BRIEF REPORTS

Brief Reports are accounts of completed research which do not warrant regular articles or the priority handling given to Rapid Communications; however, the same standards of scientific quality apply. (Addenda are included in Brief Reports.) A Brief Report may be no longer than $3\frac{1}{2}$ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Small systems have non-Maxwellian momentum distributions in the microcanonical ensemble

John R. Ray and H. W. Graben
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634-1911
(Received 19 June 1991)

The distribution of particle momentum in the canonical ensemble has the well-known Maxwell form. In the microcanonical ensemble this is not the case and the distribution of particle momentum has a different form that approaches the Maxwell form in the thermodynamic limit. Besides their intrinsic interest, these results could be of importance in studies of small systems, such as clusters. Exact results are illustrated for rigid rods, disks, and spheres.

PACS number(s): 05.20.Gg, 05.70.Ce

In the classical canonical ensemble the momentum of a particle $\mathbf{p}_a$ is distributed within $d^f p_a$ according to the Maxwell distribution w_c

$$w_c = \frac{e^{-K_a/k_B T}}{(2\pi m_a k_B T)^{f/2}} \tag{1}$$

where $K_a = p_a^2/2m_a$ is kinetic energy of particle a, m_a is the particle mass, T is the temperature of the reservoir, and f is the dimensionality of the space ($f=1$, 2, or 3). The probability distribution for the momentum of a particle in the microcanonical ensemble is not as simple as Eq. (1). In this paper we shall derive and discuss the probability distribution for momentum in the microcanonical ensemble. Since computer simulation studies, such as molecular dynamics, generate the microcanonical ensemble the form of the momentum distribution is important for the analysis of these simulations, especially in the case of small system size as, for example, cluster studies. All of our discussions refer to classical equilibrium statistical mechanics. The probability distribution of momentum in nonequilibrium processes such as collisions is not discussed.

The phase-space probability distribution for the microcanonical ensemble w_m is

$$w_m = \frac{\delta(E-H)}{\omega(E)} , \tag{2}$$

where the normalization integral has the form

$$\omega(E) = \int \delta(E-H) d^{fN}q \, d^{fN}p , \tag{3}$$

The probability density for the momentum $\mathbf{p}_a$ is obtained by integrating the probability density over all the variables except this momentum

$$w_m(\mathbf{p}_a) = \frac{\int \delta(E-H) d^{fN}q \, d^{f(N-1)}p}{\int \delta(E-H) d^{fN}q \, d^{fN}p} = \frac{N(E,\mathbf{p}_a)}{D(E)} , \tag{4}$$

where in the numerator all momenta except $\mathbf{p}_a$ are integrated over. Equation (4) can be evaluated by carrying out separate Laplace transforms, with respect to the energy, of both the numerator and denominator, evaluating the momenta integrals, which are Gaussian, and then carrying out the inverse Laplace transforms [1–3]. Here we assume the Hamiltonian has the form $H = K(p) + U(q)$, where U is the potential energy of the interacting system of N particles. Upon carrying out the Laplace transform on the numerator $N(E,\mathbf{p}_a)$, performing the momentum integrals, and inverting we obtain

$$N(E,\mathbf{p}_a) = \frac{\prod_{b=1}^{N} (2\pi m_b)^{f/2} \int (E^* - U)^{[f(N-1)-2]/2} \Theta(E^* - U) d^{fN}q}{(2\pi m_a)^{f/2} \Gamma\left[\frac{f(N-1)}{2}\right]} ; \tag{5}$$

the gamma function Γ appears in the denominator, $\Theta(x)$ is the generalized step function, and $E^* = E - K_a$. For the denominator of Eq. (4) we obtain

$$D(E)=\frac{\prod_{b=1}^{N}(2\pi m_b)^{f/2}\int(E-U)^{(fN-2)/2}\Theta(E-U)d^{fN}q}{\Gamma(fN/2)}\ . \tag{6}$$

Dividing Eq. (5) by Eq. (6) we obtain the desired momenta probability distribution in the form

$$w_m(\mathbf{p}_a)=\frac{\Gamma(fN/2)\int(E^*-U)^{[f(N-1)-2]/2}\Theta(E^*-U)d^{fN}q}{(2\pi m_a)^{f/2}\Gamma(f(N-1)/2)\int(E-U)^{(fN-2)/2}\Theta(E-U)d^{fN}q}\ . \tag{7}$$

Note that in the canonical ensemble derivation of w_c in Eq. (1) the configuration integrals cancel from the numerator and denominator, and one has the simple Maxwell form for the probability distribution. Equation (7) can be written as an average value over the configuration probability density $C(E-U)^{(fN-2)/2}$, where C is a normalization constant

$$w_m(\mathbf{p}_a)=\frac{\Gamma(fN/2)\left\langle\frac{[1-K_a/(E-U)]^{[f(N-1)-2]/2}}{(E-U)^{f/2}}\right\rangle}{(2\pi m_a)^{f/2}\Gamma(f(N-1)/2)}\ , \tag{8}$$

and the angular brackets indicate an average over the configuration probability density $C(E-U)^{(fN-2)/2}$. The configuration probability density $C(E-U)^{(fN-2)/2}$ is appropriate for microcanonical ensemble Monte Carlo calculations, as has been recently discussed [4]. Equation (8) represents the exact single-particle momentum distribution in the microcanonical ensemble in f dimensions. In order to evaluate this probability distribution for a particular value of the momentum we must calculate the configuration integrals indicated in Eq. (8). Because of this the canonical ensemble momentum distribution given in Eq. (1) is considerably simpler than the microcanonical version which depends on the potential U.

In the thermodynamic limit the microcanonical probability distribution given in Eq. (8) must merge into the Maxwell distribution since the infinite system may be considered as a temperature reservoir for the single particle. Taking the large-N limit, the leading term in Eq. (8) is

$$w_m(\mathbf{p}_a)=\frac{\Gamma(fN/2)e^{-fNK_a/2\langle K\rangle}}{(2\pi m_a)^{f/2}\Gamma(f(N-1)/2)\langle K\rangle^{f/2}}\ . \tag{9}$$

Upon inserting $\langle K\rangle=fNk_BT/2$ in Eq. (9) and using the asymptotic form of the Γ function, we see that the canonical distribution given in Eq. (1) is attained.

Since the probability distribution for momentum is different in the canonical and microcanonical ensembles, the average values of powers higher than second are in general different; however, the second-order moments are the same by the equipartition theorem. For the average of the fourth power of the momentum of a particle we obtain in the two different ensembles the exact results

$$\langle p_{ax}^4\rangle_c=3(m_ak_BT)^2 \tag{10}$$

and

$$\langle p_{ax}^4\rangle_m=3(m_ak_BT)^2\left[1+\frac{2}{fC_V^*(fN/2+1)}\right]\ , \tag{11}$$

where $C_V^*=C_V/Nk_B$ is the dimensionless specific heat. The difference in the results for the average of the fourth power of the momentum of a particle is of order $(1/N)$, which we expect for two different ensembles. Of course, the two expressions are the same in the thermodynamic limit.

The momentum distribution function in the microcanonical ensemble can be expressed explicitly for a system of nonattracting, impenetrable particles of size with $f=1$ for rigid rods, $f=2$ for rigid disks, and $f=3$ for rigid spheres. In Eq. (7) the limits of integration in the configuration integrals in the numerator and denominator are governed by the respective generalized step functions alone. For impenetrable particles, only the spatial domain with $U=0$ contributes to the volume of these configuration integrals; therefore both fN-fold integrals cover the same domain. Upon removing the constant factors of $(E^*)^{[f(N-1)-2]/2}$ and $E^{(fN-2)/2}$ from the integrands, we are left with the ratio of two equivalent integrals which need not be evaluated. The result is

$$w_m(\mathbf{p}_a)=\frac{\Gamma(fN/2)[1-p_a^2/(2m_aE)]^{[f(N-1)-2]/2}}{\Gamma(f(N-1)/2)(2\pi m_aE)^{f/2}}\ . \tag{12}$$

This expression is the same as that for an ideal gas [5] in the microcanonical ensemble. The maximum value of p_a^2 is $2m_aE$ in Eq. (12), whereas, no upper bound is required in the canonical ensemble expression Eq. (1).

To compare the microcanonical distribution function to that of the canonical ensemble, we examine the one dimensional case with $\mathbf{p}_a$ replaced by p_x. The canonical distribution function is given by

$$w_c(p_x)=e^{-p_x^2/p_0^2}/\sqrt{\pi}p_0\ , \tag{13}$$

where $p_0^2=2m_ak_BT$. For the microcanonical form we set $E=Nk_BT/2$ and $f=1$ in Eq. (12) to obtain

$$w_m(p_x,N)=\frac{C(N)[1-p_x^2/(p_0^2N/2)]^{(N-3)/2}}{\sqrt{\pi}p_0}\ , \tag{14}$$

where

$$C(N)=\frac{\Gamma(N/2)}{\sqrt{N/2}\,\Gamma((N-1)/2)}\ . \tag{15}$$

The ratio of $w_m(0,N)$ to $w_c(0)$ is just $C(N)$, which edges up from $C(4)=\sqrt{2/\pi}$ to unity as N becomes large, as shown in Fig. 1; for $N=76$ the difference is close to 1%.

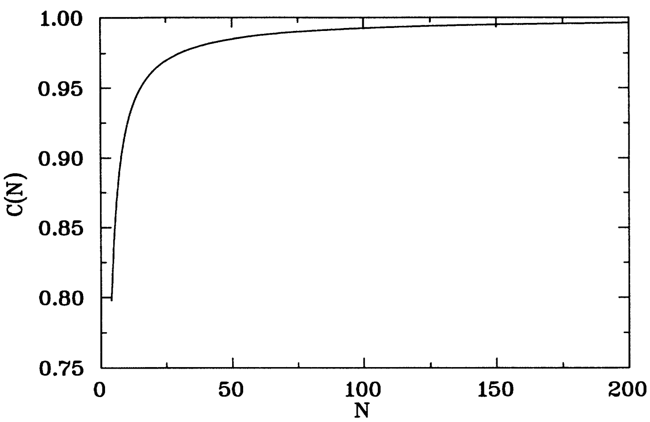

FIG. 1. The ratio of $w_m(0,N)/w_c(0)$ vs N for rigid rods.

The binomial term in Eq. (14) approaches the behavior of the exponential term in Eq. (13) as N tends to infinity. Plots of w_m and w_c vs p_x/p_0 for $N=4$, 6, 12, and 20 are shown in Fig. 2, along with the corresponding curve for the Maxwell distribution. For $N=20$ the two distributions are similar with the maximum difference being about 4% at the peak.

In this paper we have presented and discussed the momentum probability distribution for a particle in the microcanonical ensemble. Besides the intrinsic interests, some computer simulations generate the microcanonical ensemble and therefore these results are of importance for studies of small systems in these simulations. Sometimes in molecular-dynamics discussions one finds a numerical calculation of the momentum probability distribution of particles (a histogram of particle momenta) and various moments of this distribution along with a comparison of the distribution and moments to the Maxwell distribution and its moments. The agreement between the two distributions and moments is used as evidence that the system is in thermal equilibrium and generates the proper ensemble. It might be concluded from these discussions that the Maxwell distribution is the exact momentum distribution for the microcanonical ensemble. As we have shown Eq. (8) represents the exact momentum probability distribution for the microcanonical ensemble. In the thermodynamic limit, which is approximately valid in most of the molecular-dynamics discussions mentioned above, the exact microcanonical distribution goes over into the Maxwell distribution as indicated in Eq. (9) and Figs. 1 and 2. For small systems, clusters, the difference between the two distributions, could be of importance.

A comparison of w_m to w_c has been presented in detail for a one-dimensional system of rigid rods, namely, the Tonks gas; the maximum difference is about 1% for $N=76$. It is interesting to note that $w_m(\mathbf{p}_a)$ in two and three dimensions is not simply a product of component distributions, which is the case for the canonical ensemble. In canonical ensemble theory the components of $\mathbf{p}_a$ are unbounded in value, whereas the constraint $K=E-U$, with $E=$const, must be met in the microcanonical theory. The equivalence between $w_m(\mathbf{p}_a)$ and the product of the component forms holds only in the limit as N tends to infinity.

In molecular dynamics, besides the energy being constant, the total linear momentum of the system is also constant. Thus we should be dealing with the

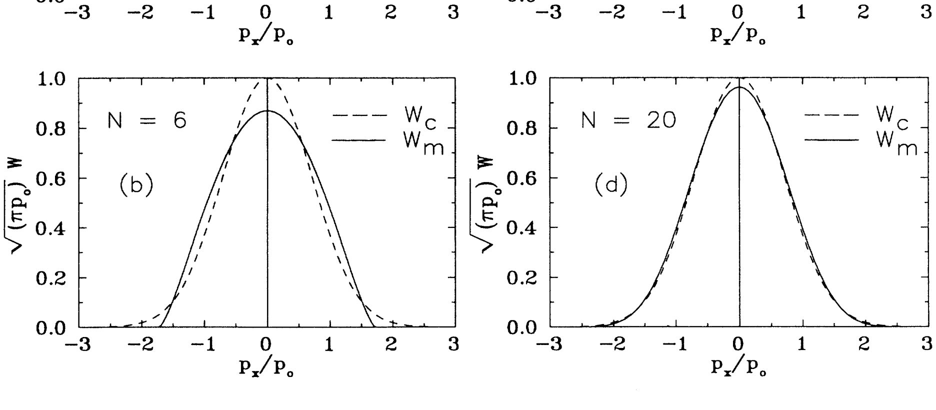

FIG. 2. The functions w_m and w_c vs p_x/p_0 for various values of N for rigid rods.

molecular-dynamics ensemble [3] instead of the microcanonical ensemble. This would give further changes in the form of Eq. (8), which we leave for the interested reader to derive.

If one carries out molecular dynamics in the canonical ensemble using Nosé's [6] approach, then the single-particle momenta would have the probability distribution given by Eq. (1) except, again, for corrections due to conservation of total linear momentum [7]. Results similar to the results of this paper could also be derived in the other microcanonical-like shell ensembles of classical statistical mechanics [8].

[1] E. M. Pearson, T. Halicioglu, and W. A. Tiller, Phys. Rev. A **32**, 3030 (1985).
[2] F. O. Raineri and H. L. Friedman, J. Chem. Phys. **91**, 5642 (1989).
[3] T. Çağin and J. R. Ray, Phys. Rev. A **37**, 247 (1988).
[4] J. R. Ray, Phys. Rev. A **44**, 4061 (1991).
[5] A. Schluter, Z. Naturforsch. A **3**, 350 (1948).
[6] S. Nosé, Mol. Phys. **52**, 255 (1984); J. Chem. Phys. **81**, 298 (1984).
[7] T. Çağin and J. R. Ray, Phys. Rev. A **37**, 4510 (1988).
[8] H. W. Graben and J. R. Ray, Phys. Rev. A **43**, 4100 (1991).