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Letter to the Editor

The Interpretation of a Theorem by Lebowitz

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Lebowitz[1] has proven that for any finite, classical, mixing system

$$\int_0^\infty \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \, dt = 0 \tag{1}$$

Due to the association of this integral with the diffusion constant, this result has led to the conclusion that such systems cannot be described by the diffusion equation. In particular, the hard-sphere gas, which Sinai[2] has proven to be mixing, has been regarded as unrealistic on this basis.

Actually, for a finite system, the infinite-time integral of the velocity autocorrelation function does not yield the diffusion constant. In fact, Eq. (1) is a consequence of diffusion in a finite system and is completely consistent with a description of the system's approach to equilibrium by the diffusion equation with a nonzero diffusion constant. This can be seen from the following physical argument.

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Suppose we have a system which does display diffusion. We wish to investigate the time dependence of the integral

$$\int_0^t \langle \mathbf{v}(t') \cdot \mathbf{v}(0) \rangle \, dt' = \langle [\mathbf{r}(t) - \mathbf{r}(0)] \cdot \mathbf{v}(0) \rangle \tag{2}$$

Consider a particular particle with an initial position $\mathbf{r}(0)$ and an initial velocity $\mathbf{v}(0)$ (we shall average over these later). The probability distribution for $\mathbf{r}(t)$ will spread out and its average position will move in the direction given by the initial velocity. After a characteristic time t_1, this average position will have essentially stopped a distance d away from the initial position. The product of $|\mathbf{v}(0)|$ and d [which is a function of $|\mathbf{v}(0)|$] averaged over all initial velocities clearly provides a measure of the diffusion. The probability distribution for $\mathbf{r}(t)$ will continue to spread out, but the average value of $\mathbf{r}(t)$ will not change appreciably until the probability distribution becomes significantly affected by the walls. This will occur after a time t_2, which depends on the size of the system (for most macroscopic systems, d is small in comparison with the dimensions of the system, so that $t_2 \gg t_1$). The probability distribution will then continue to spread throughout the system until it is uniform and the average value of $\mathbf{r}(t)$ is the center of mass of the system, $\mathbf{R}$. Since this is true for an arbitrary initial velocity, averaging over all possible directions of the initial velocity yields zero:

$$\operatorname*{Lim}_{t \to \infty} \int_0^t \langle \mathbf{v}(t') \cdot \mathbf{v}(0) \rangle \, dt' = \langle [\mathbf{R} - \mathbf{r}(0)] \cdot \mathbf{v}(0) \rangle = 0 \tag{3}$$

To obtain a proper measure of the diffusion in a finite system, we should really evaluate the integral in Eq. (2) at a time t such that $t_2 \gg t \gg t_1$. On the other hand, we can explicitly neglect the walls by taking the thermodynamic limit (so that $t_2 \to \infty$) and then let $t \to \infty$. The thermodynamic limit is, of course, just a mathematical trick for simplifying calculations and does not actually introduce diffusion into the system.

The approach to equilibrium of a finite system[3] (and, in particular, the hard-sphere gas) can therefore be described by the diffusion equation with a nonzero diffusion constant and appropriate boundary conditions. However, the uncritical use of the traditional expression for the diffusion constant is not correct.

REFERENCES

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