Velocity Correlation Functions in Two and Three Dimensions

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Velocity correlation functions $\rho(t)$ in hard-disk and hard-sphere fluids are discussed on the basis of the kinetic theory of gases. It is found in *d* dimensions that $\rho(t) \sim \alpha (t/t_0)^{-d/2}$ with $\alpha = O(\rho^{d-1}) (t_0)^{-1}$ collision frequency; ρ = reduced density). Expressions for α are given that seem correct at low densities and a good approximation at least up to half the close-packing density. The agreement with Alder and Wainwright's computer results is good.

The revived interest in the long-time behavior of time correlation functions has been stimulated by recent computer calculations by Alder and Wainwright.¹ They determined the long-time behavior of the velocity autocorrelation function for a hard-disk and hard-sphere fluid over a wide range of densities. Their main results are the following: (a) The function

$$\rho_D^{(d)}(t) = \langle v_x(0) v_x(t) \rangle / \langle v_x^2 \rangle \sim \alpha_D^{(d)}(t/t_0)^{-d/2}$$
(1)

for 30 $t_0 \ge t \gg t_0$. Here $v_x(t)$ is the *x* component of the velocity of a particle at time *t*, t_0 is the mean free time between two successive collisions (or the inverse collision frequency in the gas), angular brackets denote an average over an ensemble of systems taken in the thermodynamic limit, and *d* is the number of dimensions (d = 2, 3). (b) Expression (1) describes $\rho_D^{(2)}(t)$ over the entire range of measured densities and times within the experimental error. (c) The velocity distribution around a particle is not irrotational but shows a vortex pattern.

We investigated these results from the point of view of the kinetic theory of gases. The starting point is an expansion² of $\rho_D^{(d)}(\epsilon)$, the Laplace transform of $\rho_D^{(d)}(t)$, in powers of the number density *n*:

$$\rho_D^{(d)}(\epsilon) = \rho_{D1}^{(d)}(\epsilon) + n\rho_{D2}^{(d)}(\epsilon) + \cdots$$
(2)

In Eq. (2) only terms relevant for a discussion of the long-time behavior of $\rho_D^{(d)}$ are considered. $\rho_{D1}^{(d)}$ is the contribution to $\rho_D^{(d)}$ from sequences of uncorrelated binary collisions and can be obtained from the Boltzmann equation. This term leads to an exponential behavior $\rho_D^{(d)}(t) \sim \exp(-t/t_0)$. For $t > t_0$ the long-time behavior of $\rho_D^{(d)}$ is determined by $\rho_{D2}^{(d)}$. This term results from a summation of sequences of correlated binary collisions (characterized by ring diagrams), which are -in each order of the density - the most divergent terms in a density expansion of $\rho_D^{(d)}(\epsilon)$. It is these same collision sequences that lead to divergences in a computation of the transport coefficients.³

Recently Pomeau⁴ has concluded from a qualitative analysis of $\rho_{D2}^{(d)}$ that although this term exists in the limit $\epsilon \rightarrow 0$ in three dimensions, it diverges in this limit as $ln\epsilon$, in two dimensions. We have investigated $\rho_{D_2}^{(d)}(\epsilon)$ in the same limit along a similar line quantitatively and find the following: (a) In both two and three dimensions the ring resummation leads to a $\rho_{D2}^{(d)}$ with a time dependence of the form found by Alder and Wainwright⁵ and in two dimensions in good quantitative agreement with their computer results over the entire density range considered. (b) A similar behavior can be expected for the velocity correlation functions $\rho_{\eta}^{(d)}$ and $\rho_{\lambda}^{(d)}$ that determine the kinetic parts of the coefficients of viscosity and thermal conductivity, respectively. These conclusions were arrived at in the following way.

(a) The expression for $\rho_{D2}^{(d)}(\epsilon)$ can be evaluated in terms of the eigenfunctions and eigenvalues of the linear inhomogeneous Boltzmann operators for a gas of hard disks (or hard spheres) and for the corresponding Lorentz gas. For small ϵ the behavior of $\rho_{D2}^{(d)}(\epsilon)$ is determined by those combinations of the hydrodynamical modes of the inhomogeneous linearized Boltzmann operators for the Lorentz gas and for the real gas that lead in the expression for $\rho_{D2}^{(d)}(\epsilon)$ to integrals of the form

$$\int d^{d}k(\boldsymbol{\epsilon}+\boldsymbol{\alpha}k^{2})^{-1},$$

for small k, where α is independent of k and ϵ . On inverting the Laplace transform $\rho_{D2}^{(d)}(\epsilon)$, these integrals lead to the $t^{-d/2}$ behavior for $\rho_D^{(d)}(t)$ for $t \gg t_0$. While a Lorentz gas only has a diffusion mode, a real gas has a heat mode, two sound modes, and d-1 viscous modes. These hydrodynamical modes can be obtained for small k by a perturbation calculation from the zero eigenvalue modes of the respective linearized Boltzmann collision operators. To lowest order in n and to order k^2 , the perturbed eigenvalues are, for the Lorentz gas

$$\omega_{D} = k^{2} D_{0} (d = 2, 3),$$

$$\omega_{V}^{(i)} = k^{2} \eta_{0} / nm \ (i = 1, d-1);$$

$$\omega_{H} = k^{2} \lambda_{0} / 2nk_{B} \text{ for } d = 2;$$

$$\omega_{H} = 2k^{2} \lambda_{0} / 5nk_{B} \text{ for } d = 3;$$

$$\omega_{s}^{\pm} = \pm ikc + k^{2} (\eta_{0} / nm + \lambda_{0} / 2nk_{B}) \text{ for } d = 2;$$

$$\omega_{s}^{\pm} = \pm ikc + k^{2} (2\eta_{0} / 3nm + 2\lambda_{0} / 15nk_{B}) \text{ for } d = 3.$$

Here c is the adiabatic velocity of sound in an ideal gas, $k_{\rm B}$ is Boltzmann's constant, and η_0 , λ_0 , and D_0 are the coefficients of viscosity, thermal conductivity, and self-diffusion, respectively, of a dilute gas. Using these eigenvalues and the corresponding eigenfunctions, one finds that the long-time behavior of $\rho_D^{(a)}(t)$ is given by (1) with

$$\alpha_{D}^{(d)} = \alpha_{D,0}^{(d)} \rho^{d-1} + \alpha_{D,1}^{(d)} \rho^{d} + \cdots, \qquad (3)$$

where $\rho = na^d$; *a* is the diameter of a particle. Here

$$\alpha_{D,0}^{(2)} = \left[8\pi n\rho (D_0 + \eta_0/nm) t_0\right]^{-1} = \frac{1}{4}, \qquad (3a)$$

$$\alpha_{D,0}^{(3)} = \left[\pi \rho^{4/3} (D_0 + \eta_0 / nm) t_0\right]^{-3/2} / 12n$$
$$= (64/11)^{3/2} / 12$$
(3b)

if the first Enskog approximation to the coefficients of self-diffusion and viscosity of a dilute gas are used.

One contribution to $\alpha_{D1}^{(d)}$ and the higher terms in (3) comes from collisional transfer of momentum and, in fact, equals the change in $\alpha_D^{(d)}$ that would be obtained if the Enskog collisional transfer contribution to η due to binary collisions alone is added to η_0 in $\alpha_{D,0}^{(d)}$.⁶ In order to determine $\alpha_D^{(d)}$ further, an analysis must be made of the contributions of the dynamical events between four, five, \cdots particles, that are contained in the higher-order terms in (2). The contributions of a subclass of all these events has been evaluated and leads, together with the collisional transfer contribution mentioned before, to an expression for $\alpha_D^{(d)}$ that can be obtained by replacing η_0 and D_0 in $\alpha_{D,0}^{(d)}$ by their full values η_E and D_E , respectively, as given by the Enskog theory, viz., to

$$\alpha_{D,E}^{(2)} = [8\pi n (D_{E} + \eta_{E}/nm)t_{0}]^{-1};$$

$$\alpha_{D,E}^{(3)} = [\pi (D_{E} + \eta_{E}/nm)t_{0}]^{-3/2}/12n.$$
(4)

 $\alpha_{D,E}^{(d)}$ for d=2,3 are plotted in Fig. 1; $\alpha_{D,E}^{(2)}$ is



FIG. 1. $\alpha_{D,E}^{(d)}/(V_0/V)^{d-2}$ plotted as a function of the reduced volume V_0/V , where V_0 is the volume at close packing, for d=2 and d=3. The crosses indicate the computer results of Alder and Wainwright for d=2.

found to be in very good agreement with the available computer data for a fluid of hard disks.

We have not evaluated other dynamical events that contribute to $\alpha_D^{(d)}$. However, it is not unreasonable to suppose that their contributions might be small compared with $\alpha_{D,E}^{(d)}$. This is in view of the fact that in a number of cases (e.g., the computation of the transport coefficients) the Enskog contributions - which incorporate excluded-volume effects-are known to be dominant among the contributions of all dynamical events.⁷⁻⁹ On the basis of hydrodynamical arguments Alder and Wainwright¹ and also Ernst, Hauge, and van Leeuwen¹⁰ have derived expressions for $\alpha_{D}^{(d)}$ identical to those given in (4) except that $D_{\rm E}$ and $\eta_{\rm F}$ are replaced by the actual transport coefficients, D and η , respectively.¹¹ The two expressions for $\alpha_D^{(d)}$ give virtually indistinguishable results for d = 2 for all densities considered by Alder and Wainwright and are very close for d=3for densities up to about half the density at close packing.

(b) A behavior similar to that of $\rho_D^{(d)}$ has been found for the velocity correlation functions $\rho_{\eta}^{(d)}$ and $\rho_{\lambda}^{(d)}$ that determine the kinetic part of the viscosity and thermal conductivity coefficients and which can be obtained from (1) by replacing v_x by

$$\sum_{i=1}^{N} v_{iz} v_{iy}$$

and by

$$\sum_{i=1}^{N} v_{ix}(mv_{i}^{2}/2k_{\rm B}T - h_{0}^{(d)}/k_{\rm B}T),$$

respectively, where the summation includes all the N particles in the gas, T is the absolute temperature, m the mass of a particle, and $h_0^{(d)}$ the enthalpy per particle in an ideal gas in d dimensions $(h_0^{(2)} = 2k_{\rm B}T, h_0^{(3)} = 5k_{\rm B}T/2)$.

One finds

$$\rho_{\eta}^{(d)} = \left[\alpha_{\eta,0}^{(d)}\rho^{d-1} + \cdots\right](t/t_0)^{-d/2},\tag{5}$$

where we have calculated

$$\alpha_{\eta,0}^{(2)} = \left[(\eta_0/nm)^{-1} + (\eta_0/nm + \lambda_0/2nk_B)^{-1} \right] / 32\pi\rho nt_0 = \frac{1}{6}$$

and

$$\alpha_{n,0}^{(3)} = \left[7(2\eta_0/nm)^{-3/2} + (4\eta_0/3nm + 4\lambda_0/15nk_B)^{-3/2}\right]/120n\rho^2(\pi t_0)^{3/2} = 1.05$$
(5a)

and similarly for $\rho_{\lambda}^{(d)}$

$$\alpha_{\lambda,0}^{(2)} = [\eta_0/nm + \lambda_0/2nk_B]^{-1}/4\pi\rho nt_0 = \frac{1}{3}$$

and

$$\alpha_{\lambda,0}^{(3)} = \left[(\eta_0 / nm + 2\lambda_0 / 5nk_B)^{-3/2} + (4\lambda_0 / 15nk_B + 4\eta_0 / 3nm)^{-3/2} / 3 \right] / 12n\rho^2 (\pi t_0)^{3/2} = 1.3.$$
(5b)

This long-time behavior, (1), (5), of $\rho_D^{(d)}$, $\rho_n^{(d)}$, and $\rho_{\lambda}^{(d)}$ does not seem to be restricted to hard disks and hard spheres, but to hold for more general interparticle potentials as well, as the present calculations can be generalized immediately to more general potentials. The good quantitative agreement of the theory with experiment and the fact that the ring diagrams are responsible for the long-time behavior of $\rho_{D}^{(d)}(t)$ observed in the Alder and Wainwright experiments suggest that it is these diagrams that incorporate the correlated motions of the particles that are responsible for the vortex velocity pattern seen by Alder and Wainwright. Thus this vortex pattern may not be restricted to harddisk or hard-sphere fluids but may be found in a more general class of fluids as well.¹²

The long-time behavior of the $\rho(t)$ discussed here on the basis of Eq. (2) may only be correct up to times $t \approx 30t_0$, relevant in a typical machine calculation of Alder and Wainwright. To determine their behavior on a longer time scale and also to settle in two dimensions the question of the existence of the transport coefficients^{1,4,13} -which are related to time integrals of $\rho(t)$ -other classes of dynamical events have to be taken into account than considered here.

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¹B. J. Alder and T. E. Wainwright, Phys. Rev. Lett. <u>18</u>, 988 (1969), and J. Phys. Soc. Jap., Suppl. <u>26</u>, 267 (1968), and Phys. Rev. A <u>1</u>, 18 (1970); B. J. Alder, D. M. Gass, and T. E. Wainwright, to be published.

²K. Kawasaki and I. Oppenheim, Phys. Rev. <u>136</u>, A1519 (1964); J. R. Dorfman, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Gordon and Breach, New York, 1967), Vol. 9C, p. 443.

³Cf. J. R. Dorfman and E. G. D. Cohen, J. Math. Phys. <u>8</u>, 282 (1967); E. A. Frieman and R. Goldman, J. Math. Phys. 8, 1410 (1967).

⁴Y. Pomeau, Phys. Lett. <u>27A</u>, 601 (1968), and thesis, University of Orsay, 1969 (unpublished), and to be published.

⁵For d=3, a similar qualitative behavior has been noticed by R. Goldman, Phys. Rev. Lett. <u>17</u>, 910 (1966).

⁶I.e., η_0 is replaced by $\eta_0 (1 + \pi \rho/4)^2 + \rho^2 (\pi m k_B T)^{1/2}/4a$ for d = 2 and by $\eta_0 (1 + 4\pi \rho/15)^2 + 4\rho^2 (\pi m k_B T)^{1/2}/15a^2$ for d = 3.

⁷J. R. Dorfman and E. G. D. Cohen, Phys. Lett. <u>16</u>, 124 (1965).

⁸B. J. Alder, D. M. Gass, and T. E. Wainwright, to be published; J. V. Sengers, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Gordon and Breach, New York, 1967), Vol. 9C, p. 335.

⁹This reasoning seems also valid in two dimensions for the times considered in the Alder and Wainwright computations and is independent of the question whether transport coefficients exist in two dimensions.

¹⁰M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. Lett. <u>25</u>, 1254 (1970) (this issue).
¹¹R. Zwanzig and M. Bixon, Phys. Rev. A (to be pub-

lished), give a hydrodynamical treatment of a related problem and obtain an expression for $\alpha_D^{(3)}$ which

agrees with those obtained in Refs. 8 and 10 if the coefficient of self-diffusion is neglected.

¹²Cf. L. Brillouin, J. Phys. (Paris) 7, 153 (1936). ¹³For similar reasons the existence of the transport coefficients in the Burnett hydrodynamical equations is not clear in three dimensions.

Calorimetric Evidence for Positive Phonon Dispersion in Liquid Helium-4[†]

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The constant-volume heat capacity of liquid He⁴ has been measured from 0.3 K to above the λ point. Below 0.9 K the phonon heat capacity corresponds to a dispersion relation $\epsilon = cp (1-\gamma p^2)$ with γ varying from $-4.1 \times 10^{37} \text{ g}^{-2} \text{ cm}^{-2} \sec^2 a$ the saturated vapor pressure to $19.6 \times 10^{37} \text{ g}^{-2} \text{ cm}^{-2} \sec^2$ near the freezing pressure.

During the past few years, extensive studies¹⁻⁶ of the propagation of sound in liquid He⁴ have revealed inadequacies in the theoretical expressions for the velocity and attenuation. In a recent Letter, Maris and Massey⁷ have pointed out that the discrepancies between theory and experiment might be resolved if the coefficient γ in the equation representing the phonon region of the energy-momentum relation,

$$\epsilon = cp(1 - \gamma p^2 - \delta p^4 \cdots), \qquad (1)$$

were negative. For example, negative values would account for the observed attenuation exceeding the theoretical maximum. However, γ has generally been assumed to be positive, and no direct experimental evidence for negative values has been published previously. In this Letter we report measurements of the constantvolume heat capacity C_v that provide support for the suggestion that γ is negative. The measurements show that for pressures near the saturation vapor pressure and for low phonon energies the dispersion is positive [dominated by terms in Eq. (1) with negative coefficients] and can be approximated by $\gamma = -4.1 \times 10^{37}$ g⁻² cm⁻² sec².

During the measurements the capillary used to fill the constant-volume cell was closed by a valve at the entrance to the cell, and evacuated.⁸ This eliminated the various problems associated with a connecting capillary filled with He⁴. A germanium thermometer that had been calibrated against the susceptibility of a single crystal of cerium magnesium nitrate was used. The heat capacity of copper has been measured on the same temperature scale and the results were in good agreement with accepted values,⁹ demonstrating the reliability of the calibration. Systematic errors in C_V are believed to be less than 1%, and to vary only slowly with temperature.

The low-temperature expression for the phonon heat capacity corresponding to Eq. (1) is

$$C_{V,Ph} = \frac{\pi V (2\pi k_{\rm B})^4}{15h^3 c^3} \left[T^3 + \frac{25\gamma}{7} \left(\frac{2\pi k_{\rm B}}{c} \right)^2 T^5 + \frac{3\gamma^2 + \delta}{7} \left(\frac{2\pi k_{\rm B}}{c} \right)^4 T^7 \cdots \right] \equiv A T^3 + B T^5 + C T^7 \cdots,$$
(2)

where $k_{\rm B}$ is the Boltzmann constant and V is the molar volume. For temperatures of approximately 1 K or less the roton contribution to the heat capacity should be adequately approximated by¹⁰

$$C_{\mathbf{v},\mathbf{r}} = R \left[\left(\frac{\Delta}{k_{\mathrm{B}}T} \right)^{3/2} + \left(\frac{\Delta}{k_{\mathrm{B}}T} \right)^{1/2} + \frac{3}{4} \left(\frac{\Delta}{k_{\mathrm{B}}T} \right)^{-1/2} \right] \exp(-\Delta/k_{\mathrm{B}}T), \tag{3}$$

where $R = 2p_0^2 \mu^{1/2} k_B V/(2\pi)^{3/2} \bar{h}^3$. In the derivation of Eq. (3) the energy-momentum relation for rotons is approximated by $\epsilon = \Delta + (p - p_0)^2/2\mu$.