

Examination of Bounds on the Chemical Potential, Using a One-Dimensional System

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A recently devised method of establishing arbitrarily close upper and lower bounds on the chemical potential for certain kinds of thermodynamic systems is applied to a one-dimensional lattice system whose sites cannot accept particles as nearest neighbors, i.e., whose particles repel one another when they are nearest neighbors. The *exact* chemical potential is found to always lie within the bounds, and the convergence of the bounds is examined for lattices of increasing size. The system, of course, lacks a phase transition, but its study, which is both brief and simple, is useful for the purposes of illustration and completeness.

KEY WORDS: Equation of state; bounds; one-dimensional lattice; repulsion; thermodynamic limit.

1. INTRODUCTION

In a recent paper, Reiss and Merry⁽¹⁾ developed a method for establishing rigorous upper and lower bounds on the chemical potential of a hard sphere fluid. The bounds were applicable at any density, and could be made arbitrarily close at the expense of evaluating petite ensemble partition functions for systems containing increasing numbers of particles. Although these systems contain finite numbers of particles, the partition functions can only be evaluated numerically, e.g., by Monte Carlo methods.

A cost effective way of exploring the convergence of bounds of this type would involve deriving them for a system where petite ensemble partition functions for systems consisting of finite numbers of particles could be evaluated analytically. These partition functions, however, must correspond to systems with *free* or *cylindrical* boundary conditions,² not

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² Cylindrical conditions refer to a two-dimensional system whose boundaries are free in one direction and periodic or cyclic in the other direction.

cyclic conditions.⁽²⁾ Candidate systems are the two-dimensional ferromagnet⁽³⁾ (Ising model) whose partition functions are available for *cylindrical* conditions and the two-dimensional dimer model⁽⁴⁾ where partition functions are available for *free* boundary conditions. The Ising model possesses a phase transition.

The use of these models still involves some complexity, although they should certainly be enlisted in the near future, and it is worthwhile, for the sake of completeness, to first examine an even simpler model involving a system which is only one-dimensional. Such a system cannot, of course, undergo a phase transition, and the convergence of bounds will be unrealistically rapid (since slow convergence can be shown⁽¹⁾ to be due to surface effects, and the one-dimensional system will only have ends whose extent, unlike that of a surface, is independent of system size), but, in view of the inherent simplicity, and the associated brevity of exposition, its study is still worthwhile. In this paper we describe such a system, and examine the convergence of the bounds on its chemical potential.

2. THE SYSTEM AND ITS BOUNDS

We choose a one-dimensional system occupying a one-dimensional lattice containing N sites. The particles in this system can occupy the lattice, but two particles can never occupy adjacent (nearest neighbor) sites. Thus there is an effective "repulsion" between particles which confers on them some of the characteristics of the hard spheres treated in Ref. 1. The lower bound in Ref. 1 is specified by equation (68) of that paper, while the upper bound is determined by equation (76). Because of the repulsive interaction between the particles on our lattice it is possible to show, by arguments exactly parallel to those leading to equations (68) and (76) of Ref. 1, that for the lattice systems the lower and upper bounds are, respectively, determined by³

$$f_{\infty} N = \frac{\sum_{j=1}^N j \lambda^j q_j(N)}{1 + \sum_{j=1}^N \lambda^j q_j(N)} \quad (1)$$

$$f_{\infty}(N+2) = \frac{\sum_{j=1}^N j \lambda^{j+1} q_j(N)}{1 + \sum_{j=1}^N \lambda^{j+1} q_j(N)} \quad (2)$$

³ These equations would both be exact for $N \rightarrow \infty$ since they are then simply expressions for the average occupancy according to the conventional grand ensemble. However, for N finite, they can be shown to be inexact by the omission of interaction terms between the "system" and the constant chemical potential "surroundings" of the grand ensemble. These interaction terms depend upon whether the system is multidimensional or unidimensional. In Ref. (1) it is shown that these interaction terms render λ^{**} in Eq. (1), a lower bound, and λ^{**} in Eq. (2), an upper bound.

where

$$\lambda_* = e^{\mu_*/kT} \quad (3)$$

is a *lower* bound, thermodynamic activity related, as shown, to the *lower* bound chemical potential, μ_* . Temperature is denoted by T , and k is the Boltzmann constant. The *upper* bound activity is

$$\lambda_{**} = e^{\mu_{**}/kT} \quad (4)$$

where μ_{**} is the upper bound chemical potential. In Eqs. (1) and (2) $q_j(N)$ is the petite ensemble partition function for j particles on a lattice of N sites; j_N is the maximum number of particles allowed on a lattice of N sites, $N/2$ when N is even, and $(N + 1)/2$ when N is odd. Finally f_∞ has the following meaning:

Consider a system with $N \rightarrow \infty$, i.e., a system in the thermodynamic limit. Then f_∞ is defined as the *ratio* of the number of particles to lattice sites in this system. Given f_∞ , the chemical potential in this system is determined. In fact it is the limit to which μ_* in Eq. (1) converges as $N \rightarrow \infty$ in Eq. (1). This follows from the fact that the right-hand side of Eq. (1) is the standard grand ensemble expression for the number of particles on the lattice as $N \rightarrow \infty$, provided that μ_* is the true chemical potential for $N \rightarrow \infty$. When $N \rightarrow \infty$, $f_\infty N$ is the number of particles in the system, so the exactness in the thermodynamic limit of the grand ensemble expression guarantees that μ_* will converge on μ , the true chemical potential. Thus, $f_\infty N$ is the number of particles in the system, in the thermodynamic limit, when the true thermodynamic potential is μ . The μ_* determined by Eq. (1) (the lower bound) bears the following relation to $\mu(f_\infty)$:

$$\mu_* \leq \mu(f_\infty) \quad (5)$$

Similarly,

$$\mu_{**} \geq \mu(f_\infty) \quad (6)$$

If the *effective* grand partition function is defined as

$$Z_n(\lambda) = \sum_{j=0}^{j_N} \lambda^j q_j(N) \quad (7)$$

where $q_j(0) = 1$, then Eq. (1) may be expressed as

$$f_\infty N = \frac{\partial \ln Z_n(\lambda_*)}{\partial \ln \lambda_*} \quad (8)$$

and Eq. (2) as

$$f_\infty(N + 2) = \frac{\partial \ln Z_n(\lambda_{**})}{\partial \ln \lambda_{**}} \quad (9)$$

If we can arrive at an analytical expression for $Z_n(\lambda)$, then Eqs. (8) and (9) can be solved for λ_* and λ_{**} , respectively, thereby yielding the lower and upper bounds. The true activity, λ , in the thermodynamic limit can be obtained from

$$f_\infty = \lim_{N \rightarrow \infty} \left\{ \frac{1}{N} \frac{\partial \ln Z_n(\lambda)}{\partial \ln \lambda} \right\} \quad (10)$$

Thus we can compare λ_* , λ_{**} , and λ as functions of the particle fraction (effectively the density), f_∞ . We follow such a program in the following sections.

3. EVALUATION OF $Z_n(\lambda)$

The most convenient way to arrive at an analytical expression for $Z_n(\lambda)$ is through the transfer matrix technique.⁽⁵⁾ $Z_n(\lambda)$ consists of two "components" consisting of terms in which the N th site is unoccupied and occupied, respectively. These two components are denoted by Z_0^N and Z_1^N , respectively, and are viewed as the two components of a vector, \mathbf{Z}_N . The transfer matrix,

$$\mathbf{M} = \begin{pmatrix} 1 & 1 \\ \lambda & 0 \end{pmatrix} \quad (11)$$

maps \mathbf{Z}_{n-1} into \mathbf{Z}_n ,

$$\mathbf{Z}_n = \mathbf{M} \cdot \mathbf{Z}_{n-1} \quad (12)$$

Repeated application of this relation gives

$$\mathbf{Z}_n = \mathbf{M}^{n-1} \cdot \mathbf{Z}_1 \quad (13)$$

where \mathbf{Z}_1 is clearly

$$\mathbf{Z}_1 = \begin{pmatrix} 1 \\ \lambda \end{pmatrix} \quad (14)$$

Denoting the unit vector as

$$\mathbf{1} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad (15)$$

we find

$$\begin{aligned} Z_n(\lambda) &= Z_0^{(N)}(\lambda) + Z_1^{(N)}(\lambda) \\ &= \mathbf{1} \cdot \mathbf{Z}_n(\lambda) = \mathbf{1} \cdot \mathbf{M}^{N-1} \cdot \mathbf{Z}_1(\lambda) \end{aligned} \quad (16)$$

If \mathbf{A} is the matrix which diagonalizes \mathbf{M} such that

$$\mathbf{D} = \mathbf{A}^{-1} \mathbf{M} \mathbf{A} \quad (17)$$

where

$$D = \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \quad (18)$$

where

$$\begin{aligned} \alpha &= \frac{1}{2} + \left(\frac{1}{4} + \lambda\right)^{1/2} \\ \beta &= \frac{1}{2} - \left(\frac{1}{4} + \lambda\right)^{1/2} \end{aligned} \quad (19)$$

are the eigenvalues of M , we have

$$Z_n(\lambda) = \mathbf{1} \cdot \mathbf{A} \cdot \begin{pmatrix} \alpha^{N-1} & 0 \\ 0 & \beta^{N-1} \end{pmatrix} \cdot \mathbf{A} \cdot \mathbf{Z}_1(\lambda) \quad (20)$$

It is easily shown that

$$\mathbf{A} = \begin{pmatrix} 1 & 1 \\ \alpha - 1 & \beta - 1 \end{pmatrix} \quad (21)$$

and

$$\mathbf{A}^{-1} = \frac{1}{\beta - \alpha} \begin{pmatrix} \beta - 1 & -1 \\ 1 - \alpha & 1 \end{pmatrix} \quad (22)$$

Performing the operations implicit in Eq. (20) we arrive at the result

$$Z_n(\lambda) = \frac{\alpha^N (\beta - 1 - \lambda) + \beta^N (1 - \alpha + \lambda)}{\beta - \alpha} \quad (23)$$

We note that

$$\frac{\partial \alpha}{\partial \lambda} = \frac{1}{2\left(\frac{1}{4} + \lambda\right)^{1/2}} \quad (24)$$

$$\frac{\partial \beta}{\partial \lambda} = \frac{-1}{2\left(\frac{1}{4} + \lambda\right)^{1/2}}$$

Equation (23) may be substituted into Eqs. (8) and (9), and with the help of Eq. (24), provides equations which determine λ_* and λ_{**} .

For the case $N \rightarrow \infty$, both of these equations yield

$$f_\infty = \frac{\lambda}{\frac{1}{2} + 2\lambda + \left(\frac{1}{4} + \lambda\right)^{1/2}} \quad (25)$$

from which λ and the *true* value of μ ,

$$\mu = kT \ln \lambda \quad (26)$$

can be determined as functions of f_∞ .

4. DISCUSSION

To compare λ with λ_* and λ_{**} as functions of f_∞ , we first determine λ as a function of f_∞ , using Eq. (25). The easiest way to arrive at this curve is to simply calculate f_∞ as a function of λ , and plot the result in the form of λ as a function of f_∞ . This curve is presented in Fig. 1 as the curve marked λ . The equations derived from Eqs. (8) and (9), through substitution of Eqs. (23) and (24), can then be used to calculate f_∞ as functions of λ_* and λ_{**} for particular values of N . These relations may be expressed as

$$f_\infty = F(\lambda_*, N) \quad (27)$$

or

$$f_\infty = F(\lambda_{**}, N) \quad (28)$$

The results can again be plotted in the forms of $\lambda_*(f_\infty, N)$ and $\lambda_{**}(f_\infty, N)$ as functions of f_∞ . Such plots, denoted by the labels $\lambda_*(N)$ and $\lambda_{**}(N)$, are plotted in Figs. 1, 2, and 3, for values of N equal to 2, 10, and 40, respectively. As expected, all the λ_* curves lie below, and all the λ_{**} lie above λ . The bounds converge rapidly with increasing N , but converge with difficulty at values of f_∞ in the neighborhood of 0.5, i.e., in the neighborhood of close packing. Even so, the convergence is anomalously rapid with increasing N , since the one-dimensional system has no "surface," only ends.

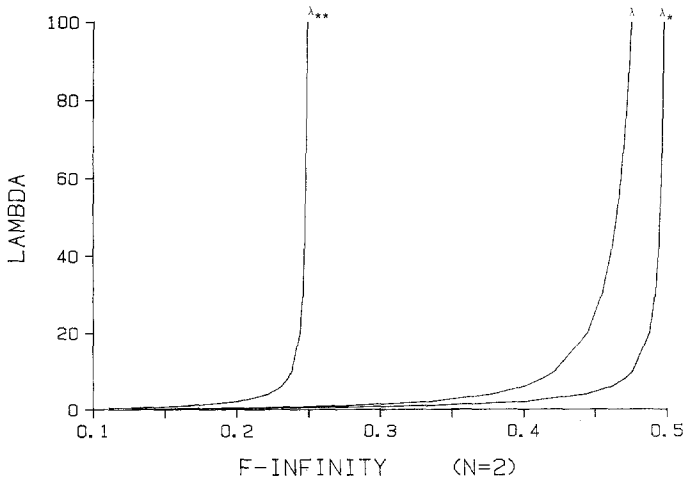


Fig. 1. Plots of λ_{**} , λ , and λ_* as functions of f_∞ for $N=2$. In this case the system can contain only a single particle, and the situation is obviously artificial. Of course the bounds are far apart.

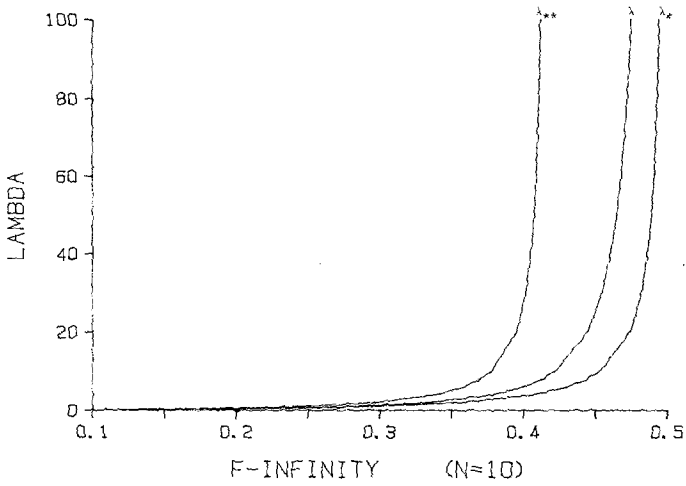


Fig. 2. Plots of λ_{**} , λ , and λ_* as functions of f_∞ for $N \approx 10$. Some convergence of the bounds may be noted.

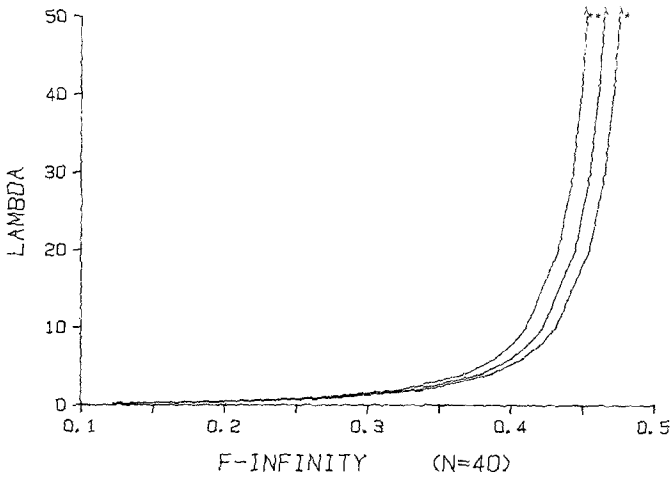


Fig. 3. Plots of λ_{**} , λ , and λ_* as functions of f_∞ for $N = 40$. Convergence is already quite good, but still difficult to achieve near $f_\infty = 0.5$ corresponding to close packing.

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