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The Velocity Autocorrelation Function of a Finite Model System

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We investigate in detail the dependence of the velocity autocorrelation function of a one-dimensional system of hard, point particles with a simple velocity distribution function (all particles have velocities $\pm c$) on the size of the system. In the thermodynamic limit, when both the number of particles N and the length of the "box" L approach infinity and $N/L \to \rho$, the velocity autocorrelation function $\psi(t)$ is given simply by $c^2 \exp(-2\rho ct)$. For a finite system, the function $\psi_N(t)$ is periodic with period $2L/c$. We also show that for more general velocity distribution functions (particles can have velocities $\pm c_i$, $i = 1,...$), $\psi_N(t)$ is an almost periodic function of t. These examples illustrate the role of the thermodynamic limit in nonequilibrium phenomena: We must keep t fixed while letting the size of the system become infinite to obtain an auto-correlation function, such as $\psi(t)$, which decays for all times and can be integrated to obtain transport coefficients. For any finite system, our $\psi_N(t)$ will be "very close" to $\psi(t)$ as long as t is small compared to the effective "size" of the system, which is $2L/c$ for the first model.

KEY WORDS: One dimension; finite system; thermodynamic limit; velocity autocorrelation function.

1. INTRODUCTION

The study of time-dependent correlation functions plays a central role in the statistical mechanics of nonequilibrium phenomena. These functions are

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defined as follows: Consider a classical system of N particles whose positions and momenta (that is, the configuration of the system) are specified by a point X, $X = (\mathbf{r}_1, ..., \mathbf{r}_N ; \mathbf{p}_1, ..., \mathbf{p}_N)$, in the phase space of the system. The position coordinates $\mathbf{r}_i$ are confined to some domain Λ with volume $V(\Lambda)$ by "rigid walls." The time evolution of the system is described by a unitary operator s_t, $s_t X = X_t$ being the phase point of the system at time t when it was X at time zero, and $s_{t_1} s_{t_2} = s_{t_1+t_2}$. Let $f(X)$ and $g(X)$ be some functions of X, the configuration of the system. For a given configuration X at time zero, the value of f at time t is given by $s_t f(X) = f(X_t)$. We define the correlation of f at time t and g at time zero as

$$\begin{aligned}\langle f(t)\, g\rangle_N &= \langle f(X_t)\, g(X)\rangle_N \\ &= \int dX\, \mu_0(X) f(X_t)\, g(X)\end{aligned} \tag{1}$$

where $\mu_0(X)$ is some stationary (equilibrium) Gibbsian ensemble density, e.g., microcanonical or canonical such that

$$\mu_0(X_t) = \mu_0(X)$$

and

$$\int dX\, \mu_0(X) = 1 \tag{2}$$

We have used the subscript N on $\langle f(t)\, g\rangle_N$ to indicate explicitly that we are dealing with systems of N particles.

One reason for the importance of time-dependent correlation functions is that linear transport coefficients may be expressed as time integrals over appropriate correlation functions. For example, Einstein related the self-diffusion constant D to the integral of the velocity autocorrelation function by

$$D = (1/d) \int_0^\infty dt\, \langle \mathbf{v}(t) \cdot \mathbf{v}\rangle \tag{3}$$

where d is the dimensionality of the system and $\mathbf{v}$ is the velocity of some *specified* particle in the system.

The function $\psi(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}\rangle$ appearing in (3) (and different correlation functions appearing in other formulas of this type) has to be interpreted as the limit of the velocity autocorrelation $\langle \mathbf{v}(t) \cdot \mathbf{v}\rangle_N$ for a system of N particles in a domain Λ, when $N \to \infty$ and $V(\Lambda) \to \infty$ in such a way that $N/V(\Lambda) = \rho$, the density of the system. This limit is usually called the "thermodynamic limit." The taking of such an infinite volume limit is *always* necessary, since for a finite system, the integral of $\langle \mathbf{v}(t)\cdot\mathbf{v}\rangle_N$, *if it exists*, is equal to zero.(1) This is due to the fact that

$$\int_0^t dt' \, \langle \mathbf{v}(t')\cdot\mathbf{v}\rangle_N = \tfrac{1}{2}(\partial/\partial t)\langle\{\mathbf{r}(t)-\mathbf{r}\}^2\rangle_N \tag{4}$$

where $\mathbf{r}$ is the position coordinate conjugate to the velocity (momentum) $\mathbf{v}$. Now, since the right side of (4) is the derivative of a bounded function (since $\mathbf{r}$ is confined to a bounded domain Λ), it cannot have a limit as $t\to\infty$ different from zero. For the model system we shall consider in this paper, the existence of the limit $t\to\infty$ depends on the type of stationary ensemble $\mu_0(X)$ we choose.

The use of the thermodynamic limit of the correlation functions in defining transport coefficients forces us to consider the existence of limits such as

$$\psi(t) = \lim_{N\to\infty} \langle \mathbf{v}(t)\cdot\mathbf{v}\rangle_N \tag{5}$$

While the existence of the thermodynamic limit for different equilibrium quantities has been established under fairly general conditions, there are few results for nonequilibrium quantities. Indeed, the only "fluid" system for which $\psi(t)$ is known to exist is the one-dimensional system of hard point particles studied by Jepsen[2] and others(3–5) for which D can be found explicitly. (The ideal gas(6) and perfect harmonic crystal are the only other dynamical model systems for which the correlation functions can be computed exactly.(1)) It is the purpose of this note to study the behavior of $\psi_N(t)$ and its approach to $\psi(t)$ for this system.

The system of hard, point particles is described in Section 2. Due to the simplicity of the dynamics of this system, we can readily find a large class of stationary distributions. In particular, we can choose $\mu_0(X)$ in such a way that the ensemble density is concentrated in regions of the phase space in which the velocities of the particles only assume a denumerable (or finite) set of values. Since the phase space has $2N$ dimensions and these regions have an N-dimensional volume, this is only possible because this system is not ergodic on its energy surfaces, which are of $2N-1$ dimensions.

We show in Section 3 that for all stationary distributions of the above type, $\psi_N(t)$ will be an almost periodic function of t. It will therefore not decay as $t\to\infty$ and therefore the upper limit of integration in (4) cannot be extended to infinity. To see what happens in the thermodynamic limit, we study, in Section 4, a particularly simple stationary distribution. For this distribution, the configuration of the system and hence all time-dependent correlation functions are periodic functions of the time with a period which is proportional to the length of the box. We obtain $\psi_N(t)$ explicitly for this $\mu_0(X)$ and observe how it approaches its limit $\psi(t)$ which decays to zero as

$t \to \infty$ yielding a finite diffusion coefficient D. Finally, the extension of these results to some other equilibrium distributions $\mu_0(X)$ is discussed in Section 5.

2. THE ONE-DIMENSIONAL SYSTEM OF HARD POINT PARTICLES

We consider a system of N hard, point particles of unit mass moving in one dimension, like a row of beads on an abacus. The particles are confined to a "box" of length L and we impose reflecting boundary conditions so that when a particle strikes a wall of the box, it is specularly reflected. Since all the particles are hard, when two of them collide, they simply exchange velocities. Thus, any initial distribution of velocities will be preserved at all later times (apart from changes in sign caused by collisions with the walls). This means that any distribution function of the form

$$\mu_0(X) = (1/L^N) \prod_{i=1}^{N} h_0(v_i) \tag{6}$$

with $h_0(v)$ an arbitrary, nonnegative, even function of v normalized to unity,

$$h_0(v) = h_0(-v) \geqslant 0$$

and

$$\int_{-\infty}^{\infty} dv\, h_0(v) = 1 \tag{7}$$

is stationary.

The method used for calculating $\psi_N(t)$ will follow closely the paper of Lebowitz and Percus,[4] who solved the same problem in the thermodynamic limit. A formal expression can be obtained for $\psi_N(t)$ by noticing that the order of the particles in the box is maintained at all times: If a particle is initially the ith particle from the left wall of the box, then it will always be the ith particle because there is no mechanism by which it can pass either of its nearest neighbors. We can thus calculate $\psi_N(t)$ by allowing the particles to evolve independently on free-particle trajectories provided the correct ordering of the particles is maintained. The resulting expression is

$$\psi_N(t) = (1/N) \sum_{i=1}^{N} \sum_{j=1}^{N} \langle v_j(t)\, v_i\, \delta_{\sigma_j(t),\sigma_i} \rangle \tag{8}$$

Here, $\sigma_j(t)$ is the order of the jth particle at time t and is given by

$$\sigma_j(t) = \sum_{l=1}^{N} \epsilon(r_j(t) - r_l(t)) \tag{9}$$

where

$$\epsilon(x) = \begin{cases} 0 & \text{for} \quad x < 0 \\ 1 & \text{for} \quad 0 < x \end{cases} \tag{10}$$

and $\{r_i(t), v_i(t)\}$ are the positions and velocities of a set of *free particles* (ideal gas) moving in the box of length L, that is,

$$v_i(t) = v_i\,; \qquad r_i(t) = r_i + v_i t \tag{11}$$

subject to the reflecting boundary conditions.

Equation (8) can be handled more easily by writing the δ-function as

$$\delta_{\sigma_j(t),\sigma_i} = (1/2\pi) \int_0^{2\pi} d\theta \exp\{i\theta[\sigma_j(t) - \sigma_i]\} \tag{12}$$

Then by using Eq. (9), separating the summations in (8) into two parts depending on whether $i = j$ or $i \neq j$, using the symmetry properties of the average, and defining

$$\begin{aligned} E_\theta(R, r \mid t) = {} & \int_0^L \frac{dr_l}{L} \int_{-\infty}^{\infty} dv_l\, h_0(v_l) \\ & \times \exp\{i\theta[\epsilon(R - r_l(t)) - \epsilon(r - r_l)]\} \end{aligned} \tag{13}$$

which from (11) is only a function of R, r, θ, and t, we find

$$\begin{aligned} \psi_N(t) = {} & \frac{1}{2\pi L} \int_0^L dr_1 \int_{-\infty}^{\infty} dv_1\, h_0(v_1)\, v_1(t)\, v_1 \int_0^{2\pi} d\theta\, E_\theta(r_1(t), r_1 \mid t)^{N-1} \\ & + \frac{(N-1)}{2\pi L^2} \int_0^L dr_1 \int_{-\infty}^{\infty} dv_1\, h_0(v_1) \int_0^L dr_2 \int_{-\infty}^{\infty} dv_2\, h_0(v_2)\, v_2(t)\, v_1 \\ & \times \int_0^{2\pi} d\theta \exp\{i\theta[\epsilon(r_2(t) - r_1(t)) - \epsilon(r_1 - r_2)]\}\, E_\theta(r_2(t), r_1 \mid t)^{N-2} \end{aligned} \tag{14}$$

When $t = 0$,

$$E_\theta(R, r \mid 0) = 1 + i(\sin\theta)[(R - r)/L] - (1 - \cos\theta)(|R - r|/L)$$

and from Eq. (14),

$$\psi_N(0) = \int_{-\infty}^{\infty} dv_1\, h_0(v_1)\, v_1^2 = \langle v^2 \rangle$$

as expected.

We note here that these formulas remain valid when the particles have hard cores$^{(4)}$ (rigid-rod system). If the minimum distance of approach between the centers of two particles is a then we merely have to replace L by $L - Na$ everywhere.

3. DISCRETE VELOCITY DISTRIBUTIONS

In order to discuss the dynamics of the system, we follow Jepsen[2] and construct a phase diagram. A simple diagram showing the motion of two particles with velocities $\pm c$, $c > 0$, is given in Fig. 1. The trajectory which starts at position a with velocity c passes through $L - a$ with velocity $-c$ at $t = L/c$ and returns to a with velocity c at $t = 2L/c$. Similar results hold for the trajectory which started at b with velocity $-c$. It is clear that after a time $t = 2L/c$, the two particles have returned exactly to their initial $t = 0$ configurations. The particles then follow the same trajectories as before. Thus the time dependence of the functions $r_i(t)$ and $v_i(t)$ in (11) is periodic with a period $T_i = 2L/|v_i|$.

Consider now the case in which the equilibrium velocity distribution function $h_0(v)$ is purely discrete, i.e.,

$$h_0(v) = \tfrac{1}{2} \sum_{l=1}^{\infty} K_l[\delta(v - c_l) + \delta(v + c_l)] \tag{15}$$

with $0 \leqslant c_1 < c_2 < c_3 \cdots$, $K_l > 0$, and $\sum_{l=1}^{\infty} K_l = 1$. We assume further that the mean energy per particle is finite,

$$\langle v^2 \rangle = \sum_{l=1}^{\infty} K_l c_l^2 < \infty \tag{16}$$

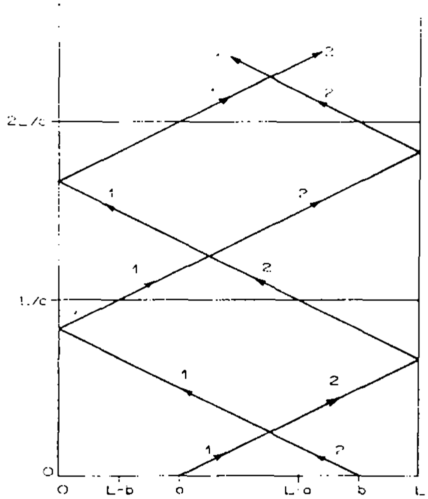

Fig. 1. Phase diagram for two particles.

The velocity autocorrelation function can be written in the form (as can be inferred from the appendix)

$$\psi_N(t) = \sum_{l_1=1}^{\infty} \cdots \sum_{l_N=1}^{\infty} K_{l_1} \cdots K_{l_N} F_{l_1 \cdots l_N}(\tau_{l_1}, \ldots, \tau_{l_N}) \tag{17}$$

where

$$\tau_j = c_j t/2L = t/T_j$$

and $F_{l_1 \cdots l_N}$ is a continuous, symmetric, periodic function in the τ_{l_i},

$$F_{l_1 \cdots l_N}(\tau_{l_1} + m_{l_1}, \ldots, \tau_{l_N} + m_{l_N}) = F_{l_1 \cdots l_N}(\tau_{l_1}, \ldots, \tau_{l_N}) \tag{18}$$

with $\{m_{l_i}\}$, $i = 1, \ldots, N$, a set of integers. The function $F_{l_1 \cdots l_N}(\tau_{l_1}, \ldots, \tau_{l_N})$ (which is of the type called "quasiperiodic" by Moser$^{(7)}$ and "Bohl function" by Bohr$^{(8)}$) is the velocity autocorrelation function of a system of N hard, point particles on a line segment of length L in which there is exactly one particle with velocity $\pm c_{l_1}$, one particle with velocity $\pm c_{l_2}$, etc., corresponding to a stationary distribution

$$\mu_0(X) = (1/N!)\, S \left\{(1/L^N) \prod_{i=1}^{N} \tfrac{1}{2}[\delta(v_i - c_{l_i}) + \delta(v_i + c_{l_i})]\right\} \tag{19}$$

where S stands for symmetrization in the l_i. Hence, $F_{l_1 \cdots l_N}$ is bounded by its value at $t = 0$,[3]

$$|F_{l_1 \cdots l_N}(\tau_{l_1}, \ldots, \tau_{l_N})| \leqslant (1/N) \sum_{i=1}^{N} c_{l_i}^2 \tag{20}$$

and the series in (17) is uniformly convergent. It follows now from the general theory of almost periodic functions$^{(8)}$ that $\psi_N(t)$, obtained from an arbitrary discrete velocity distribution, is almost periodic and therefore, in particular, cannot decay to zero as $t \to \infty$.

The situation is quite different when $h_0(v)$ is an absolutely continuous function of v. In that case, the summations in (17) are replaced by integrals and we expect $\psi_N(t)$ to decay as $t \to \infty$. When $h_0(v)$ contains both a discrete and a continuous part, then $\psi_N(t)$ should also have an almost periodic part and a decaying part.

4. EXPLICIT RESULTS FOR $h_0(v) = \frac{1}{2}[\delta(v - c) + \delta(v + c)]$

In order to see in detail the effect which an increase in the size of the system has on its nonequilibrium properties, we shall now compute $\psi_N(t)$ explicitly for the case in which all the particles have the same speed, i.e.,

$$h_0(v) = \tfrac{1}{2}[\delta(v - c) + \delta(v + c)], \qquad c > 0 \tag{21}$$

[3] This follows from $\langle f(t)f\rangle \leqslant \langle f^2(t)\rangle^{1/2}\langle f^2\rangle^{1/2} = \langle f^2\rangle$.

Since the period of all the particles is now the same, we have

$$\psi_N(t+T) = \psi_N(t), \qquad T = 2L/c \tag{22}$$

and we need only calculate $\psi_N(t)$ for times t in the range $0 < t < T$.

Let us now consider the trajectories in Fig. 1 during the first cycle. If the trajectories are reflected in the line at $t = L/c$ ($= T/2$), then the first trajectory starts at a with velocity $-c$ and the second at b with velocity c. The motion of two particles along the reflected trajectories in the forward time direction from $t = 0$ to $t = T$ is exactly the same as the motion of the two particles along the original trajectories in the backward time direction from $t = T$ to $t = 0$. Since $\psi_N(t)$ contains an average over all possible velocities (as well as positions), both the original and the reflected trajectories give contributions to $\psi_N(t)$. If the contribution of the original trajectories in Fig. 1 is $h_N(t)$, then the reflected trajectories give $h_N(T-t)$ and the total contribution is $h_N(t) + h_N(T-t)$. As all possible configurations can be arranged in pairs as the above simple example, $\psi_N(t)$ must be of the form

$$\psi_N(t) = H_N(t) + H_N(T-t)$$

Thus, for $0 < t < T$,

$$\psi_N(T-t) = \psi_N(t) \tag{23}$$

which means we need only determine $\psi_N(t)$ in the range $0 < t < T/2$.

This is as far as we can go with general arguments and we must return to Eq. (14) to obtain an explicit expression for $\psi_N(t)$. As the calculation is simple but rather long, we give the details in the appendix and quote the result here:

$$\psi_N(t) = c^2\{(1-x)(1-2x)^{N-1} - (1/2N)[1-(1-2x)^N]\} \tag{24}$$

where

$$x = ct/L = 2t/T \tag{25}$$

and $0 \leqslant x \leqslant 1$ or $0 \leqslant t \leqslant T/2$. Outside this range, $\psi_N(t)$ can be found by using Eqs. (22) and (23). In particular,

$$\psi_N(0) = \psi_N(T) = c^2$$

For small values of N, $\psi_N(t)$ is very simple. For example, when $N = 1$,

$$\psi_1(t) = c^2(1-2x) \qquad \text{for} \quad 0 \leqslant x \leqslant 1$$

or

$$\psi_1(t)/\psi_1(0) = 1 - (4t/T) \qquad \text{for} \quad 0 \leqslant t \leqslant T/2$$

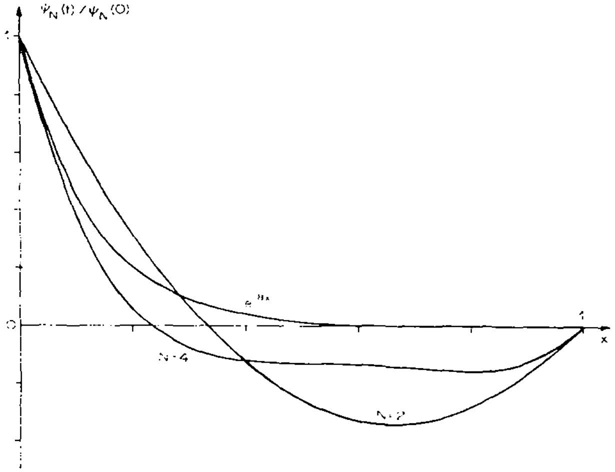

Fig. 2. Plots of $\psi_N(t)/\psi_N(0)$ for $N = 2$ and 4 and $\psi(t)/\psi(0)$ for $\rho = 4/L$ as functions of $x = ct/L$ for $h_0(v)$ given in Eq. (21).

Thus, when t increases from 0 to $T/2$, $\psi_1(t)/\psi_1(0)$ decreases linearly from 1 to -1 and when t increases from $T/2$ to T, $\psi_1(t)/\psi_1(0)$ increases linearly from -1 to 1. The first cycle has now been completed and the system starts again from its initial ($t = 0$) state. For $N \geqslant 2$, $\psi_N(t)/\psi_N(0)$ is still exactly periodic with period T, but it no longer decays linearly in the first half-period. The results for $N = 2$ are shown in Fig. 2 in the range $0 \leqslant x \leqslant 1$.

When $N \geqslant 4$, $\psi_N(t)/\psi_N(0)$ has turning values at $x = 1/2$ and $x = N/(N+1)$. At $x = 1/2$, the first $N - 2$ derivatives of $\psi_N(t)$ vanish, and at $x = N/(N+1)$, $\psi_N(t)$ is negative and has a maximum for odd values of N and a minimum for even values of N. Finally, when $x = 1/2$,

$$\psi_N(T/4)/\psi_N(0) = -1/2N$$

and when $x = 1$,

$$\psi_N(T/2)/\psi_N(0) = -(1/2N)[1 - (-1)^N]$$

Therefore, $\psi_N(t)$ passes through zero and becomes negative somewhere in the range $0 < t < T/4$ and then remains negative through the remainder of the half-period until $t = T/2$. The largest negative value $\psi_N(t)/\psi_N(0)$ can achieve is $-1/N$, so that

$$-1/N \leqslant \psi_N(t)/\psi_N(0) \leqslant 0$$

for $T/4 \leqslant t \leqslant T/2$.

To investigate the thermodynamic limit, we put $\rho = N/L$ and express $\psi_N(t)$ as a function of t, ρ, and N. Then,

$$\frac{\psi_N(t)}{\psi_N(0)} = \left(1 - \frac{\rho ct}{N}\right)\left(1 - \frac{2\rho ct}{N}\right)^{N-1} - \frac{1}{2N}\left[1 - \left(1 - \frac{2\rho ct}{N}\right)^{N}\right] \tag{26}$$

for $0 < \rho ct < N$. Now, in most problems in statistical mechanics, we are interested in the long-time behavior of a many-particle system of fixed density ρ. If we hold N fixed, then the limit $t \to \infty$ is not defined because $\psi_N(t)$ is a periodic function in t. Thus, we must keep t fixed and take the thermodynamic limit first. Since

$$\lim_{n\to\infty} [1 + (x/n)]^n = e^x$$

we find from Eq. (26) for fixed t and ρ,

$$\begin{aligned}\lim_{N\to\infty} \psi_N(t) &= \psi(t)\\ &= c^2 e^{-2\rho ct}\end{aligned} \tag{27}$$

which is just the result obtained by Lebowitz and Percus.(4) If we now let $t \to \infty$, then $\psi(t) \to 0$, as expected.

In Fig. 2, we compare $\psi_N(t)/\psi_N(0)$ with $\psi(t)/\psi(0)$ for $N = 4$. Clearly, these functions are identical near $t = 0$ and differ as t (or x) increases until one becomes negative and the other remains positive. However, in the thermodynamic limit, only the initial part of the x axis is important and in this region, $\psi_N(t)$ decays monotonically toward zero.

Since $\psi_N(t)$ is a periodic function and

$$\int_0^{T/2} dt'\, \psi_N(t') = 0$$

then $\int_0^t dt'\, \psi_N(t')$ is also a periodic function, so that the limit of $t \to \infty$ does not exist. However, in the thermodynamic limit, $\int_0^t dt'\, \psi(t')$ is a monotonically decreasing function; the limit $t \to \infty$ exists and the self-diffusion coefficient is given by

$$\begin{aligned}D &= \lim_{t\to\infty} \int_0^t dt'\, \psi(t')\\ &= c/2\rho\end{aligned}$$

It is seen from Fig. 2 that even for N as small as four, there is an interval near $t = 0$, proportional to L, in which $\psi_N(t)$ is very close to its limiting value $\psi(t)$. As N increases, this interval becomes larger. It is quite *reasonable to assume* that from the measurement of the velocity autocorrelation function in a finite system over a fixed time interval t, (as is done in the machine computations of Alder, Rahman, Verlet, and others[9]) one can extrapolate to find the infinite volume $\psi(t)$ with good accuracy.

5. DISCUSSION

Other correlation functions of interest, such as the Van Hove self-distribution function, can also be calculated for $v_i = \pm c$ by the methods used in the appendix. It again is exactly periodic, but is much more complicated than $\psi_N(t)$ and so will not be given here.

There is no reason why the ensemble density should be limited to that given in (6). Another simple possibility is

$$\mu_0(X) = \frac{1}{N}\frac{1}{L^N}\sum_{i=1}^{N}\frac{H_0(v_i)}{h_0(v_i)}\prod_{j=1}^{N} h_0(v_j) \tag{28}$$

If we now choose

$$h_0(v) = \delta(v) \tag{29}$$

i.e., all particles but one are initially at rest, then

$$\psi_N(t) = \frac{1}{N}\frac{1}{L^N}\int_0^L dr \int_{-\infty}^{\infty} dv\; H_0(v)\, v(t)\, v[L - |r(t) - r|]^{N-1} \tag{30}$$

This model suffers from the drawback that $\psi_N(t) \sim 1/N$, but if we notice that

$$\psi_N(0) = (1/N)\int_{-\infty}^{\infty} dv\; H_0(v)\, v^2$$

then $\psi_N(t)/\psi_N(0)$ will approach a nonzero value in the thermodynamic limit.

In order to illustrate the role of $\mu_0(X)$, let us briefly consider two choices for $H_0(v)$ in the above model and reflecting boundary conditions: (a) for the first choice,

$$H_0(v) = \tfrac{1}{2}[\delta(v - c) + \delta(v + c)] \tag{31}$$

$\psi_N(t)$ is periodic with period $2L/c$ as before and in the thermodynamic limit,

$$\psi_N(t)/\psi_N(0) \to e^{-\rho ct}$$

(b) For the second choice,

$$H_0(v) = (\alpha/2)\, e^{-\alpha|v|} \tag{32}$$

$\psi_N(t)$ is no longer periodic. As $t \to \infty$,

$$\psi_N(t) \sim -1/t^4$$

in such a way that

$$\lim_{t\to\infty} \int_0^t dt'\, \psi_N(t') = 0$$

These two cases illustrate the two possibilities discussed in the introduction: either $\lim_{t\to\infty} \int_0^t dt'\, \psi_N(t')$ does not exist (case *a*) or if it does exist, it must be zero (case *b*).

APPENDIX

In this appendix, we calculate $\psi_N(t)$ for times t in the range $0 \leqslant t \leqslant T/2 = L/c$ and $h_0(v)$ given in Eq. (21).

First of all, we must use the reflecting boundary conditions to specify the equations of motion. In the time interval $[0, T/2]$, each trajectory makes one and only one intersection with the walls of the system. For a trajectory which starts at r with velocity c,

$$v(t) = c, \qquad r(t) = r + ct \qquad \text{for} \quad 0 \leqslant t \leqslant (L - r)/c$$

and

$$v(t) = -c, \qquad r(t) = 2L - r - ct \qquad \text{for} \quad (L - r)/c \leqslant t \leqslant L/c$$

At this point, it is convenient to define a length λ by $t = \lambda/c$ so that $0 \leqslant \lambda \leqslant L$. Then, the previous equations can be written as

$$v(t) = +c, \qquad r(t) = r + \lambda \qquad \text{for} \quad 0 \leqslant r \leqslant L - \lambda \tag{A.1}$$

and

$$v(t) = -c, \qquad r(t) = 2L - r - \lambda \qquad \text{for} \quad L - \lambda \leqslant r \leqslant L \tag{A.2}$$

Similarly, for a trajectory which starts at r with velocity $-c$,

$$v(t) = -c, \qquad r(t) = r - \lambda \qquad \text{for} \quad \lambda \leqslant r \leqslant L \tag{A.3}$$

and

$$v(t) = c, \qquad r(t) = \lambda - r \qquad \text{for} \quad 0 \leqslant r \leqslant \lambda \tag{A.4}$$

In calculating the statistical average of any quantity, we first do the velocity integrals which determine whether the trajectories start with velocities $+c$ or $-c$. The integrals over positions are then divided into ranges according to Eqs. (A.1) and (A.2) or Eqs. (A.3) and (A.4) and the corresponding equations of motion are used. As an example, from Eq. (13),

$$\begin{aligned}E_\theta(R, r \mid \lambda/c) = (1/2L) \int_0^L dy\, [&\epsilon(\lambda - y)\, e^{i\theta\epsilon(R+y-\lambda)} \\ &+ \epsilon(y - \lambda)\, e^{i\theta\epsilon(R+\lambda-y)} + \epsilon(L - \lambda - y)\, e^{i\theta\epsilon(R-\lambda-y)} \\ &+ \epsilon(y + \lambda - L)\, e^{i\theta\epsilon(R+\lambda+y-2L)}]\, e^{-i\theta\epsilon(r-y)}\end{aligned}$$

where ϵ is the step function defined in Eq. (10). When the integrals are evaluated, we find

$$\begin{aligned}&E_\theta(R, r \mid \lambda/c) \\ &\quad = 1 + i(\sin\theta)[(R - r)/L] \\ &\qquad - (1 - \cos\theta)(1/L)[\lambda + \epsilon(R - \lambda - r)(R - \lambda - r) + \epsilon(r - \lambda - R)(r - \lambda - R) \\ &\qquad - \epsilon(\lambda - R - r)(\lambda - R - r) - \epsilon(\lambda + R + r - 2L)(\lambda + R + r - 2L)]\end{aligned} \tag{A.5}$$

so that

$$\begin{aligned}E_\theta(R, r \mid \lambda/c) &= E_\theta(L - r, L - R \mid \lambda/c) \\ &= E_\theta{}^*(r, R \mid \lambda/c)\end{aligned} \tag{A.6}$$

We now go back to Eq. (14) for $\psi_N(t)$, substitute $h_0(v)$ from Eq. (21), do the velocity integrals, divide the position integrals into ranges, and use the equations of motions and the properties of E_θ above. Then we get

$$\begin{aligned}\psi_N(\lambda/c) = \frac{c^2}{L}\, \frac{Re}{2\pi} \int_0^{2\pi} d\theta \int_0^L dy\, [&\epsilon(y - \lambda)\, E_\theta(y - \lambda, y \mid \lambda/c)^{N-1} \\ &- \epsilon(\lambda - y)\, E_\theta(\lambda - y, y \mid \lambda/c)^{N-1}] \\ &+ (N - 1)\frac{c^2}{2L^2}\, \frac{\mathrm{Re}}{2\pi} \int_0^{2\pi} d\theta \int_0^L dy \int_0^L dz\, \{\epsilon(y - \lambda) \\ &\times [-\epsilon(\lambda - z)\, e^{-i\theta\epsilon(y-z-\lambda)} + \epsilon(L - \lambda - z)\, e^{i\theta[\epsilon(z+\lambda-y)-\epsilon(y-z-\lambda)]} \\ &- \epsilon(z - \lambda)\, e^{i\theta[\epsilon(\lambda+z-y)-\epsilon(y+\lambda-z)]} + \epsilon(z + \lambda - L)\, e^{i\theta\epsilon(2L-\lambda-y-z)}] \\ &+ \epsilon(\lambda - y)[-\epsilon(\lambda - z) + \epsilon(L - \lambda - z)\, e^{i\theta\epsilon(y+z-\lambda)} \\ &- \epsilon(z - \lambda)\, e^{i\theta\epsilon(z-\lambda-y)} + \epsilon(z + \lambda - L)\, e^{i\theta[\epsilon(y+z-\lambda)-\epsilon(y+z+\lambda-2L)]}]\} \\ &\times E_\theta(z, y \mid \lambda/c)^{N-2}\end{aligned} \tag{A.7}$$

The curly bracket in the second term of this equation can be reduced to

$$-\epsilon(y + \lambda - z)\, \epsilon(z + \lambda - y)\, \epsilon(y + z - \lambda)\, \epsilon(2L - y - z - \lambda)(1 - e^{i\theta})$$

so that when Eq. (A.5) is used for E_θ and the step functions eliminated, $\psi_N(\lambda/c)$ becomes

$$\begin{aligned}\psi_N(\lambda/c) = \frac{c^2}{L^N}\frac{\text{Re}}{2\pi}\int_0^{2\pi} d\theta \Big[&(L-\lambda)(L-\lambda+\lambda e^{i\theta})^{N-1} \\ &-\int_0^\lambda dx\,[L-\lambda+(\lambda-x)\,e^{i\theta}+xe^{-i\theta}]^{N-1} \\ &-(N-1)(1-\cos\theta)(L-\lambda) \\ &\times\int_0^\lambda dx\,(L-\lambda+(\lambda-x)\,e^{i\theta}+xe^{-i\theta})^{N-2}\Big]. \end{aligned} \tag{A.8}$$

If we define

$$g_{N-1}(\lambda) = (1/2\pi)\,\text{Re}\int_0^{2\pi} d\theta \int_0^\lambda dx\,[L-\lambda+(\lambda-x)\,e^{i\theta}+xe^{-i\theta}]^{N-1} \tag{A.9}$$

then Eq. (A.8) can be written in the compact form

$$\psi_N(\lambda/c) = (c^2/L^N)(d/d\lambda)[(L-\lambda)\,g_{N-1}(\lambda)] \tag{A.10}$$

It is now a simple matter to evaluate the integrals in (A.9) and obtain $\psi_N(\lambda/c)$ from (A.10). The result is

$$g_{N-1}(\lambda) = (1/2N)[L^N-(L-2\lambda)^N]$$

so that

$$\psi_N\left(\frac{\lambda}{c}\right) = c^2\left\{\left(1-\frac{\lambda}{L}\right)\left(1-\frac{2\lambda}{L}\right)^{N-1}-\frac{1}{2N}\left[1-\left(1-\frac{2\lambda}{L}\right)^N\right]\right\} \tag{A.11}$$

If we now put

$$t = \lambda/c = xL/c$$

then

$$\psi_N(t) = c^2\{(1-x)(1-2x)^{N-1}-(1/2N)[1-(1-2x)^N]\} \tag{A.12}$$

which is the expression quoted in the text.

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