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One-dimensional soft rods: exact partition and thermodynamic functions

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Abstract. We apply the theory of classical canonical ensembles to a one-dimensional system of 'soft rods' and obtain an exact expression for the partition function. In our model, each particle is composed of two mass points attracting or repelling one another according to a potential linearly dependent on their separation. Mass points, whether they constitute a given particle or are members of different particles, are presumed to be unable to pass one another. This is a very simple model, therefore, of a system whose internal and external degrees of freedom interact. In order to eliminate end effects without appealing to the thermodynamic limit, we employ a coordinate system with periodic boundary conditions. Our methodology of evaluation is more general than the solution for our particular model which, for a finite system, involves in the partition function a modified Bessel function of half-integral order.

In the limit of vanishing intraparticle potential, we recover the correct partition function for mass points. We derive explicit formulae for one-dimensional pressure, chemical potential, and entropy for finite systems. We also obtain the partition function in the thermodynamic limit, and explicit formulae for three thermodynamic functions, which we show to be approached by those for finite systems. This involves establishing an apparently new asymptotic expression for the ratio of two Bessel functions of large but slightly different orders.

1. Introduction

The central problem in rigorous classical statistical mechanics of systems of 'particles' is the evaluation of partition functions and configuration integrals. Formally, these are merely multiple integrals, but in practice, only rarely is their evaluation possible. As a review by Barker and Henderson (1976) shows, a number of approximate methods have been developed to predict quantities of interest in statistical thermodynamics without obtaining the relevant partition functions. Although approximate methods provide fairly accurate numerical data for the prediction of physical properties, the *a priori* selection of the best approximation for a given system under a given set of conditions is difficult (Andrews 1975). From the theoretician's viewpoint, obtaining an exact expression for the partition function is essential to the analysis of approximate theories, and to the development of a comprehensive understanding of the behaviour of molecules. The mathematical complexity of the evaluation of the integral forms of the partition functions for systems of interacting particles has restricted research in exact classical statistical mechanics to a very few cases, perhaps the best known of which is the Tonks gas (Tonks 1936). Another notable example, exact in the thermodynamic limit, is the system studied by Kac *et al* (1963), in which the potential is a hard core plus an

exponential attraction. The entire field of one-dimensional statistical mechanics has been reviewed by Lieb and Mattis (1966).

We examine a one-dimensional model of a system of particles similar to that of Tonks, but incorporating an interaction between the internal and external degrees of freedom of the particles, obtaining an exact expression for the partition function. In order to simplify the mathematics involved in the expression for the partition function, we array $N + 1$ particles on a circle of radius R and circumference $2\pi R \equiv L$. The $N + 1$ th particle acts as a marker for the imposition of periodic boundary conditions. By altering the properties of this particle, we intend to show in a work in preparation (J C Poirier and J K Swadesh 1979 unpublished) that we may examine end effects without difficulty. For the present, we assume that all particles are composed of two identical mass points, or 'subparticles'. The separation of the two subparticles comprising particle i is given by $2R\phi_i$. The centre of mass of the i th particle, from which each of its subparticles is separated by a distance of magnitude $R\phi_i$, is separated from the centre of mass of the $N + 1$ th particle by a distance of magnitude $R\theta_i$. In turn, the centre of mass of the $N + 1$ th particle is at a distance $R\theta_{N+1}$ from an arbitrary zero. No subparticle may pass another, but otherwise there is no interaction between the subparticles of different particles. In mathematical terms, we may write the energy of the i th particle as

$$E_i = 2cR\phi_i + V_{jj'}^i + P_i^2/2M' + 2p_i^2/M' \quad (1.1)$$

where c is any real constant, $V_{jj'}^i$ is a potential function which becomes infinite should the subparticles j and j' (at least one of which is part of particle i) attempt to pass one another and is otherwise zero, P_i is the momentum of the centre of mass relative to that of the $N + 1$ th particle, M' is the mass of the particle, p_i is the momentum of either subparticle with respect to the centre of mass of the particle, and $m = M'/2$ is the mass of a subparticle. The additional factor of two in the numerator of the right-most term arises during the derivation according to the Lagrangian formulation, and reflects the constraint of symmetrical motion implied by the choice of a centre-of-mass coordinate system. For the $N + 1$ th particle, P_{N+1} is the momentum of the centre of mass of that particle with respect to an arbitrary zero. In our exposition, we will not write $V_{jj'}^i$ explicitly, but the limits of integration will depend on this potential, excluding prohibited configurations from phase space.

Our method of solution is to integrate first over the set $\{R\theta\}$, obtaining an expression comparable to that of Tonks' (1936) hard rod case. We then transform $\{2R\phi\}$ to a new set of coordinates $\{y\}$, in terms of which the intermediate result may be evaluated. Finally, we merge the resultant expression with that obtained by integrating over all momenta and multiply by $h^{-(2N+2)}$ to obtain the complete expression for the partition function.

2. The configuration integral: external degrees of freedom

The system configuration integral, Z , resulting from the particle energies summarised by (1.1) is

$$Z = \int_{\{2R\phi\}} \dots \int_{\{R\theta\}} \dots \int \prod_{i=1}^{N+1} \exp(-2\beta cR\phi_i) dR\theta_i d(2R\phi_i) \quad (2.1)$$

where β is the inverse of the product of Boltzmann's constant with the absolute

temperature. The lower limit on the integration over $R\theta_k$ is $R\theta_{N+1} + 2 \sum_{j=1}^{k-1} R\phi_j + R\phi_k + R\phi_{N+1}$ and the upper limit is $R\theta_{k+1} - R\phi_{k+1} - R\phi_k$; for the integration over $R\theta_{N+1}$, the limits are zero and L . The lower limit for the integration over $2R\phi_k$ is zero and the upper limit is $L - 2 \sum_{j=k+1}^{N+1} R\phi_j$ for $1 \leq k \leq N$; when $k = N + 1$, the lower limit is zero and the upper is L . Overlaps of the k th particle with particles of lower index are prevented by the conditions imposed by the ranges of integration of those particles. If the integrations are performed in the order indicated, we systematically exclude first those configurations in which two particles have centres of mass closer than the sum of their radii of extension, and then those configurations in which the extension of a particle exceeds the free length of the line, i.e. the length of line not occupied by other particles. Taken in conjunction, the limits of integration fulfil the requirements of the function V_{ij}^i .

The integration over the $\{R\theta\}$ simplifies (2.1) to

$$Z = \int_{\{2R\phi\}} \dots \int (L/N!) \left(L - 2 \sum_{i=1}^{N+1} R\phi_i \right)^N \prod_{i=1}^{N+1} \exp(-2\beta c R\phi_i) d(2R\phi_i). \tag{2.2}$$

For a system of N hard rods on a line, Tonks (1936) obtained $(L - N\sigma)^N/N!$ for the configuration integral, where σ is the length of the hard rod. This compares with our result of $L(L - 2 \sum_{i=1}^{N+1} R\phi_i)^N/N!$ after the integration over the $\{R\theta\}$. Our extra factor of L comes from the integration over $R\theta_{N+1}$ from zero to L , and would arise in Tonks' formulation if $N + 1$ hard rods were arrayed on a circle. Because $2R\phi_i$ represents the arc length or extension of the i th 'soft rod', our result becomes identical with that of Tonks in the case that $2R\phi_1 = 2R\phi_2 = \dots = 2R\phi_{N+1} = \sigma$, a constant.

Our next step is to transform the $\{2R\phi\}$ to the more convenient set of coordinates, $\{y\}$, whose members are defined by $y_k = L - 2 \sum_{i=k}^{N+1} R\phi_i$; $1 \leq k \leq N + 1$. This procedure gives us $N + 1$ linearly independent coordinates, which we may insert into (2.2) as both variables and limits of integration; to complete the transformation, we multiply (2.2) by the appropriate value of one, namely $\exp[\beta(cL - cL)]$; the Jacobian of transformation is unity. The new limits for the integration over y_k are 0 and y_{k+1} for $1 \leq k \leq N$, and 0 and L for $k = N + 1$. The transformed expression for the configuration integral becomes

$$Z = e^{-bL}(L/N!) \int_0^L \dots \int_0^{y_2} y_1^N \exp(by_1) \prod_{i=1}^{N+1} dy_i \tag{2.3}$$

where $b \equiv \beta c$. The procedure for transforming a set of coordinates is presented in Taylor (1955).

3. The configuration integral: internal degrees of freedom

There are $N + 1$ integrations to be performed in (2.3), and the exponent of y_1 is N . It is possible, however, to obtain a generalised solution for any number of integrations, and for any non-negative integral value of the exponent of y_1 . Because, as we have previously noted, a general solution will allow us to examine end effects, we simplify the general integral, of which a special case appears in (2.3).

Define $y_1, \dots, y_B, \dots, y_D$ as D independent, real, continuous variables, M as a non-negative integer, and L and b as real constants. The generalised integral to be

evaluated is

$$I(D, M, L, b) = \int_{0(y_D)}^L \dots \int_{0(y_j)}^{y_{j+1}} \dots \int_{0(y_1)}^{y_2} y_1^M \exp(by_1) \prod_{i=1}^D dy_i. \tag{3.1}$$

Application of the technique of Laplace transforms (Abramowitz and Stegun 1964, 29.2.7, p 1020; 29.3.11, p 1022) to (3.1) gives

$$\mathcal{L}I(D, M, L, b) = M!/s^D (s - b)^{M+1}$$

where \mathcal{L} is the transform operator, and s is the variable associated with the image function. The convolution theorem (Abramowitz and Stegun 1964, 29.2.8, p 1020; 29.3.3, 29.3.11, p 1022) allows us to perform the inverse transformation, giving

$$I(D, M, L, b) = \int_0^L \frac{(L - y_D)^{D-1} y_D^M \exp(by_D)}{(D - 1)!} dy_D. \tag{3.2}$$

If $D - 1 = M = N$, as in (2.3), (3.2) simplifies to $I(N + 1, N, L, b) = \int_0^L [y_D(L - y_D)]^N \exp(by_D) dy_D/N!$ If $Lx_D \equiv y_D$, the expression is transformed to

$$I(N + 1, N, L, b) = L^{2N+1} \int_0^1 [x_D(1 - x_D)]^N \exp(2\alpha x_D) dx_D/N!$$

where $\alpha = bL/2$, and the Jacobian of transformation is L . This may again be transformed, now using $x_D \equiv (z_D + 1)/2$, and including the Jacobian of $\frac{1}{2}$, we obtain

$$I(N + 1, N, L, b) = (L/2)^{2N+1} e^\alpha \int_{-1}^1 (1 - z_D^2)^N \exp(\alpha z_D) dz_D/N!.$$

This may be written (Abramowitz and Stegun 1964, 9.6.18, p 376) as

$$I(N + 1, N, L, b) = e^\alpha L^{2N+1} \pi^{1/2} I_{N+1/2}(\alpha)/(2\alpha)^{N+1/2}$$

where $I_{N+1/2}(\alpha)$ is a modified Bessel function of order $N + \frac{1}{2}$. Inserting this expression into (2.3), we obtain

$$Z = \frac{e^{-\alpha} L^{N+1} (2\pi\alpha)^{1/2} I_{N+1/2}(\alpha)}{N! b^{N+1}}. \tag{3.3}$$

We may obtain an explicit expression for the configuration integral by invoking a formula from Abramowitz and Stegun (1964, 10.2.9, p 443), given as

$$(\pi/2z)^{1/2} I_{N+1/2}(z) = (2z)^{-1} [R(N + \frac{1}{2}, -z) e^z - (-1)^N R(N + \frac{1}{2}, z) e^{-z}]$$

where $R(N + \frac{1}{2}, z)$ is defined (Abramowitz and Stegun 1964, 10.2.11, p 443) as $\sum_{k=0}^N (N + \frac{1}{2}, k)(2z)^{-k}$, and $(N + \frac{1}{2}, k)$ is defined (Abramowitz and Stegun 1964, 10.1.9, p 437) as $(N + k)!/k!(N - k)!$. So we obtain

$$Z = (L/b)^{N+1} \sum_{j=0}^N \binom{N+j}{j} \frac{[(-1)^j + (-1)^{N+1} e^{-bL}]}{(N-j)!(bL)^j}. \tag{3.4}$$

4. The momentum integrals and the partition function

The integrals over centre-of-mass momenta

$$P' = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \prod_{i=1}^{N+1} \exp(-\beta P_i^2 / 2M') \, dP_i$$

reduce to $(2\pi M' / \beta)^{(N+1)/2}$. The integrals over the momenta of the subparticles relative to the respective centres of mass reduce from

$$P'' = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \prod_{i=1}^{N+1} \exp(-2\beta p_i^2 / M') \, dp_i$$

to $(\pi M' / 2\beta)^{(N+1)/2}$. Therefore, the expression for the momentum integrals, P' by P'' , gives us the net expression

$$P = (\pi M' / \beta)^{N+1}. \tag{4.1}$$

To obtain the partition function, we merely multiply Z as expressed by (3.3) by P as expressed by (4.1) and divide by the correction to classical phase space, h^{2N+2} , to obtain the major result of this paper:

$$Q = \left(\frac{\pi M' L}{\beta b h^2} \right)^{N+1} \frac{\exp(-\alpha) (\pi b L)^{1/2} I_{N+1/2}(\alpha)}{N!}. \tag{4.2}$$

Similarly, an explicit expression may be obtained for the partition function by the use of (3.4).

5. Limiting forms of the partition function

In this section, we show that the partition function (4.2) reduces to that of a system of $2N + 2$ mass points as c approaches zero, and also exhibit the form of the partition function in the thermodynamic limit.

5.1. Reduction of the soft rod system to a system of mass points

Using the definitions $\alpha \equiv bL/2$ and $b \equiv \beta c$, we may rewrite (4.2) as

$$Q = \left(\frac{\pi M' L}{\beta^2 h^2} \right)^{N+1} \frac{(\pi \beta L)^{1/2} \exp(-\beta c L / 2) I_{N+1/2}(\beta c L / 2)}{N! c^{N+1/2}}.$$

It is found (Abramowitz and Stegun 1964, 9.6.7, p 375) that, as c approaches zero, $I_{N+1/2}(\beta c L / 2) \sim (\beta c L / 4)^{N+1/2} / (N + \frac{1}{2})!$. The powers of c cancel and the exponential term approaches unity. Using the definition (Abramowitz and Stegun 1964, 6.1.2, p 255; 6.1.8, p 255) of $(N + \frac{1}{2})! = (N + \frac{1}{2}) [1 \times 3 \times 5 \times 7 \times \dots \times (2N - 1)] \pi^{1/2} / 2^N$, it is easily found that

$$\lim_{c \rightarrow 0} Q = \left(\frac{2\pi m L^2}{\beta h^2} \right)^{N+1} \left(\frac{1}{(2N + 1)!} \right) \tag{5.1}$$

which is the partition function for $2N + 2$ mass points, of mass $m = M' / 2$, on a circle.

5.2. *The thermodynamic limit*

In Olver (1974, p 390), we find that when ν is positive, and $|\text{ph } z| \leq 1/2\pi - \delta$, where δ is a small positive number, and $|\text{ph } z|$ is the absolute value of the phase of z , that the modified Bessel function $I_\nu(\nu z)$ asymptotically approaches

$$\frac{e^{\nu\xi(z)}[1 + O(\nu^{-1})]}{(2\pi\nu)^{1/2}(1+z^2)^{1/4}} \tag{5.2}$$

as ν approaches infinity. In (5.2), $O(\nu^{-1})$ implies that the term in square brackets is bounded by $1 + K/\nu$, where K is a constant (Olver 1974, p 4). Olver (1974, p 375) defines $\xi(z)$ as $(1+z^2)^{1/2} + \ln z [1 + (1+z^2)^{1/2}]^{-1}$.

In (4.2), we notice that if we define $L = (N + 1)/\rho$, where ρ is the number density, the order of the Bessel function is not quite proportional to the argument. But, if N is assumed to be large, we may approximate the order of the modified Bessel function of (4.2) as $I_{N+1/2}(bL/2) \approx I_{N+1}[b(N + 1)/2\rho]$ to conform with (5.2). With $z = b/2\rho$ and $\nu = N + 1$, (5.2) may be substituted into (4.2) to give an expression valid for large $N + 1$. Then, taking the thermodynamic limit, all terms involving $O(\nu^{-1})$ vanish, and with the use of Stirling's approximation on $N!$ (Abramowitz and Stegun 1964, 6.1.38, p 257), we find from (4.2)

$$\lim_{\substack{N+1 \rightarrow \infty \\ (N+1)/L = \rho}} \frac{\ln Q}{(N + 1)} = \ln \left(\frac{\pi M' \exp\{1 - b/2\rho + [1 + (b/2\rho)^2]^{1/2}\}}{2\beta h^2 \rho^2 \{1 + [1 + (b/2\rho)^2]^{1/2}\}} \right). \tag{5.3}$$

The same result is obtained if we define $(N + \frac{1}{2})/L = \rho$, so that the order and argument of the Bessel function may be directly proportional.

If, in (5.3), the intersubparticle potential is allowed to vanish ($c = b/\beta \rightarrow 0$), (5.3) reduces to the thermodynamic limit for $N + 1$ mass point 'pairs' on a circle. The same expression results from (5.1) if $\rho = (N + 1)/L$ is defined as the 'pair point density' in (5.1) and the thermodynamic limit is taken. By contrast, (5.1) leads to a different expression, correct for mass points if, in (5.1), $\rho = (2N + 2)/L$ and the thermodynamic limit is taken in the conventional fashion.

6. The thermodynamic functions F , μ and S

In this section, we exhibit expressions for the one-dimensional pressure, F , for the chemical potential, μ , and for the entropy, S . We present formulae for these functions both for a system of finite extension, and also in the thermodynamic limit under the condition that $b/2\rho$ remains finite.

A great deal of literature exists on the interchangeability of the order of taking the thermodynamic limit, and the taking of various partial derivatives of the partition function; two works especially deserving of mention in this regard are Münster (1969) and Balescu (1975). For simplicity, we prefer to demonstrate by direct methods that the taking of the thermodynamic limit and the taking of the relevant derivatives is interchangeable for our system. To do this, we must examine the ratio $I_{N-1/2}(\alpha)/I_{N+1/2}(\alpha)$, which occurs in the formulae for F , μ and S of the soft rod system not in the thermodynamic limit.

In examining this ratio, we notice that the order and the argument of each of the two Bessel functions are slightly different, if we use the definition of density used in (5.3). In

§ 5.2 this proved to be no difficulty, because terms arising from the mismatch of order and argument of the Bessel function vanished in the limit. Such is not the case in the ratio of Bessel functions; more care is needed.

Suppose that we define $(N + \frac{1}{2})/L = \rho$. Set $x = b/2\rho$; then $z = (N + \frac{1}{2})x(N - \frac{1}{2})^{-1}$. Because z varies very slowly as N increases, we may use expression (5.2) to establish the limit of the ratio of Bessel functions as N goes to infinity. The full expression is

$$A \frac{\exp[(N - \frac{1}{2})(1 + z^2)^{1/2}]}{\exp[(N + \frac{1}{2})(1 + x^2)^{1/2}]} \left[\left(\frac{z}{x} \right)^N (xz)^{-1/2} \right] \left(\frac{1 + (1 + z^2)^{1/2}}{1 + (1 + x^2)^{1/2}} \right)^N \left(\frac{1 + (1 + z^2)^{1/2}}{[1 + (1 + x^2)^{1/2}]^{-1}} \right) \quad (6.1)$$

where $A = [2\pi(N + \frac{1}{2})]^{1/2}(1 + x^2)^{1/4}/[2\pi(N - \frac{1}{2})]^{1/2}(1 + z^2)^{1/4} \sim 1$ as $N \rightarrow \infty$. The first bracketed term asymptotically approaches e/x as N approaches infinity. Using the binomial expansion (Jolley 1961) for z in terms of x and N , tedious algebra reduces the second bracketed term to $\{1 + x^2 N^{-1}(1 + x^2)^{-1/2}[1 + (1 + x^2)^{1/2}]\}^{-N}$ if terms of order N^{-2} and smaller are dropped. Similarly, the final term is found to be $[1 + (1 + x^2)^{1/2} + O(N^{-1})]$. With some algebraic manipulation, the result is

$$\lim_{N \rightarrow \infty} \frac{I_{N-1/2}[(N + \frac{1}{2})b/2\rho]}{I_{N+1/2}[(N + \frac{1}{2})b/2\rho]} = \frac{1 + [1 + (b/2\rho)^2]^{1/2}}{b/2\rho} \quad (6.2)$$

using $b/2\rho$ as x .

6.1. The one-dimensional pressure

By analogy with the formula for pressure (Tolman 1967), $F_1 = \beta^{-1}(\partial \ln Q/\partial L)_{T,N}$, where T is the temperature and Q is given by (4.2), and the subscript on F_1 simply denotes a finite system. From the general statement $(z^{-1} d/dz)^k z^\nu I_\nu(z) = z^{\nu-k} I_{\nu-k}(z)$ found in Abramowitz and Stegun (1964, 9.6.28, p 376), we readily deduce that $dI_\nu(z)/dz = I_{\nu-1}(z) - (\nu/z)I_\nu(z)$. With $z = \alpha$, $\nu = N + \frac{1}{2}$ and $k = 1$, we find that the one-dimensional pressure of a system *not* in the thermodynamic limit is

$$F_1 = \beta^{-1} \left[\frac{1}{bL} - \frac{b}{2} \left(1 - \frac{I_{N+1/2}(bL/2)}{I_{N-1/2}(bL/2)} \right) \right]. \quad (6.3)$$

The one-dimensional pressure F_2 exerted by a system in the thermodynamic limit may be obtained by multiplying (5.3) by $-\beta^{-1}$ to obtain the free energy per particle, and then differentiating with respect to $-\rho^{-1}$ (the length per particle), giving

$$F_2 = \beta^{-1} \left\{ \rho - \frac{b}{2} + \rho \left[1 + \left(\frac{b}{2\rho} \right)^2 \right]^{1/2} \right\}. \quad (6.4)$$

Insertion of (6.2) into (6.3), and passage to the thermodynamic limit results in (6.4), as expected.

6.2. The chemical potential

In a finite system, the number of particles, N , is not a continuous variable. Only in the thermodynamic limit is it strictly permissible to obtain the chemical potential μ as a derivative of $\ln Q$ with respect to N . To avoid this in obtaining μ for a finite system, we may assume that the system is not extremely small (Hill 1963) and adopt a procedure employed by Andrews (1975), setting $\mu_1 = -\beta^{-1} \ln(Q_{N+1}/Q_N)$, where the subscripts to

Q indicate the number of particles in each system. From (4.2), we then have

$$\mu_1 = -\beta^{-1} \ln\left(\frac{\pi M' L I_{N+1/2}(bL/2)}{b\beta h^2 N I_{N-1/2}(bL/2)}\right) \tag{6.5}$$

for a relatively small system.

If we wish to obtain the chemical potential μ_2 for a system in the thermodynamic limit, we may take

$$\left(\frac{\partial \ln Q}{\partial(N+1)}\right)_{L,T} = \rho \left(\frac{\partial[\ln Q/(N+1)]}{\partial \rho}\right)_{\beta} + \frac{\ln Q}{N+1}.$$

Use of (5.3) for $\ln Q/(N+1)$ and multiplication by $-\beta^{-1}$ leads to

$$\mu_2 = -\beta^{-1} \ln\left(\frac{\pi M'}{2\beta h^2 \rho^2 \{1 + [1 + (b/2\rho)^2]^{1/2}\}}\right). \tag{6.6}$$

Again, we note that if (6.5) is taken into the limit as $N \rightarrow \infty$, one obtains (6.6) using (6.2).

6.3. The entropy

Finally, we consider the entropy of the soft rod system. The entropy of a finite system is defined (Tolman 1967) as $S_1 = k_B \ln Q + \beta^{-1}(\partial \ln Q/\partial T)_{N,L}$, where k_B is Boltzmann's constant. Using (4.2) in this definition, and recalling that $b = \beta c$ and $\alpha = \beta cL/2$,

$$S_1 = k_B \left[\ln Q + 2N + \frac{3}{2} + \frac{bL}{2} \left(1 - \frac{I_{N-1/2}(bL/2)}{I_{N+1/2}(bL/2)} + \frac{2N+1}{bL} \right) \right]. \tag{6.7}$$

The entropy per particle, s_1 , is simply $S_1/(N+1)^{-1}$.

In order to relate the entropy to (5.3), one must consider the entropy per particle, which can be obtained by defining the specific entropy:

$$s_2 \equiv S_2/(N+1)^{-1} = k_B \ln(Q)/(N+1) + \beta^{-1}\{\partial[\ln Q/(N+1)]/\partial T\}_{N,L}.$$

This affords us

$$s_2 = k_B \ln\left(\frac{\pi M' e^3}{2\beta h^2 \rho^2 \{1 + [1 + (b/2\rho)^2]^{1/2}\}}\right). \tag{6.8}$$

The same expression may be obtained from (6.7) by dividing by $N+1$ and invoking the expression given for the ratio of Bessel functions given in (6.2).

7. Conclusions

In this work, we derived the partition function for a system of soft rods in the absence of end effects. We showed that this partition function reduced to the correct partition function for a corresponding system of mass points as the intraparticle potential approached zero. We then obtained the thermodynamic limit of the soft rod partition function, which had a simple mathematical form. Finally, we derived the one-dimensional pressure, the chemical potential, and the entropy per particle for both finite and macroscopic systems, and showed that the expressions for the thermodynamic functions of the finite system converge to the corresponding functions of the macroscopic system in the thermodynamic limit.

The procedure we employed to integrate over the positional coordinates of the centre of mass is general for any intraparticle potential. We compared the soft rod configuration integral prior to integration over the coordinates relative to the centres of mass with the configuration integral of a corresponding hard rod system. A similar comparison may be made with the configuration integral of hard rod mixtures (David 1964). If the potential in (2.2) is replaced by a potential of different form, one may obtain the correct expression for the configuration integral of the corresponding system.

We leave consideration of end effects and other interesting properties of the soft rod system to a work in preparation (J C Poirier and J K Swadesh 1979 unpublished), and we remark here only that end effects may be included by modification of the properties of the $N + 1$ th particle.

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