Σ-Π interactions. Not only have our data provided substantial evidence for the essential correctness of the dual pseudocrossing molecular picture, but we have also provided basic parameters and conclusions about the molecular levels participating in the collision process which constitute important experimental facts for future calculations dealing with collision spectroscopy.

The authors acknowledge helpful discussions with F. J. deHeer, H. H. Michels, R. Novick, H. Rosenthal, and F. T. Smith.

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Asymptotic Time Behavior of Correlation Functions

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The asymptotic time behavior of the velocity autocorrelation function and of the kinetic parts of the correlation functions for the shear viscosity and the heat conductivity is derived. The results are expressed in terms of the transport coefficients and the specific heats and are valid for all densities.

In a recent publication Alder and Wainwright[1] reported on molecular dynamics calculations of the velocity autocorrelation function for a two- and three-dimensional system of hard spheres. The asymptotic decay was observed to be of the form $t^{-d/2}$ (where d is the dimensionality of the system). They also proposed a hydrodynamical explanation of their observations on the basis of a numerical solution of the Navier-Stokes equations. It is the purpose of this Letter to show that the asymptotic time behavior of such correlation functions can be established precisely in terms of the transport coefficients and equilibrium thermodynamic quantities.

As a typical example consider the normalized velocity autocorrelation function

$$C_D(t) = \langle v_{1x}(0)v_{1x}(t)\rangle / \langle v_{1x}{}^2(0)\rangle, \tag{1}$$

where $\vec{v}_1(t)$ is the velocity of particle 1 at time t. The average $\langle\rangle$ refers to an equilibrium ensemble and the thermodynamic limit is always taken as the final step. The numerator of (1) can be written as

$$\langle v_{1x}(0)v_{1x}(t)\rangle = \int d^3v_0 v_{0x} \int d^3r_0 \int d^3r \langle v_{1x}(t)\,\delta(\vec{r}_1(t)-\vec{r})\delta(\vec{v}_1(0)-\vec{v}_0)P(\vec{r}_1(0)-\vec{r}_0)\rangle, \tag{2}$$

where $P(\vec{r})$ is a function which integrates to unity. The form of $P(\vec{r})$ is in principle arbitrary, and we shall choose it to be slowly varying (on a macroscopic scale). The insertion $\delta(\vec{v}_1(0)-\vec{v}_0)P(\vec{r}_1(0)-\vec{r}_0)$ in the average selects out of the equilibrium ensemble those initial configurations in which the velocity of particle 1 is precisely determined as $\vec{v}_0$, while its position is given only by the extended probability

distribution $P(\vec{r}_1(0)-\vec{r}_0)$ around $\vec{r}_0$. By this selection one has constructed a nonequilibrium ensemble on which one can define the hydrodynamical variables: $P(\vec{r}, t)$ as the probability distribution for particle 1 at time t, $n(\vec{r}, t)$ as the particle density, $\vec{u}(\vec{r}, t)$ as the average velocity field, and $T(\vec{r}, t)$ as the temperature. Using the fact that $P(\vec{r}-\vec{r}_0)$ can be chosen as a smooth function of macroscopic extension, one computes the initial deviations of these variables from their overall equilibrium values to be

$$P(\vec{r}, 0) = P(\vec{r}-\vec{r}_0), \quad n(\vec{r}, 0)-n = k_B T(\partial n/\partial p)_T P(\vec{r}-\vec{r}_0), \quad \vec{u}(\vec{r}, 0) = (\vec{v}_0/n)P(\vec{r}-\vec{r}_0),$$

$$T(\vec{r}, 0)-T = (1/2nC_V)(mv_0^2-dk_B T)P(\vec{r}-\vec{r}_0). \tag{3}$$

Here p is the equilibrium pressure, C_V is the specific heat per particle at constant volume, m is the particle mass, and $k_B = (\beta T)^{-1}$ is Boltzmann's constant.

The smoothness of $P(\vec{r}-\vec{r}_0)$ implies that the initial deviations from equilibrium are small and slowly varying in space, and for a computation of their time dependence one is thus justified in using the linearized equations of hydrodynamics. We split $\vec{v}_1(t)$ in two parts:

$$\vec{v}_1(t) = \vec{u}(\vec{r}_1(t), t) + \vec{V}_1(t), \tag{4}$$

where $\vec{v}_1(t)$ is the peculiar velicity of particle 1 with respect to the local average $\vec{u}(\vec{r}_1(t), t)$. From the assumption that a system in any initial nonequilibrium state comes close to a state of local equilibrium after a relatively short time (which is a necessary requirement for the existence of hydrodynamics), it follows that to lowest order in the deviations from equilibrium, $\vec{V}_1(t)$ for long times becomes random as far as its direction is concerned, and with average magnitude given by the local temperature $T(\vec{r}_1(t), t)$. Thus we find for the leading terms for long times

$$\langle v_{1x}(t)\delta(\vec{r}_1(t)-\vec{r})\delta(\vec{v}_1(0)-\vec{v}_0)P(\vec{r}_1(0)-\vec{r}_0)\rangle \simeq u_x(\vec{r}, t)\langle\delta(\vec{r}_1(t)-\vec{r})\delta(\vec{v}_1(0)-\vec{v}_0)P(\vec{r}_1(0)-\vec{r}_0)\rangle$$

$$= u_x(\vec{r}, t)P(\vec{r}, t)f^0(v_0)/V, \tag{5}$$

where $f^0(v)$ is the normalized equilibrium Maxwell velocity distribution function and V is the volume of the system. Combination of (2) and (5) gives the asymptotic expression

$$\langle v_{1x}(0)v_{1x}(t)\rangle \simeq \int d^3v_0 f^0(v_0)v_{0x}\int d^3r u_x(\vec{r}, t)P(\vec{r}, t). \tag{6}$$

With the initial condition (3), $u_x(\vec{r}, t)$ and $P(\vec{r}, t)$ now follow from the linearized Navier-Stokes and diffusion equations, respectively. Asymptotically one finds

$$C_D(t) \simeq (d-1)d^{-1}n^{-1}(2\pi)^{-d}\int d^3k\,|P_k|^2\exp[-(D+\nu)k^2t] \simeq (d-1)d^{-1}n^{-1}[4\pi(D+\nu)t]^{-d/2}. \tag{7}$$

Here P_k is the kth Fourier component of $P(\vec{r}-\vec{r}_0)$, D is the self-diffusion coefficient, $\nu = \eta/nm$ is the kinematic and η the shear viscosity. Note that the asymptotic behavior of $C_D(t)$ is independent of the shape and spatial extent of $P(\vec{r}-\vec{r}_0)$, as it should be.

Exactly the same arguments apply to the kinetic parts of the correlation functions for the shear viscosity η and the heat conductivity λ. The normalized kinetic parts of these correlation functions are given by

$$C_\eta^K(t) = \langle v_{1x}(0)v_{1y}(0)\sum_{j=1}^N v_{jx}(t)v_{jy}(t)\rangle/\langle v_{1x}^2(0)v_{1y}^2(0)\rangle,$$

$$C_\lambda^K(t) = \left\langle\left[v_1^2(0)-\frac{d+2}{m\beta}\right]v_{1x}(0)\sum_{j=1}^N\left[v_j^2(t)-\frac{d+2}{m\beta}\right]v_{jx}(t)\right\rangle\left\langle\left[v_1^2(0)-\frac{d+2}{m\beta}\right]^2 v_{1x}^2(0)\right\rangle^{-1}. \tag{8}$$

For long times one may effectively make the following identifications inside the averages:

$$\sum_{j=1}^N v_{jx}(t)v_{jy}(t)\delta(\vec{r}_j(t)-\vec{r}) \simeq u_x(\vec{r}, t)u_y(\vec{r}, t)\sum_{j=1}^N\delta(\vec{r}_j(t)-\vec{r}),$$

$$\sum_{j=1}^N\left[v_j^2(t)-\frac{d+2}{m\beta}\right]v_{jx}(t)\delta(\vec{r}_j(t)-\vec{r}) \simeq (d+2)k_B m^{-1}[T(\vec{r}, t)-T]u_x(\vec{r}, t)\sum_{j=1}^N\delta(\vec{r}_j(t)-\vec{r}). \tag{9}$$

Again the time dependence of $\vec{u}(\vec{r}, t)$ and $T(\vec{r}, t)$ follows from linearized hydrodynamics with initial conditions (3). One finds asymptotically

$$C_\eta^K(t) \simeq \frac{1}{nd(d+2)}\left[\frac{d^2-2}{(8\pi\nu t)^{d/2}} + \frac{1}{(4\pi\Gamma t)^{d/2}}\right], \quad C_\lambda^K(t) \simeq \frac{k_B(d+2)}{2ndC_p}\left[\frac{d-1}{[4\pi(\nu+D_T)t]^{d/2}} + \frac{\gamma-1}{[4\pi\Gamma t]^{d/2}}\right], \tag{10}$$

where $D_T = \lambda/(nC_p)$ is the thermal diffusivity and Γ is the sound-wave damping constant given by

$$\Gamma = 2(d-1)d^{-1}\nu + n^{-1}m^{-1}\zeta + (\gamma-1)D_T. \tag{11}$$

Here ζ is the bulk viscosity and $\gamma = C_p/C_V$ the ratio of the specific heats.

In conclusion we make the following remarks:

(1) The expressions (7) and (10) agree in the low-density limit with those obtained by Dorfman and Cohen[2] from kinetic theory.

(2) The density dependence of $C_D(t)$ and $C_\eta^K(t)$, apart from a trivial factor n^{-1}, manifests itself solely through that of the damping constants D, ν, and Γ, whereas the formula for $C_\lambda^K(t)$ explicitly contains the specific heats.

(3) The only assumptions involved in the calculations above are (a) that the approach to a state close to local equilibrium precedes the hydrodynamical decay, and (b) existence of the Navier-Stokes equations as a valid hydrodynamical description in the long-wavelength limit.

(4) The assumption 3(b) invalidates our results in two dimensions since the integral over a long-time tail $\sim t^{-1}$ does not exist. From (7) it follows that the self-diffusion coefficient does not exist in two dimensions. On the basis of the conjecture that the long-time behavior of the complete $C_\eta(t)$ and $C_\lambda(t)$ does not differ qualitatively from that of their kinetic parts, the same conclusion is reached for η and λ. Thus hydrodynamics in the conventional sense does not exist in two dimensions.

(5) Although the existence of Navier-Stokes hydrodynamics is not challenged for $d \geq 3$, a similar argument as sub 4 shows that the first correction to Navier-Stokes, as given by the Burnett equations, is meaningless for $d = 3$ and $d = 4$.

(6) The transport coefficients are proportional to the time integral over the corresponding correlation functions. Clearly our asymptotic formulas (7) and (10) cannot be integrated from 0 to ∞. From assumption 3(a) it follows, however, that the contributions leading to the asymptotic tail have a meaning only after a state close to local equilibrium has been established (we do not assume that these contributions become dominant on this time scale!). The time needed to approach local equilibrium is of the order of the mean time between collisions, i.e., for low densities of $O(n^{-1})$. One therefore concludes that the contribution of the asymptotic tail to the transport coefficients has the order (Boltzmann value) $\times O(n^{d-1})$. This is precisely the order in which the well-known divergences in the density expansion of the transport coefficients manifest themselves.[3]

(7) No reference to the nature of the intermolecular forces [other than that implied by the assumptions 3(a) and 3(b)] has been made in the above calculations.

(8) In particular, forces with a repulsive and an attractive part that produce phase transitions are not excluded. However, the assumptions 3(a) and 3(b) break down close to the critical point, and our analysis is thus not valid in the critical region.

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