Probability Densities for Some One-Dimensional Problems in Statistical Mechanics

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1. Introduction

The statistical mechanics of the real three-dimensional world is generally too difficult to allow us to obtain analytic results for the structural and other properties of matter. A few problems, most of them variants of the Ising model, can be solved for two-dimensional systems, but it is only for one-dimensional systems that analytic results can be obtained in profusion (Lieb and Mattis 1966). There is a heavy price to pay for this simplification since many features of the real world, such as transitions between the different phases of matter, are absent in one-dimensional systems with intermolecular forces of realistic range. If, however, we are interested in the behaviour of fluids near planar solid walls or in slits between parallel walls (e.g. Kjellander and Sarman 1988) then we wish to know only how the properties change with distance in the one direction perpendicular to the wall(s), since the system will generally be translationally invariant in the two directions parallel to the wall(s). The behaviour of one-dimensional systems mimics these three-dimensional systems reasonably realistically. Here we consider several such systems, in different thermodynamic ensembles, in order to obtain explicit expressions for the probability densities for the number of molecules in a system of fixed length or for the length in a system of fixed number of molecules. Most previous work on one-dimensional systems has considered only the so-called thermodynamic limit, that is the limit of infinite size but finite non-zero density. Here the emphasis is on finite systems although comparisons are made with infinite systems. The analogy of such systems with the counting rates of Geiger counters is also explored. Such devices have for a long time aroused the interest of those working on probability theory (Kosten 1943; Malmquist 1947; Feller 1948; Hammersley 1953; Albert and Nelson 1953).

2. Thermodynamic Ensembles

The most primitive thermodynamic ensemble is a totally closed system of fixed number of molecules of each species, N_α, of fixed volume, V, and of fixed energy, U. Its characteristic function is the entropy $S(\mathbf{N}, V, U)$. Here $\mathbf{N}$ denotes the set of N_α. More useful are the two canonical ensembles of fixed temperature, T, one of constant volume and the other of constant pressure, for which the characteristic functions are the Helmholtz and Gibbs free energies, $A(\mathbf{N}, V, T)$ and $G(\mathbf{N}, p, T)$. The pressure fluctuates about its mean value in the constant volume ensemble, and vice versa. In the grand canonical ensemble the activity ζ_α (or its logarithm, the ratio of chemical potential to temperature, $\mu_\alpha/kT = \ln \zeta_\alpha$) is specified for each species but the numbers of molecules fluctuate; the characteristic function is the grand potential, $\Omega(\zeta, V, T)$. In the thermodynamic limit this is equal to $-pV$ in a homogeneous system, but in a finite inhomogeneous system it can also contain terms proportional to area, length etc. (see below). The reduced variance of the number of molecules in a one-component grand ensemble, $(\overline{N^2} - \overline{N}^2)/\overline{N}^2$, is proportional to N^{-1}, but is nevertheless of physical interest. Thus if k is Boltzmann's constant we have in the thermodynamic limit

$$\frac{\overline{N^2} - \overline{N}^2}{\overline{N}^2} = -\frac{kT}{V^2}\left(\frac{\partial V}{\partial p}\right)_{T,\overline{N}}, \tag{2.1}$$

and so the variance is proportional to the compressibility.

The grand ensemble of fixed pressure is not properly specified since all its variables, ζ, p and T, are intensive and so its size is undetermined. Moreover its characteristic function would be zero by virtue of the Gibbs-Duhem equation which requires that

$$\sum_\alpha N_\alpha d(\ln \zeta_\alpha) - V dp + S dT = 0. \tag{2.2}$$

Each characteristic function is related to the energy $\mathcal{U}(\mathbf{r}^N)$ of N molecules at positions $\mathbf{r}^N$ through the appropriate partition function, Z. Thus

$$\begin{aligned} A &= -kT \ln Z(\mathbf{N}, V, T), \\ G &= -kT \ln Z(\mathbf{N}, p, T), \\ \Omega &= -kT \ln Z(\zeta, V, T); \end{aligned} \tag{2.3}$$

$$\begin{aligned} Z(\mathbf{N}, V, T) &= n_0^N \bigl(\prod_\alpha N_\alpha!\bigr)^{-1} \int_V d\mathbf{r}^N e^{-\mathcal{U}(\mathbf{r}^N)/kT}, \\ Z(\mathbf{N}, p, T) &= n_0 \int_0^\infty dV \; Z(\mathbf{N}, V, T) e^{-pV/kT}, \\ Z(\zeta, V, T) &= \sum_{N=0} Z(\mathbf{N}, V, T) \prod_\alpha \zeta_\alpha^{N_\alpha}. \end{aligned} \tag{2.4}$$

The density n_0 is introduced to ensure that all the partition functions are dimensionless. We shall see that its size does not affect the value of observable thermodynamic properties. The sum in $Z(\zeta, V, T)$ is over all values of N_α, N_β etc. The Laplace transform that defines $Z(\mathbf{N}, V, T)$ was used in the treatment of one-dimensional systems by Takahashi (1942) and, more recently, by Percus (1982), Bishop and Boonstra (1983) and Finn and Monson (1988).

Since $\Omega = -pV$ for a homogeneous system, it follows that $Z(\zeta, V, T)$ diverges exponentially with volume, that is, as $\exp(pV/kT)$. So we can introduce a function $Z(\zeta, P, T)$ by the equation

$$Z(\zeta, P, T) = n_0 \int_0^\infty dV \; Z(\zeta, V, T) e^{-PV/kT}, \tag{2.5}$$

which becomes infinite as P approaches p. From the nature of this approach one can deduce the behaviour of a one-dimensional system in the thermodynamic limit (Rushbrooke and Ursell 1948; Longuet-Higgins 1958). The important result, for a system of pair-wise additive intermolecular potentials is

$$\Delta(\zeta, p, T) \equiv \begin{vmatrix} \zeta_a \eta_{aa} - 1 & \zeta_a \eta_{ab} & \cdots \\ \zeta_b \eta_{ba} & \zeta_b \eta_{bb} - 1 & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0, \tag{2.6}$$

where

$$\eta_{\alpha\beta} = n_0 \int_0^\infty dr \; e^{-u_{\alpha\beta}(r)/kT} e^{-pr/kT}, \tag{2.7}$$

where $u_{\alpha\beta}(r)$ is the energy of a pair of molecules on a line with α to the left of β, and separated by a distance r. If the line forms a circle then we speak of clockwise and anti-clockwise interactions. The canonical partition function for the line is a $(N+1)$-fold convolution, and for the circle a N-fold convolution of the Boltzmann factors $\exp[-u_{\alpha\beta}(r)/kT]$. The extra factor in the first case arises from the interaction of the molecules with the fixed boundaries. Hence $Z(\mathbf{N}, p, T)$ is the $(N+1)$- or N-fold product of the appropriate factors $\eta_{\alpha\beta}$, and, from the relation of Z to the Gibbs free energy, it follows that for a pure substance η^{-1} is the activity ζ. For a binary system with $\eta_{ab} = \eta_{ba}$, we have

$$\Delta = 1 - \zeta_a \eta_{aa} - \zeta_b \eta_{bb} + \zeta_a \zeta_b (\eta_{aa} \eta_{bb} - \eta_{ab}^2) = 0. \tag{2.8}$$

There is an important class of systems for which the last term vanishes. For example, if we have a mixture of hard rods of lengths ρ_a and ρ_b then

$$u_{aa}(r) = \infty \;\; \text{if } r < \rho_a, \quad u_{bb} = \infty \;\; \text{if } r < \rho_b, \tag{2.9}$$

and

$$u_{ab}(r) = \infty \quad \text{if } r < \tfrac{1}{2}(\rho_a + \rho_b),$$

and all are zero otherwise. For such a system

$$\eta_{ab} = \pi^{-1} \exp\left[-\tfrac{1}{2}\pi n_0(\rho_a + \rho_b)\right] = (\eta_{aa}\eta_{bb})^{1/2}, \quad \pi = p/n_0kT. \qquad (2.10)$$

If there are c components then

$$\Delta = 1 - \pi^{-1} \sum_{\alpha=1}^{c} \zeta_\alpha e^{-\pi\rho_\alpha} = 0. \qquad (2.11)$$

This equation and that for the densities, n_α,

$$n_\alpha = -(\partial\Delta/\partial \ln \zeta_\alpha)/(\partial\Delta/\partial\pi), \qquad (2.12)$$

have the solutions

$$\begin{aligned} n_0\pi &= \sum_\alpha n_\alpha \bigg/ \left(1 - \sum_\alpha \rho_\alpha n_\alpha\right), \\ \zeta_\alpha &= \pi n_\alpha e^{\pi\rho_\alpha} \bigg/ \sum_\alpha n_\alpha. \end{aligned} \qquad (2.13)$$

Another system of interest is the penetrable sphere model (Widom and Rowlinson 1970; Hammersley, Lewis and Rowlinson 1975; Rowlinson 1980) the primitive form of which is a binary mixture with

$$\begin{aligned} u_{aa}(r) = u_{bb}(r) &= 0 \quad \text{for all } \ r, \\ u_{ab}(r) = \infty \ \text{ if } \ r < \rho/2 &\ \text{ and zero otherwise.} \end{aligned} \qquad (2.14)$$

It is now convenient to choose $n_0 = \rho^{-1}$, so that n is a dimensionless density. The equation $\Delta = 0$ takes the form

$$(\pi - \zeta_a)(\pi - \zeta_b) = \zeta_a\zeta_b e^{-\pi}, \qquad (2.15)$$

and

$$\pi = \frac{n_a\zeta_a - n_b\zeta_b}{n_a - n_b}, \qquad (2.16)$$

$$n_a^{-1} = \pi^{-1} + \frac{(1 + \pi - \zeta_b)}{(\pi - \zeta_b)(1 + e^\pi(\pi - \zeta_b)/\zeta_b)}, \qquad (2.17)$$

together with a corresponding equation for n_b^{-1} in terms of ζ_a.

These results are for the primitive or two-component version of the penetrable sphere model. The name itself belongs to the transcribed or one-component version which is obtained by integrating over all positions of the molecules of one species (say b) in the grand partition function. We have then a system with an intermolecular energy that is now negative (or attractive) for all configurations. It is given by

$$\mathcal{U}(\mathbf{r}^N) = \mathcal{W}(\mathbf{r}^N) - N, \tag{2.18}$$

where $\mathcal{W}(\mathbf{r}^N)$ is the total volume covered by N freely penetrating spheres of unit volume (or rods of unit length, etc.) at positions denoted by $\mathbf{r}^N$. If the molecules are well separated then $\mathcal{U}$ is zero, but if they are close it is negative, and it has a minimum value of $(1-N)$ when all the molecules are at the same position.

3. Finite Systems

The results above are either already known or are simple extensions of what is known. Of more current interest are finite systems for which the properties calculated from the several thermodynamic ensembles are significantly different. It is now difficult to handle a multi-component system of hard rods with any generality since the maximum number of molecules that can be accommodated on a line of finite length is a discontinuous function of composition. A case for which there is a simple explicit solution is a binary mixture of rods of unit length (species a) and points of zero length (species b), the centres of the former of which are confined to a line of length L_a, and the latter to the same line, but to a length L_b of it, symmetrically chosen with respect to L_a. If the boundaries are formed from fixed molecules, of either species, then $L_b = L_a + 1$, but we can equally well consider the slightly more general case $L_b \geq L_a + 1$. We have now

$$Z(N_a, N_b, L_a, L_b) = (L_a - N_a + 1)^{N_a}(L_b - N_a)^{N_b}/N_a!\,N_b!, \qquad L_a \geq N_a - 1. \tag{3.1}$$

The partition function is not a function of temperature, because of the nature of the potential energy of a system of hard rods, and so this variable is omitted. The grand partition function is

$$Z(\zeta_a, \zeta_b, L_a, L_b) = \sum_{N_a=0}^{[L_a+1]} \sum_{N_b=0}^{\infty} \frac{[\zeta_a(L_a - N_a + 1)]^{N_a}[\zeta_b(L_b - N_a)]^{N_b}}{N_a!\,N_b!} \tag{3.2}$$

where $[L_a + 1]$ is the integral part of $L_a + 1$. The summation over N_b can be made at once to give

$$Z(\zeta_a, \zeta_b, L_a, L_b) = e^{\zeta_b L_b} \sum_{N_a=0}^{[L_a+1]} \frac{[\zeta_a e^{-\zeta_b}(L_a - N_a + 1)]^{N_a}}{N_a!}. \tag{3.3}$$

The sum is now the partition function for a one-component system of rods of unit length, on a line of length L_a, at an activity of $\zeta_a e^{-\zeta_b}$. This we know already (Robledo and Rowlinson 1986).

$$\begin{aligned} Z(\zeta_a, \zeta_b, L_a, L_b) &= e^{\zeta_b L_b} Z(\zeta_a e^{-\zeta_b}, L_a) \\ &= n_a^* \left(\frac{1-n_a}{n_a}\right) \exp\left[\zeta_b L_b + \frac{n_a(L_a+1)}{1-n_a}\right], \end{aligned} \tag{3.4}$$

where n_a is the density of this pure substance in an infinite system at an activity $\zeta_a e^{-\zeta_b}$, and n_a^* is the density of the same substance at the same activity in a semi-infinite system at a distance L_a+1 from the one boundary. If L_a is greater than about 4 then n_a^* is almost indistinguishable from n_a, but it is very different in smaller systems.

It follows from equation (3.4) that in the thermodynamic limit we have

$$\zeta_a e^{-\zeta_b} = \left(\frac{n_a}{1-n_a}\right) \exp\left(\frac{n_a}{1-n_a}\right), \quad \zeta_b = \frac{n_b}{1-n_a}, \tag{3.5}$$

or

$$\zeta_a = \left(\frac{n_a}{1-n_a}\right) \exp\left(\frac{n_a+n_b}{1-n_a}\right). \tag{3.6}$$

It follows from equation (2.13), that ζ_a is therefore also the activity of component a in the original mixture (in the thermodynamic limit) at densities n_a and n_b. Thus n_a is both the density of a in the original system at an activity ζ_a, and that of substance a in the hypothetical one-component system at an activity $\zeta_a e^{-\zeta_b}$.

In the finite system

$$Z(\zeta_a, \zeta_b, L_a, L_b) = \frac{n_a^*(1-n_a)}{n_a} \exp\left[\frac{n_a(L_a+1)+n_b L_b}{1-n_a}\right], \tag{3.7}$$

and

$$\pi = \frac{n_a+n_b}{1-n_a} = \zeta_a e^{-\pi} + \zeta_b, \tag{3.8}$$

where π, n_a, and n_b are the pressure-to-temperature ratio and the densities of the infinite system at the same activities, ζ_a and ζ_b, as the finite system. The negative of the grand potential, $-\Omega$, is equal to pL, where $L \sim L_a$, L_b, together with two 'end-effects' that are the one-dimensional analogues of the surface tension, γ, of a fluid against a wall. We can re-write equation (3.7) as

$$-\Omega(\zeta_a, \zeta_b, L_a, L_b)/kT = \pi L - 2\gamma/kT + O(L)^{-1}, \tag{3.9}$$

where π is given by equation (3.8) and

$$2\gamma/kT = \frac{n_a(L_a-L+1)+n_b(L_b-L)}{(1-n_a)} + \ln(1-n_a), \tag{3.10}$$

and where the difference between n_a^* and n_a has been lost in the term of $O(L)^{-1}$. Clearly if γ is defined as an 'excess' or surface contribution to the grand potential then it is not determined precisely, since L is arbitrary, a conclusion that has been drawn also for more general cases (McQuarrie and Rowlinson 1987). If $\zeta_b = 0$ then the natural choice is $L = L_a$, when

$$2\gamma/kT = \frac{n_a}{1-n_a} + \ln(1-n_a) < 0, \tag{3.11}$$

a result that has been obtained also by Henderson (1983) by a different route. If $\zeta_a = 0$ then we choose $L = L_b$ to give $\gamma = 0$. There is no obviously natural choice for a mixture.

4. Probability Densities

We now obtain the probability densities for grand and constant-pressure ensembles, which may be written $\mathcal{P}_V(N)$ and $\mathcal{P}_N(V)$ respectively since the first is the probability of finding N molecules in a system of fixed V (at specified ζ and T), and the second is the probability density of finding V to lie between V and $V + dV$ in a system of fixed N (at specified π and T). In the thermodynamic limit we can show that these functions have the same algebraic form. (We cannot say that they are the same function, since the first is a discrete function of N and the second a continuous function of V.)

The general expressions are, for a system of one component,

$$\mathcal{P}_{V,T,\zeta}(N) = \frac{Z(N,V,T)\zeta^N}{\sum_{N=0}^{\infty} Z(N,V,T)\zeta^N} = \frac{Z(N,V,T)\zeta^N}{Z(\zeta,V,T)}, \tag{4.1}$$

$$\mathcal{P}_{N,T,\pi}(V) = \frac{Z(N,V,T)e^{-pV/kT}}{\int_0^{\infty} dV\, Z(n,V,T)e^{-pV/kT}} = \frac{n_0 Z(N,V,T)e^{-pV/kT}}{Z(N,\pi,T)}, \tag{4.2}$$

where n_0 is the density introduced in the definition of the partition functions in equation (2.4). In the thermodynamic limit the partition functions are related to the thermodynamic functions by equation (2.3), so, with an abbreviation of the subscripts,

$$\frac{\mathcal{P}_N(V)}{\mathcal{P}_V(N)} = n_0 \exp[-(pV + N\mu)/kT] \exp[(G-\Omega)/kT] = n_0. \tag{4.3}$$

Here $\zeta = \exp(\mu/kT)$ has been written out in full to show its relation to the function $G = N\mu$ in the thermodynamic limit. Thus $\mathcal{P}_N(V)$ and $\mathcal{P}_V(N)$ are the same thing, their ratio being a fixed density (see below). We shall see that this simple relation between the two probability densities is only slightly modified in the finite one-dimensional system.

The probability, in the binary system discussed above, of there being N_a molecules (rods) and N_b molecules (points) on a line of lengths L_a, L_b is proportional to the appropriate term in the grand partition function, as in equation (4.1).

$$\mathcal{P}_{\zeta_a,\zeta_b,L_a,L_b}(N_a,N_b) = \frac{[\zeta_a(L_a-N_a+1)]^{N_a}[\zeta_b(L_b-N_a)]^{N_b}}{N_a!\,N_b!\,Z(\zeta_a,\zeta_b,L_a,L_b)}, \qquad N_a \le [L_a+1]. \tag{4.4}$$

It follows that the conditional probability of there being N_b molecules, if the number of species a is fixed at N_a, is a Poisson distribution,

$$\mathcal{P}(N_b \mid N_a) = \frac{[\zeta_b(L_b-N_a)]^{N_b}}{N_b!} e^{-\zeta_b(L_b-N_a)}. \tag{4.5}$$

Since

$$\mathcal{P}(N_a,N_b) = \mathcal{P}(N_b \mid N_a)\cdot\mathcal{P}(N_a), \tag{4.6}$$

it follows that the absolute probability of there being N_a molecules in the system is

$$\begin{aligned}\mathcal{P}(N_a) &= \frac{e^{\zeta_b L_b}[\zeta_a e^{-\zeta_b}(L_a-N_a+1)]^{N_a}}{N_a!\,Z(\zeta_a,\zeta_b,L_a,L_b)}\\ &= \frac{(\pi-\zeta_b)^{N_a+1}(L_a-N_a+1)^{N_a}}{n_a^* N_a!}\exp[-(\pi-\zeta_b)(L_a-N_a+1)],\\ &\qquad N_a \le [L_a+1],\end{aligned} \tag{4.7}$$

where π is given by equation (3.8). This probability is independent of L_b since it has been assumed that $L_b \ge L_a + 1$.

If ζ_b is zero this reduces to the probability of finding N rods of unit length on a line of length L when the activity is ζ and where the pressure in an infinite system of the same activity is given by π;

$$\mathcal{P}_L(N) = \frac{\pi^{N+1}(L-N+1)^N}{n^* N!}\exp[-\pi(L-N+1)], \quad N \le [L+1], \tag{4.8}$$

where

$$\pi = \frac{n}{(1-n)} \quad \text{and} \quad \zeta = \pi e^{\pi}. \tag{4.9}$$

I cannot obtain the absolute probability $\mathcal{P}(N_b)$ in closed form but its lower cumulants can be found. We have, for fixed ζ_a, ζ_b, L_a, L_b,

$$\overline{N_b} = \zeta_b(L_b - \overline{N_a}) \tag{4.10}$$

$$\overline{N_b^2} - \overline{N_b}^2 = \zeta_b(L_b-\overline{N_a}) + \zeta_b^2(\overline{N_a^2} - \overline{N_a}^2). \tag{4.11}$$

Thus the variance of N_b comprises two terms, the first of which is the variance of a Poisson distribution of N_b for a fixed value of N_a, and the second of which is the additional fluctuation in N_b caused by the fluctuations in N_a. The higher cumulants separate similarly into an intrinsic term and a contribution from the fluctuations in N_a. The covariance is negative;

$$\overline{N_a N_b} - \overline{N_a}\,\overline{N_b} = -\zeta_b(\overline{N_a^2} - \overline{N_a}^2). \tag{4.12}$$

The more rods there are in the system, the fewer points, and vice versa.

To obtain the distribution of the length of the system in the constant pressure ensemble we choose $L_b = L_a + 1$ so that $L_a = -1$ corresponds formally to $N_a = N_b = 0$. We have then

$$\begin{aligned} Z(N_a, N_b, \pi) &= \int_{N_a-1}^{\infty} dL_a\, \frac{(L_a - N_a + 1)^{N_a+N_b}}{N_a!\, N_b!} e^{-\pi L_a}, \\ &= \frac{(N_a+N_b)!}{N_a!\, N_b!} \pi^{-(N_a+N_b+1)} \exp[-\pi(N_a - 1)]. \end{aligned} \tag{4.13}$$

(Since our rods have 'unit' length we take $n_0 = 1$.) Hence

$$\mathcal{P}_{N_a,N_b}(L_a) = \frac{\pi^{N_a+N_b+1}}{(N_a+N_b)!}(L_a - N_a + 1)^{N_a+N_b} \exp[-\pi(L_a - N_a + 1)], \qquad L_a \geq N_a - 1, \tag{4.14}$$

which is a gamma distribution. If $N_a = 0$ then this is the probability distribution for a line of length $L_b = L_a + 1$ with N_b molecules of a perfect gas;

$$\mathcal{P}_{N_b}(L_b) = \frac{\pi^{N_b+1}}{N_b!} L_b^{N_b} e^{\pi L_b}. \tag{4.15}$$

If $N_b = 0$, and if we abbreviate N_a and L_a to N and L, then

$$\mathcal{P}_N(L) = \frac{\pi^{N+1}}{N!}(L - N + 1)^N e^{-\pi(L-N+1)}, \quad L \geq N + 1. \tag{4.16}$$

So we have a simple relation between $\mathcal{P}_L(N)$, the discrete distribution in the grand ensemble, and $\mathcal{P}_N(L)$, the continuous distribution function in the constant pressure ensemble, namely

$$n^* \mathcal{P}_L(N) = \mathcal{P}_N(L). \tag{4.17}$$

We recall, however, that the density n^*, which first appeared in equation (3.4), is the local density at a distance $L + 1$ from the wall in a semi-infinite grand ensemble of the same activity or pressure, $\zeta = \pi e^{\pi}$. This density is, therefore, a function of L and of ζ (or π), and equation (4.17) does not have the simplicity of equation (4.3), where n_0 is a constant. In the thermodynamic limit n^* in equation (4.17) does become constant and is equal to the actual density at activity ζ. The normalisations of $\mathcal{P}_N(L)$ and $\mathcal{P}_L(N)$ are

$$\int_{N-1}^{\infty} dL\,\mathcal{P}_N(L) = \sum_{N=0}^{[L+1]} \mathcal{P}_L(N) = 1. \tag{4.18}$$

The local densities, $n(l)$, at distance l from a wall are known for the grand ensemble (Robledo and Rowlinson 1986) and for the constant pressure ensemble (Finn and Monson 1988), in the latter case both analytically and by Monte Carlo computer simulation. Figure 1 shows the Monte Carlo results, the exact curve, the mean $\overline{L}$, and the square root of the variance $(\overline{L^2} - \overline{L}^2)^{1/2}$ calculated from $\mathcal{P}_N(L)$. It is seen that the local density is highest in contact with the fixed wall, $n(0)$, and then oscillates about $n = \pi/(1+\pi)$, its thermodynamic limit. The density falls to zero for lengths much beyond $\overline{L}$; that is, the 'floating' piston or wall that exerts a constant force on the finite system rarely makes excursions much beyond $L = \overline{L}$. For each instantaneous position of the piston we should expect to see a symmetric distribution of the local density, $n(l)$, about $l = L/2$, and so sharp peaks against both walls. The right-hand peak is, however, smoothed out by the fluctuations in the position of the piston, but the underlying symmetry is revealed by a calculation of the mean position of the centre of mass of the fluid. We have

$$n_N(l) = \sum_{q=0} \frac{(l-q)^2}{q!} \pi^{q+1} e^{-\pi(l-q)}, \tag{4.19}$$

where $n_N(l)$ is the local density at distance l from the left-hand (fixed) wall, and where the upper limit of the sum is $\min(N-1, [l])$. As π becomes infinite the distribution becomes a sum of delta-functions

$$n_N(l) = \sum_{q=0} \delta(l-q). \tag{4.20}$$

In general,

$$\bar{l} = N^{-1} \int_0^{\infty} dl\, l\; n_N(l) = \frac{1}{2}\left(N - 1 + \frac{N+1}{\pi}\right) = \frac{1}{2}\overline{L}; \tag{4.21}$$

that is, the mean of l is half of the mean of the total length.

FIG. 1. The density in a constant pressure ensemble with $N = 10$ and $\pi = 3$. The points are the results of a Monte Carlo simulation by Finn and Monson (1988) and the line through them is the calculated density. The horizontal line, n, is the density in the thermodynamic limit, and the vertical line, $\overline{L}$, the mean length of the assembly. The square root of the variance is shown by the short line between the arrowheads.

The difference between $\overline{N}$ at fixed L in the grand ensemble and $\overline{L}$ at fixed N in the constant-pressure ensemble is seen by writing the equations for these quantities in the form

$$\overline{N} = L\left(\frac{\pi}{1+\pi}\right) + \left(\frac{\pi}{1+\pi}\right)^2, \quad N = \overline{L}\left(\frac{\pi}{1+\pi}\right) - \left(\frac{1-\pi}{1+\pi}\right). \tag{4.22}$$

The difference is of the order unity and so negligible in the thermodynamic limit.

Since L has a gamma distribution it exhibits the property of convolution, which can be given a physical interpretation. We have, from equation (4.16),

$$\mathcal{P}_{M+N+1}(L) = \int_M^{L-N} dl\, \mathcal{P}_M(l-1)\mathcal{P}_N(L-l-1). \tag{4.23}$$

Let us number the molecules from the left in a system of $(M+N+1)$ molecules, and single out the $(M+1)$th molecule. We can regard this as an internal piston that divides the system into two parts, with M molecules to the left of it and N to the right. The equation above then tells us that, at a fixed external pressure, the probability that the total length is L the convolution of the probability that the length of the left part of the system is $(l-1)$ and the right part $(L-l-1)$. The internal piston can occupy any position from $l = M$ to $l = L - N$, and it excludes other molecules from a length of two units, thus giving a total length to the system of $(l-1)+(L-l-1)+2 = L$.

The one-dimensional system of hard rods has an obvious analogy with a Type I Geiger counter. In this instrument the emissions of a radioactive source are counted, but after each successful count the instrument is dead for a fixed time, and any emissions in that interval go unrecorded. If the emission is a Poisson process of rate π (in units of reciprocal dead time) then the rate at which counts are recorded is $n = \pi/(1+\pi)$. Thus in the language of statistical physics, the rate of emission is the pressure π and the rate of counting is the density in the thermodynamic limit, n. If the dead-time is zero then these rates are the same — the counter 'obeys Boyle's Law'.

The recorded counts do not have a Poisson distribution, as is shown above. From these results we have for the variance of a finite system

$$\overline{N^2} - \overline{N}^2 = n(1-n)^2(L+2n) = \pi(1+\pi)^{-3}\left(L + \frac{2\pi}{1+\pi}\right). \tag{4.24}$$

In the limit of L becoming infinite this is the expression for the variance of a Type I counter given by Feller (1971).

5. Penetrable Sphere Model

There are no obviously simple boundary conditions for the transcribed version of this model, so the finite system is best studied by placing the molecules on the circumference of a ring. The reciprocal of the activity η

is given by

$$\eta = \int_0^\infty dr\, e^{-\pi r} e^{\theta[1-\min(1,r)]} \tag{5.1}$$

$$= \frac{\pi e^\theta + \theta e^{-\pi}}{\pi(\pi+\theta)} = \zeta^{-1}, \tag{5.2}$$

where θ is a dimensionless measure of the reciprocal temperature, and π is, as before, the dimensionless ratio of pressure to temperature. The constant-pressure partition function is

$$Z(N,\pi,\theta) = \eta^N. \tag{5.3}$$

In principle we could obtain the constant-volume partition function by inverting the Laplace transform $Z(N,\pi,\theta)$. Since η has a pole only at $\pi = 0$, and since the contribution to $Z(N,L,\theta)$ of the first molecule is L, we have

$$Z(N,L,\theta) = \frac{L}{N!}\left(\frac{\partial^{N-1}}{\partial\pi^{N-1}}\left[\pi^N\eta^N e^{\pi L}\right]\right)_{\pi=0}. \tag{5.4}$$

This route is practicable for a system of hard rods for which it gives

$$Z(N,L) = \frac{L(L-N)^N}{N!}, \tag{5.5}$$

but not for the penetrable sphere model. We can, however, use the constant pressure ensemble to obtain the moments of the length of the system. If the length per molecule is denoted $\lambda \equiv L/N$, then

$$\begin{aligned}\eta\overline{\lambda^n} &= \int_0^\infty d\lambda\, \lambda^n \exp[-\pi\lambda + \theta(1-\min(1,\lambda))] \\ &= \frac{n!\, e^\theta}{(\pi+\theta)^{n+1}} + \frac{n!}{e^\pi}\sum_{i=0}^{n}\frac{1}{i!}\left[\pi^{i-n+1} - (\pi+\theta)^{i-n+1}\right].\end{aligned} \tag{5.6}$$

The cumulants of the length are obtained by differentiating the Gibbs free energy,

$$C_n(\lambda) = (-)^n\left(\frac{\partial^n \ln\eta}{\partial\pi^n}\right)_\theta. \tag{5.7}$$

We have

$$\overline{\lambda} = \frac{\overline{L}}{N} = \frac{1}{\pi+\theta} + \frac{1+\pi}{\pi(1+\pi e^{\pi+\theta}/\theta)}, \tag{5.8}$$

$$\overline{\lambda^2} - \overline{\lambda}^2 = \frac{\overline{L^2} - \overline{L}^2}{N} = \frac{1}{(\pi+\theta)^2} + \frac{\theta + 2\pi e^{\theta+2\pi}(1+\pi+\pi^2/2)}{\pi^2(1+\pi e^{\pi+\theta}/\theta)^2}. \tag{5.9}$$

The limits of these expressions as $\theta \to 0$ give the mean-field results,

$$\overline{\lambda} = \frac{1}{\pi}\left[1 + \frac{\theta}{\pi}\left(e^{-\pi}(1+\pi) - 1\right)\right] + O(\theta^2), \tag{5.10}$$

$$\overline{\lambda^2} - \overline{\lambda}^2 = \frac{1}{\pi^2}\left[1 + \frac{2\theta}{\pi}\left(e^{-\pi}(1+\pi+\pi^2/2) - 1\right)\right] + O(\theta^2). \tag{5.11}$$

The complexity of these results does not make it seem likely that there is any simple expression for $\mathcal{P}_N(\lambda)$ for this system.

A Type II Geiger counter has a dead time that runs for a fixed interval after each emission, not after each count. There is, therefore, an analogy with the one-dimensional penetrable sphere model in its mean-field or random distribution limit. Each emission is a molecule and now the analogue of the total dead time is the covered length $\mathcal{W}$ of equation (2.18). The count rate of the instrument is the analogue of the number of blocks into which $\mathcal{W}$ is divided, since each block, followed by a covered interval (dead time) of variable length is one recorded count. The ratio of the number of ends of blocks (and so twice the number of blocks) to the sum of total lengths of the blocks is an analogue of the ratio of the covered area to the covered volume in a three-dimensional system. So we can use Widom's (1971) result for the mean areas of systems of arbitrary dimensionality to show that an emission rate of n gives a count rate of ne^{-n}. This result was obtained by other means by Levert and Scheen (1943) and by Kosten (1943). More generally, from Widom's result and the equations above, the mean density of blocks, $\overline{\nu}$, in a one-dimensional system is

$$\overline{\nu} = \frac{\zeta\pi(\pi+\theta)}{\pi^2 e^{\pi} + \zeta\theta(1+\pi)}. \tag{5.12}$$

The random or mean-field limit of $\overline{\nu} = \pi e^{-\pi} = ne^{-n}$, is attained at $\theta = 0$. However high the density or pressure, $\overline{\nu}$ remains non-zero; that is, the blocks never coalesce, or there is no percolation limit. A Type II counter never records once and then stays dead for all time, however high the rate of emission. Even when the penetrable sphere model has the additional incentive of an attractive intermolecular potential ($\theta > 0$) an infinite number of molecules never forms a single cluster in a one-dimensional system.

Thus the analogy of the hard-rod problem with a Type I counter requires that the count rate is the number of molecules and the emission rate is the pressure, while that between the penetrable sphere model and a Type II counter requires that the emission rate is the number of molecules and the count rate is the number of blocks into which the penetrating molecules are grouped. If, to choose a neutral symbol, the emission rate is r, in units of the reciprocal of the dead time caused by an isolated emission, then a

Type I instrument has a count rate of $r(1+r)^{-1}$ and a Type II instrument of re^{-r}. The Type I instrument is the more efficient.

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References

Albert, G.E. and Nelson, L. (1953). Contributions to the statistical theory of counter data. *Annals of Mathematical Statistics* 24, 9–22.

Bishop, M. and Boonstra, M.A. (1983). Exact partition functions for some one-dimensional models via the isobaric ensemble. *American Journal of Physics* 51, 564–566.

Feller, W. (1948). On probability problems in the theory of counters, in *Studies and Essays presented to R. Courant on his 60th birthday, January 8 1948*, 105–115, ed. K.O. Friedrichs, O.E. Neugebauer and J.J. Stoker, Interscience, New York.

——— (1971). *An Introduction to Probability Theory and Its Applications*, Volume 2. 2nd edition, 372–373. John Wiley and Sons, New York.

Finn, J.E. and Monson, P.A. (1988). Adsorption equilibria in an isobaric ensemble. *Molecular Physics* 65, 1345–1361.

Hammersley, J.M. (1953). On counters with random dead time. *Proceedings of the Cambridge Philosophical Society* 49, 623–637.

Hammersley, J.M., Lewis, J.W.E. and Rowlinson, J.S. (1975). Relationships between the multinomial and Poisson models of stochastic processes, and between the canonical and grand canonical ensembles in statistical mechanics, with illustrations and Monte Carlo methods for the penetrable sphere model of liquid-vapour equilibrium. *Sankhyā A* 37, 457–491.

Henderson, J.R. (1983). Statistical mechanics of fluids at spherical structureless walls. *Molecular Physics* 50, 741–762.

Kjellander, R. and Sarman, S. (1988). On the statistical mechanics of inhomogeneous fluids in narrow slits. An application to a hard-sphere fluid between hard walls. *Chemical Physics Letters* 149, 102–108.

Kosten, L. (1943). On the frequency distribution of the number of discharges counted by a Geiger-Müller counter in a constant interval. *Physica* 10, 749–756.

Levert, C. and Scheen, W.L. (1943). Probability fluctuations of discharges in a Geiger-Müller counter produced by cosmic radiation. *Physica* 10, 225–238.

Lieb, E.H. and Mattis, C.C. (1966). *Mathematical Physics in One Dimension. Exactly Soluble Models of Interacting Particles.* Academic Press, New York.

Longuet-Higgins, H.C. (1958). One-dimensional multicomponent mixtures. *Molecular Physics* 1, 83–92.

McQuarrie, D.A. and Rowlinson, J.S. (1987). The virial expansion of the grand potential at spherical and planar walls. *Molecular Physics* 60, 977–989.

Malmquist, S. (1947). A statistical problem connected with the counting of radioactive particles. *Annals of Mathematical Statistics* 18, 255–264.

Percus, J.K. (1982). Non-uniform fluids. In *The Liquid State of Matter*, 31–140, ed. E.W. Montroll and J.L. Lebowitz, North-Holland, Amsterdam.

Robledo, A. and Rowlinson, J.S. (1986). The distribution of hard rods on a line of finite length. *Molecular Physics* 58, 711–721.

Rowlinson, J.S. (1980). Penetrable sphere models of liquid-vapor equilibrium. *Advances in Chemical Physics* 41, 1–57.

Rushbrooke, G.S. and Ursell, H.D. (1948). One-dimensional regular assemblies. *Proceedings of the Cambridge Philosophical Society* 44, 263–271.

Takahashi, H. (1942). Eine einfache Methode zur Behandlung der statistischen Mechanik eindimensionaler Substanzen. *Proceedings of the Physical-Mathematical Society of Japan* 24, 60–62. Reprinted in English in Lieb and Mattis (1966, pp. 25–27).

Widom, B. (1971). Geometrical aspects of the penetrable-sphere model. *Journal of Chemical Physics* 54, 3950–3957.

Widom, B. and Rowlinson, J.S. (1970). New model for the study of liquid-vapor phase transitions. *Journal of Chemical Physics* 52, 1670–1684.

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