for D^B only when the radius of the tagged sphere, R_B , is smaller than the mean free path l of a gas molecule. For small values of R_B , contributions from other types of events such as the iterated-ring and repeated-ring events can be neglected, but these events must be taken into account when R_B is large.

To obtain an expression for D^B that can be used when R_B/l is very large, Mehaffey and Cukier sum the ring, iterated-ring, and repeated-ring terms, illustrated in Fig. 1(f). The main features of their evaluation of this sum are reported in their Appendix C. There, these authors take into account the hydrodynamic shear-mode contribution to the terms in the repeated-ring sum, they then limit themselves to the lowest-order term in the wave-number expansion of the shear-mode eigenfunctions, and they evaluate the repeated-ring sum as an ordinary geometric series. The approximations made in their analysis of the repeated-ring sum are sufficient to allow Mehaffey and Cukier to obtain the correct long-time behavior of the velocity-autocorrelation function, although the same result can be obtained from the ring terms alone.³ However, Mehaffey and Cukier do not carry out their evaluation of the repeated-ring contribution to the diffusion coefficient far enough, and as a result they do not obtain the proper hydrodynamic Stokes-Einstein relation, Eq. (3).

A calculation along the same lines by Dorfman, van Beijeren, and McClure⁴ for a closely related but somewhat simpler problem shows that when the gas molecules make specular collisions with the tagged sphere, the first-order wave-number corrections to the shear-mode eigenfunction must also be taken into account. Moreover, the series that must be summed is more complicated than the geometric series considered by Mehaffey and Cukier. Instead, the series must be formulated as a geometric series in powers of a matrix. When this matrix series is summed, and the diffusion coefficient of the tagged particle is computed, the proper Stokes-Einstein relation is obtained.

We note in passing that for the case considered by Mehaffey and Cukier, it remains an open problem to show that the various ring events they considered are the only important events that contribute to D^B when R_B is large. For the case discussed in Ref. 4, namely, the flow of a dilute gas around a large heavy sphere or cylinder, this problem does not arise since one can show that these are the only events that must be considered.

¹J. R. Mehaffey and R. J. Cukier, Phys. Rev. Lett. 38, 1039 (1977); Phys. Rev. A 17, 1181 (1978).

²J. R. Dorfman and E. G. D. Cohen, Phys. Rev. A 6, 776 (1972); 12, 292 (1975); I. M. de Schepper and M. H. Ernst, Physica A 87, 35 (1977); I. M. de Schepper, H. van Beijeren, and M. H. Ernst, Physica A 75, 1 (1974).

³It is worth mentioning that the correct ring approxima-

tion to the long-time behavior of the velocity-auto-correlation function does not lead to Eq. (3.33) in Ref. 1, but rather to Eq. (3.44). Equation (3.33) is the result one obtains by including the iterated-ring but not the repeated-ring terms.

⁴J. R. Dorfman, H. van Beijeren, and C. F. McClure, Arch. Mech. Stosow 28, 33 (1976), and (unpublished).