

## **A Case Study of the MSA Approach to Quantized Polarizable Media**

**R. Hübner,<sup>1</sup> J. S. Høye,<sup>1</sup> and K. Olaussen<sup>1</sup>**

*Received February 12, 1985*

---

The mean spherical approximation (MSA) has proved to be a very general and flexible method to analyze equilibrium statistical mechanical systems. In this note we test its accuracy against a simple one-dimensional model, i.e., a lattice gas of polarizable molecules where the internal degree of freedom is treated as quantized harmonic oscillators which interact via harmonic forces. This model can be solved exactly. We find a very good agreement between the MSA and exact solutions.

---

**KEY WORDS:** Random one-dimensional system; coupled quantized harmonic oscillators; path integral method; mean spherical approximation.

### **1. INTRODUCTION**

Previously a model for a fluid of quantized interacting polarizable particles has been solved approximately using a path integral representation of the partition function.<sup>(1,2)</sup> This path integral may be regarded as the classical partition function for a system of interacting polymers. The system could then be analyzed by a generalization of the MSA (mean spherical approximation) method that has been widely employed on classical systems. In this model the center-of-mass motion of the molecules was treated classically, while the fluctuating (oscillating) dipole moments and their dipole-dipole interaction were quantized. When the dipole moment fluctuates in a harmonic potential, the result is a system of coupled har-

---

<sup>1</sup> Institutt for teoretisk fysikk, 7034 Trondheim-NTH, Norway.

<sup>2</sup> The corresponding classical problem of polarizable particles was first solved in a mean spherical approximation (MSA) by M. Wertheim [*J. Chem. Phys.* **26**:1425 (1973)]. He considered the model with nonfluctuating dipole moments. Later L. Pratt [*Mol. Phys.* **40**:347 (1980)] and J. S. Høye and G. Stell [*J. Chem. Phys.* **73**:461 (1980)] solved the corresponding classical problem in the MSA for particles with fluctuating dipole moments.

monic oscillators. If the oscillators are located on the sites of a close-packed regular lattice, this model can be solved in a straightforward way by computing the eigenfrequencies of the system. However, in other cases, with disordered location of the oscillators, the problem becomes highly nontrivial. In the book by Lieb and Mattis the situation for disordered chains of harmonic oscillators is reviewed.<sup>(3)</sup> (The system we shall consider here is actually a special case of the models described there.)

From the MSA solution for thermodynamic quantities like the internal energy it is possible to derive the corresponding frequency spectrum.<sup>(4,5)</sup> For a close-packed lattice the MSA yields the exact result.

In this work we want to check the accuracy of the MSA solution against a simple one-dimensional model that can be solved exactly. The model consists of harmonic oscillators placed randomly on the lattice sites of a linear chain, and the oscillators interact only when they are nearest neighbors. In Section 2 we define the model more precisely, and in Section 3 we evaluate the exact solution. In Section 4 we make explicit the MSA solution for this special case, and in Section 5 we compare the MSA result with the exact solution. From this comparison we conclude that the agreement is remarkably good. The situation with greatest disagreement is illustrated in Figs. 1 and 2, where the full curves are computed numerically.

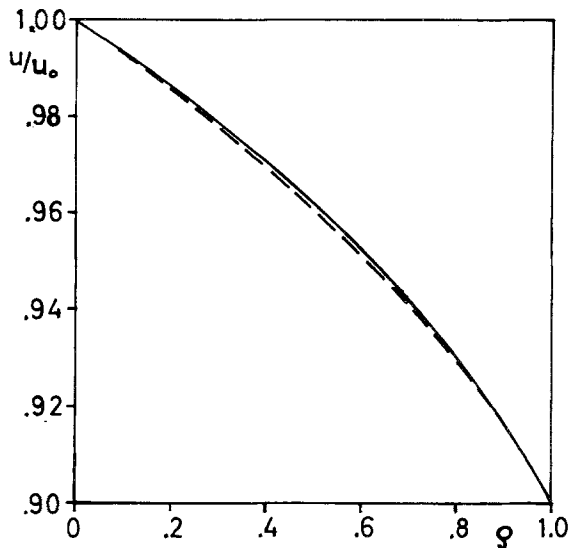


Fig. 1. The internal energy  $u$  per particle at  $T=0$  is shown as function of the density  $\rho$  of occupied sites. It is plotted relative to the ground state energy  $u_0 = (1/2)\hbar\omega_0$  of a single oscillator. The fully drawn curve is the MSA solution while the dashed curve represents the exact solution with the particles (oscillators) randomly distributed along the one-dimensional chain. The curves are made for the extreme case with relative strength of interaction  $\epsilon = 1$ .

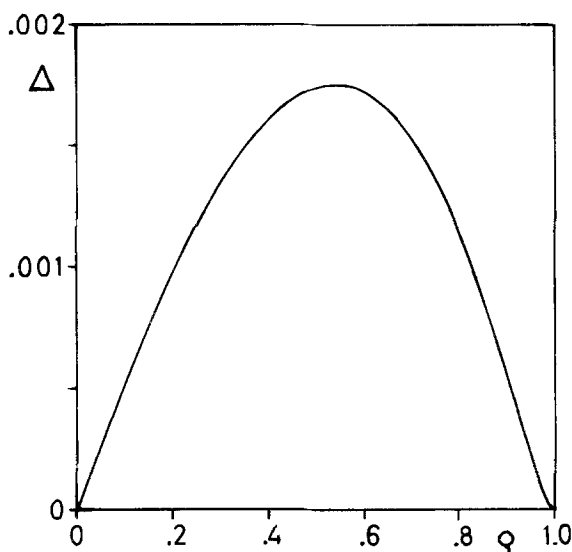


Fig. 2. The relative difference between the MSA solution and exact solution is shown enlarged for the same situation as in Fig. 1, i.e.,  $T=0$  and  $\epsilon=1$ . The  $\Delta = u_{\text{MSA}}/u_{\text{EX}} - 1$  where  $u_{\text{MSA}}$  is the MSA internal energy while  $u_{\text{EX}}$  is the exact one.

It should be noted here that the exact solution is performed for a quenched system where the occupied positions along the chain are fixed. By annealing the system the occupied positions will be thermally rearranged to favour some lowering of the energy. This would then increase the deviation from the MSA result somewhat. However, the exact annealed result requires more numerical work to evaluate, and we have for this reason not tried to obtain it.

For other models in one, two, or three dimensions we in general expect MSA results to be even closer to the exact solution than in the case considered here. This is clearly so when the interaction goes beyond nearest neighbors, since MSA improves with increasing range of interaction until the exact mean field result is reproduced in the limit of infinitely long-ranged interaction. However, in these other situations exact results, by which comparisons can be made, are usually not available.

## 2. MODEL

The model we shall consider is a one-dimensional lattice gas of polarizable molecules, each of which consist of two masses,  $m_e \ll m_n$ , with opposite charges of magnitude  $e$ . Their relative motion is associated with the reduced mass,

$$m_r = m_e m_n / (m_e + m_n)$$

while the center of mass is assumed to be bound to a lattice site. We assume the relative motion to be represented by a quantized harmonic (Drude) oscillator.<sup>(6)</sup> For the interaction between molecules we take into account only nearest-neighbor dipole-dipole interaction. By that the model can be solved exactly. Thus, with a fixed set of sites occupied by molecules, the system is described by the Hamiltonian

$$H = \sum_i \left( \frac{1}{2m_r} \mathbf{p}_i^2 + \frac{1}{2\alpha} \mathbf{q}_i^2 \right) + \frac{1}{2} \sum_{i,j} \frac{1}{a^3} [\mathbf{q}_i \cdot \mathbf{q}_j - 3(\hat{n} \cdot \mathbf{q}_i)(\hat{n} \cdot \mathbf{q}_j)] \quad (2.1)$$

where  $a$  is the lattice spacing and  $\hat{n}$  a unit vector in the lattice direction. The latter sum in (2.1) is only over oscillator pairs  $(i, j)$  that are nearest neighbors. (The factor  $1/2$  in front of it compensates for double counting.) The spring constant is chosen such that  $\alpha$  is the polarizability of a single molecule. (We use units such that the electric charge  $e = 1$ .)

Note that the system is not genuine one-dimensional, since so far we are using the dipole-dipole interaction of a three-dimensional world. Also, it is consistent to use the dipole-dipole interaction only when  $\langle q^2 \rangle \ll a^2$ .

The lattice, of total length  $N \rightarrow \infty$ , is assumed to be filled to a density  $\rho$ , such that

$$\rho = \frac{1}{N} \sum n P_n \quad (2.2)$$

Then  $P_n$  is the number of segments of length  $n$ , since for a given configuration of oscillators, the lattice breaks up into filled segments of different lengths.

With,

$$\lambda = \frac{1}{\rho N} \sum_{n \geq 1} P_n \quad (2.3)$$

the length distribution function is

$$p_n = P_n / (\lambda \rho N) \quad (2.4)$$

The  $\lambda^{-1}$  will be the average length of a filled segment. The model may now be considered in two versions: (i) quenched, the length distribution is predetermined; (ii) annealed, the length distribution function is adjusted so that the free energy of the system is minimized. We shall in this paper mostly consider the quenched case. In the MSA treatment of this problem

these two cases are not distinguishable, since spatial correlations are not accounted for in the MSA.

The Hamiltonian (2.1) can obviously be separated into three parts, each of which represents independent modes of oscillation, one parallel to  $\hat{n}$  and two transverse to it. Thus it is sufficient to consider only one of these parts. So, instead of (2.1) we now write the Hamiltonian as

$$H = \sum_i \left( \frac{1}{2m_r} p_i^2 + \frac{1}{2\alpha} x_i^2 \right) - \frac{1}{2} \sum_{i,j} \frac{1}{2\alpha} \varepsilon x_i x_j \quad (2.5)$$

where  $\varepsilon$  is the relative strength of interaction. Again  $\sum_{i,j}$  is only over nearest-neighbor pairs  $(i, j)$ . Mechanical stability requires  $|\varepsilon| < 1$ .

### 3. EXACT SOLUTION

#### 3.1. General Features

The thermodynamic properties of the model can be deduced from the partition function,

$$Z = e^{-\beta F} = \sum \text{Tr}[e^{-\beta H}] \quad (3.1)$$

where  $H$  is given by Eq. (2.5), and the summation runs over either (i) all configurations, consistent with a given length distribution function in the case of a quenched system, or (ii) all configurations, in the case of an annealed system. However, in the thermodynamic limit only a single length distribution function will contribute to the bulk free energy,  $F/\rho N$ .

Let  $H_n$  be the Hamiltonian (2.5) restricted to a filled segment of length  $n$ , and define

$$e^{-\beta n f_n} = \text{Tr}[e^{-\beta H_n}] \quad (3.2)$$

so that  $n$  times  $f_n$  is the free energy for a filled segment of length  $n$ . Since there is no interaction between different filled segments in the lattice, Eq. (3.1) may be rewritten

$$Z = \sum_{\{P\}} \exp \left[ S\{P\}/k - \beta \sum_{n \geq 1} n f_n P_n \right] \quad (3.3)$$

where  $P_n$  is the number of filled segments of length  $n$ . There is no summation over  $\{P\}$  in the quenched case. The factor

$$v\{P\} \equiv e^{S\{P\}/k} \quad (3.4)$$

counts the number of configurations consistent with a length distribution,  $\{P\}$ . As the notation suggests,  $S\{P\}$  is an entropy term (but there are additional contributions to the entropy from the internal degrees of freedom, included in the  $f_n$ 's). A simple counting argument<sup>3</sup>) shows that

$$v\{P\} = \frac{(N+1-M)!}{(N+1-M-C)! \prod_{n \geq 1} P_n!}$$

$$\ln v\{P\} = S\{P_n\}/k = N \left[ (1-\rho) \ln(1-\rho) - (1-\rho-\lambda\rho) \ln(1-\rho-\lambda\rho) \right. \\ \left. - \lambda\rho \ln(\lambda\rho) - \lambda_\rho \sum_{i \geq 1} p_i \ln p_i \right] \quad (3.5)$$

where

$$M = \rho N = \sum_n n P_n, \quad C = \lambda\rho N = \sum_n P_n$$

The counting argument goes as follows. There are  $M$  sites occupied by segments. Associate the neighboring empty site on the left-hand side of the segment to it. (It must always be accompanied by an empty site to separate it from other segments except for the segment at the left end of the chain). Thus we are left with  $N - M - (C - 1)$  empty sites that can be interchanged with  $C$  segments of varied lengths to yield different configurations. Straightforward combinatorics then give the result above for  $v\{P\}$ .

Result (3.5) may also be obtained by a more elaborate evaluation by regarding the filled segments (including an empty site at one end of each of them) as a mixture of hard rods whose entropy can be found from the equation of state.

In the quenched case, with the sites on the lattice filled at random, the length distribution function is found by direct arguments to be

$$p_n = (1-\rho)\rho^{n-1} \quad (3.6)$$

It is also straightforward to verify that this is the distribution which maximizes  $S\{P\}$  with respect to  $P_n$  when  $\rho$  is kept constant, leading to

$$S\{P\} = -Nk[\rho \ln \rho + (1-\rho) \ln(1-\rho)] \quad (3.7)$$

in agreement with the entropy of a noninteracting lattice gas.

In the annealed case one would have to determine the length distribution  $\{p_n\}$  which maximizes the exponential of expression (3.3) under the constraint  $\rho = \text{const}$ .

<sup>3</sup> We are indebted to Prof. P. C. Hemmer for demonstrating this to us.

Analogous to (3.6) the solution is now found to be of the form

$$p_n = c_0 e^{-n(c_1 + \beta f_n)} \quad (3.8)$$

where  $c_0$  and  $c_1$  are constants that can be determined. But clearly with a general form of  $f_n$  the problem can no longer be handled by purely analytic means. So, for the rest of this paper, we shall consider only the quenched version of the model.

### 3.2. Solution of the Finite Segments

We next turn to the task of finding the exact solution.

With the Hamiltonian (2.5) the equations of motion are

$$\begin{aligned} m_r \ddot{x}_j &= -[(x_j - \frac{1}{2}\varepsilon(x_{j-1} + x_{j+1}))]/\alpha, & \text{for } 1 < j < n \\ m_r \ddot{x}_1 &= -(x_1 - \frac{1}{2}\varepsilon x_2)/\alpha \\ m_r \ddot{x}_n &= -(x_n - \frac{1}{2}\varepsilon x_{n-1})/\alpha \end{aligned} \quad (3.9)$$

For an infinite chain ( $n \rightarrow \infty$ ) the end effects vanish, and it is straightforward to solve Eqs. (3.9).

A solution is then

$$x_j = A e^{i(pj - \omega t)} + A^* e^{-i(pj - \omega t)} \quad (3.10)$$

(The general solution is of course a sum of such solutions.) By insertion the relation between  $q$  and the frequencies  $\omega$  for the eigenmode (3.10) is found to be

$$m_r \omega^2 = [1 - \varepsilon \cos(p)]/\alpha \quad (3.11)$$

With end effects (i.e., finite  $n$ ) one notes the set of equations (3.9) may be extended with oscillators at both ends, provided  $x_0$  and  $x_{n+1}$  are held fixed, i.e.,  $x_0 = x_{n+1} = 0$ . By that the end effects vanish in (3.9). Instead, they appear as the boundary conditions  $x_0 = x_{n+1} = 0$ . Imposing this on Eq. (3.10) implies

$$x_j = C \sin(pj) \quad (3.12)$$

where  $p$  is restricted to

$$p = \pi \frac{k}{n+1} \quad \text{with } k = 1, 2, \dots, n \quad (3.13)$$

Thus, the eigenenergies  $\hbar\omega_k$  for a segment of  $n$  units are

$$\begin{aligned}\hbar\omega_k &= \hbar\omega_0 D\left(\frac{k}{n+1}\pi\right), & k &= 1, 2, \dots, n \\ \hbar\omega_0 &= \hbar/\alpha m_r, & D(x) &= [1 - \cos(x)]^{1/2}\end{aligned}\quad (3.14)$$

The quantized internal energy  $u_n$  for such a segment of  $n$  units is then

$$u_n = \frac{1}{2} \sum_{k=1}^n \hbar\omega_k \coth\left(\frac{1}{2}\beta\hbar\omega_k\right) \quad (3.15)$$

With  $P_n$  segments of length  $n$  the total internal energy becomes  $\sum_n P_n u_n$ . Now from (2.4)  $P_n = \lambda\rho N p_n$  with  $p_n$  given by (3.6). Thus from (2.2)

$$1 = \frac{1}{\rho N} \sum_n n P_n = \frac{\lambda}{1 - \rho} \quad (3.16)$$

i.e.,

$$P_n = \rho N (1 - \rho)^2 \rho^{n-1} \quad (3.17)$$

The exact average internal energy per particle is accordingly

$$u = \frac{1}{\rho N} \sum_n P_n u_n = (1 - \rho)^2 \sum_{n=1}^{\infty} \rho^{n-1} u_n \quad (3.18)$$

with  $u_n$  given by (3.15).

#### 4. THE MSA SOLUTION

Now we want to solve the problem of the random linear chain approximately by the MSA approach in classical statistical mechanics, as generalized to (semi)quantized polarizable fluids.<sup>(1,2,4,5)</sup> To find the MSA results we will utilize the equations obtained in Refs. 1 and 4 specialized to the linear chain considered here. When referring to the equations of Refs. 1 and 4 we will precede them by the numerals I and II, respectively, and we will not rederive them here, only evaluate general results more explicitly for the case considered.

The quantum partition function for a single oscillator is given by the path integral (I.16). In the present case it reads

$$Z^{(N)} = \int \exp \left\{ - \sum_{p=0}^{N-1} \left[ \frac{1}{2} \frac{\sigma}{\eta} (x_{p+1} - x_p)^2 + \eta \phi(x_p) \right] \right\} \prod_{q=0}^{N-1} (A dx_q) \quad (4.1)$$



where now

$$\sigma = \frac{m_r}{\hbar^2}, \quad A = \left( \frac{\sigma}{2\pi\eta} \right)^{1/2}, \quad \text{and} \quad x_N = x_0$$

The path is discretized with intervals of length  $\eta$ , such that  $\beta = N\eta$ , and the limit  $N \rightarrow \infty$  (or  $\eta \rightarrow 0$ ) is implicit. The single oscillator potential  $\phi(x)$  is found from the Hamiltonian (2.5),

$$\phi(x) = \frac{1}{2\alpha} x^2 \quad (4.2)$$

The path integral (4.1) can be interpreted as the classical partition function of a flexible polymer of length  $\beta$ . Thus each oscillator of the one-dimensional chain may be regarded as a classical polymer, and the interaction between the oscillators may be considered as interaction between polymers. In the present case this pair interaction (I.17) for two oscillators 1 and 2 is

$$\psi(12) = -\frac{\eta}{\beta} \frac{\varepsilon}{2\alpha} \sum_{p,q=1}^N x_{p1} x_{p2} \delta_{pq} \quad (4.3)$$

when they are nearest neighbors on the lattice. Otherwise it is zero in accordance with the last sum of the Hamiltonian (2.5).

To do the MSA on the polymer problem we again have to solve the OZ equation (I.18), modified to the situation where  $\psi(12)$  is given by (4.3) instead of (I.17). This simplifies matters. For example, there are no  $c_D$  and  $h_D$  terms, and we can thus replace  $c_A$  with  $c$  and  $h_A$  with  $h$ . So the transformed OZ equation (I.31) becomes

$$\tilde{h}^K(k) = \tilde{c}^K(k) + R_K \tilde{c}^K(k) \tilde{h}^K(k) \quad (4.4)$$

where

$$K = 2\pi(n/\eta N), \quad n = 1, 2, \dots, N$$

is the Fourier transform variable along the polymers, while the tilde denote Fourier transform on the lattice points in space. With (4.3) the boundary conditions for (4.4) instead of (I.35) become

$$c^K(p) = \begin{cases} \frac{\varepsilon}{2\alpha}, & |p| = 1 \\ 0, & |p| > 1 \end{cases} \quad (4.5)$$

$$h^K(p) = 0$$

when the distance  $a$  between lattice points is set equal to 1. The  $R_K$  is determined by (I.47)

$$R_K = \frac{\rho}{\sigma K^2 + 1/\alpha + c^K(0)} \quad (\eta \rightarrow 0) \quad (4.6)$$

Compared to (I.47) the factor 3 has been deleted in (4.6) since the  $x_p$  in (4.3) are scalar amplitudes while in (I.17) they are vectors with three components. So far the  $c^K(0)$  is unknown, but (4.4) with conditions (4.5) will determine it. With (4.5) the Fourier transform of  $c^K(p)$  is

$$\tilde{c}^K(k) = c + \frac{\varepsilon}{\alpha} \cos(k) \quad (4.7)$$

with  $c = c^K(0)$ . So (4.4) and (4.5) yield the following equation:

$$\begin{aligned} 0 = h^K(0) &= \frac{1}{2\pi} \int_{-\pi}^{\pi} \tilde{h}^K(k) dk = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\tilde{c}^K(k)}{1 - R_K \tilde{c}^K(k)} dk \\ &= -\frac{1}{R_K} \left[ 1 - \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{dk}{1 - R_K \tilde{c}^K(k)} \right] \end{aligned} \quad (4.8)$$

This integral can be evaluated explicitly, since

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{dk}{1 - \tau \cos k} = \frac{1}{(1 - \tau^2)^{1/2}} \quad (4.9)$$

With (4.7) inserted we thus find from (4.8)

$$1 = \frac{1}{1 - R_K c} \frac{1}{(1 - \tau^2)^{1/2}} \quad \text{with } \tau = \frac{\varepsilon}{\alpha} \frac{R_K}{1 - R_K c} \quad (4.10)$$

which gives

$$(1 - R_K c)^2 - \left( \frac{\varepsilon}{\alpha} R_K \right)^2 = 1 \quad (4.11)$$

Inserting (4.6) for  $R_K$  further gives (with  $z = \sigma K^2 + 1/\alpha$ )

$$[z + (1 - \rho)c]^2 - \left( \frac{\varepsilon}{\alpha} \rho \right)^2 = (z + c)^2 \quad (4.12)$$

or

$$(2 - \rho)c^2 + 2zc + \rho \left( \frac{\varepsilon}{\alpha} \right)^2 = 0$$

It is required that  $1 - R_K c > 0$  so only the positive square root is of interest. Therefore [ $c = c^K(0)$ ],

$$c^K(0) = \frac{1}{2 - \rho} \left\{ - \left( \sigma K^2 + \frac{1}{\alpha} \right) + \left[ \left( \sigma K^2 + \frac{1}{\alpha} \right)^2 - \rho(2 - \rho) \left( \frac{\epsilon}{\alpha} \right)^2 \right]^{1/2} \right\} \quad (4.13)$$

With  $c^K(0)$  known it is now possible to obtain thermodynamic quantities like the internal energy  $u$  per particle. From Eq. (I.76) or Eq. (II.1) we in the present case find

$$\beta u = \sum_K f(K^2) \quad (4.14)$$

where

$$f(K^2) = 1 - \sigma K^2 \frac{R_K}{\rho} = 1 - \frac{\sigma K^2}{\sigma K^2 + (1/\alpha) + c^K(0)} \quad (4.15)$$

and  $K = 2\pi(n/\beta)$ ,  $n = 1, 2, 3, \dots$  ( $\beta = \eta N$ ,  $N \rightarrow \infty$ ). For the same reason as with Eq. (4.6) the factor of 3 does not appear here. Like (II.7) it is possible to write

$$f(K^2) = \int \frac{g(m^2)}{K^2 + m^2} d(m^2) \quad (4.16)$$

where  $g(m^2)/m^2$  is the frequency distribution for the disordered chain of interacting harmonic oscillators. With (4.16) inserted into (4.15) the summation with respect to  $K$  can be performed (e.g., see Appendix of Ref. 1). So like (II.13)<sup>4</sup> we find

$$u = \frac{1}{2} \int m \coth \left( \frac{1}{2} \beta m \right) \frac{g(m^2)}{m^2} d(m^2) \quad (4.17)$$

where

$$\overline{m} = \hbar \omega \quad (4.18)$$

and  $\omega$  is the frequency. The distribution  $g(m^2)$  fulfills (II.14),

$$1 = f(0) = \int \frac{g(m^2)}{m^2} d(m^2) \quad (4.19)$$

Equation (II.11) determines  $g(m^2)$  in terms of  $f(K^2)$ , i.e.,

$$g(m^2) = -\frac{1}{\pi} \text{Im} f(-m^2 + i\gamma) \quad (\gamma \rightarrow 0+) \quad (4.20)$$

<sup>4</sup> There is a misprint in Eq. (II.13): The  $\cosh(\frac{1}{2}\beta m)$  in the denominator should be replaced by  $\sinh(\frac{1}{2}\beta m)$ .

For convenience we introduce the variable

$$q = \frac{1}{\varepsilon} (1 - \alpha \sigma m^2) = \frac{1}{\varepsilon} \left( 1 - \frac{\omega^2}{\omega_0^2} \right) \quad (4.21)$$

and the distribution  $\hat{g}(q)$  such that

$$\frac{g(m^2)}{m^2} dm^2 = \hat{g}(q) dq \quad (4.22)$$

Inserting (4.13) into (4.15), utilizing (4.20)–(4.22), we obtain

$$\hat{g}(q) = \begin{cases} \frac{1}{\pi \rho} \frac{[\rho(2-\rho) - q^2]^{1/2}}{1 - q^2}, & q^2 < \rho(2-\rho) \\ 0, & \text{otherwise} \end{cases} \quad (4.23)$$

## 5. COMPARISON OF MSA AND THE EXACT SOLUTION

The most detailed comparison between MSA and the exact result would be to compare the resulting frequency distributions since other quantities will follow from these. As expected, it is immediately clear that the MSA distribution (4.23) will deviate from the exact one when  $0 < \rho < 1$ , since the former is continuous while the latter is discretized when  $\rho < 1$ . This qualitative difference makes it somewhat difficult to compare them directly. Thus we will focus on integrated quantities. However, for a completely filled chain,  $\rho = 1$ , the distributions are identical, as has already been concluded. From the exact eigenfrequencies for a segment of  $n$  units [Eq. (3.14)] we find

$$q = \cos \left( \frac{k}{n+1} \pi \right) \quad (5.1)$$

For  $\rho \rightarrow 1$  the segments become longer and longer, i.e.,  $n \rightarrow \infty$ , such that (5.1) become continuous. Differentiation yields the frequency distribution

$$\hat{g}(q) = \frac{d \left( \frac{k}{n+1} \right)}{dq} = \frac{1}{\pi \sin \left( \frac{k}{n+1} \pi \right)} = \frac{1}{\pi} (1 - q^2)^{-1/2} \quad (5.2)$$

This is identical to the MSA result (4.23) when  $\rho = 1$ . Likewise (4.23) yields the exact result when  $\rho = 0$ , since then it reduces to a  $\delta$  function at  $\sigma m^2 = 1/\alpha$ , which is the frequency of the uncoupled oscillators.

The width of the frequency distribution (4.23) increases with density  $\rho$ . This width is a natural quantity to compare with the exact result. The average width squared becomes

$$\langle q^2 \rangle = \int dq q^2 \hat{g}(q) \quad (5.3)$$

[As may be verified by direct integration,  $\hat{g}(q)$  is normalized in accordance with (4.19).] Inserting Eq. (4.23) into (5.3) gives an integral, which can be evaluated in a straightforward way by first substituting  $q = [\rho(2 - \rho)]^{1/2} \sin \phi$  and then  $u = (1 - \rho) \tan \phi$ . The result is

$$\langle q^2 \rangle = \frac{1}{2} \rho \quad (5.4)$$

The corresponding width for the exact solution is found by summing over the different frequencies of a segment of  $n$  units and then summing over the distribution of segments. With the eigenfrequencies (5.1) it is straightforward to show that

$$a_n = \sum_{k=1}^n \cos^2 \left( \frac{k}{n+1} \pi \right) = \frac{1}{2}(n-1) \quad (5.5)$$

Weighing this over the distribution (3.17) of segments then yields for the exact solution

$$\langle q^2 \rangle = (1 - \rho)^2 \sum_{n=1}^{\infty} a_n \rho^{n-1} = \frac{1}{2} \rho \quad (5.6)$$

which coincides with the MSA result (5.4).

We may now compare some thermodynamic quantity. In view of the fact that the exact and approximate frequency distribution have the same width, which we just showed, it is reason to believe that other integrated quantities will deviate little when comparing the MSA and exact solutions. We choose to study the internal energy per particle,  $u$ . It is already clear that the MSA becomes exact when  $\rho \rightarrow 0$  and  $\rho \rightarrow 1$ . Furthermore, it becomes exact for large temperatures ( $\beta \rightarrow 0$ ), and of course when the relative strength of interaction  $\varepsilon \rightarrow 0$ . The limit  $\beta \rightarrow 0$  is obvious since this is the classical limit in which the energy of each oscillation mode is  $kT$ , independent of frequency. (On the other hand, the free energy will depend on the frequencies when  $\beta \rightarrow 0$ .) Thus we may concentrate on low temperatures (i.e.,  $\beta \rightarrow \infty$ ) where the deviations are most significant, and where the internal energy becomes the ground state energy (and also equal to the free energy).

For limiting cases the  $u$  may be computed explicitly by analytic means. Otherwise it can be done numerically. When  $\beta \rightarrow \infty$  Eq. (4.17) becomes, with use of (4.21),

$$u = \frac{1}{2} \hbar \omega_0 \int dq (1 - \varepsilon q)^{1/2} \hat{g}(q) \quad (5.7)$$

When  $\rho$  is small, the  $\hat{g}(q)$  is narrow, and one may expand

$$(1 - \varepsilon q)^{1/2} = \left[ 1 - \frac{1}{2} \varepsilon q - \frac{1}{8} (\varepsilon q)^2 \cdots \right] \quad (5.8)$$

Use of (5.4) thus yields for small  $\rho$  for the MSA,

$$u = u_0 \left[ 1 - \frac{1}{16} \varepsilon^2 \rho + \cdots \right], \quad u_0 = \frac{1}{2} \hbar \omega_0 \quad (5.9)$$

For the exact solution Eq. (3.18) with frequencies (5.1) we find

$$\begin{aligned} u &= u_0 (1 - \rho)^2 \left\{ 1 + \rho \left[ \left( 1 - \frac{1}{2} \varepsilon \right)^{1/2} + \left( 1 + \frac{1}{2} \varepsilon \right)^{1/2} \right] + \cdots \right\} \\ &= u_0 \left\{ 1 - \left( 1 - \frac{1}{2} \varepsilon \right)^{1/2} - \left( 1 + \frac{1}{2} \varepsilon \right)^{1/2} \right\} \rho + \cdots \\ &= u_0 \left[ 1 - \frac{1}{16} \varepsilon^2 \left( 1 + \frac{5}{64} \varepsilon^3 \cdots \right) \rho + \cdots \right] \end{aligned} \quad (5.10)$$

To have a stable system it is necessary that  $|\varepsilon| \leq 1$ . Thus the magnitude of the  $\rho$  terms of (5.9) and (5.10) cannot differ much.

When  $\rho = 1$  one finds from Eq. (5.2) that the MSA yields the exact result. In this case one finds for the internal energy (5.7) [utilizing Eqs. (4.23) and (5.3)]

$$\begin{aligned} u &= \frac{1}{2\pi} \hbar \omega_0 \int_{-1}^1 dq \left( \frac{1 - \varepsilon q}{1 - q^2} \right)^{1/2} \\ &= \frac{1}{2} \hbar \omega_0 \frac{2}{\pi} (1 + \varepsilon)^{1/2} E \left( \frac{2\varepsilon}{1 + \varepsilon} \right) \end{aligned} \quad (5.11)$$

where

$$E(\tau) = \int_0^{\pi/2} (1 - \tau \sin^2 \Theta)^{1/2} d\Theta \quad (5.12)$$

is the complete elliptic integral of the second kind. For the extreme case  $\varepsilon = 1$  one easily computes  $E(1) = 1$ , or from (5.1) ( $\rho = 1$ )

$$u = \frac{1}{2} \hbar \omega_0 \frac{2}{\pi} \sqrt{2} = \frac{1}{2} \hbar \omega_0 \cdot 0.9003 \quad (5.13)$$

This shows that the internal energy per particle does not vary much with  $\varepsilon$  within its stability range. We may also expand (5.11) for small  $\varepsilon$  (putting  $q = \sin \phi$  by integration)

$$u = \frac{1}{2} \hbar \omega_0 \left( 1 - \frac{1}{16} \varepsilon^3 - \frac{15}{1024} \varepsilon^2 \dots \right) \quad (5.14)$$

It is also possible to compute  $u$  analytically when  $\rho$  is close to 1. By extension to a full period of the cosine function the sum that yields  $u$  can be considered as a Simpson rule approximation to the result for  $\rho = 1$ . From this we obtain

$$\begin{aligned} u_n &= \frac{1}{2} \hbar \omega_0 \sum_{k=1}^h D \left( \frac{k}{n+1} \pi \right) \\ &= \frac{1}{2} \hbar \omega_0 [(n+1)\bar{D}] - \frac{1}{2} [D(0) + D(\pi)] + O\left(\frac{1}{n^3}\right) \end{aligned} \quad (5.15)$$

However, by a more careful analysis with application of the Euler-Maclaurin summation formula, it can be shown that the last term in (5.15) can be replaced by  $O(e^{-An})$  when  $|\varepsilon| < 1$ . (It turns out that *all* the higher-order terms in the summation formula vanish due to periodicity, leaving only the remainder term which can be shown to be exponentially small. The coefficient  $A$  will increase with decreasing  $|\varepsilon|$ .)

The average internal energy per particle thus becomes

$$\begin{aligned} u &= (1-\rho)^2 \sum_{n=1}^{\infty} \rho^{n-1} u_n \\ &= \frac{1}{2} \hbar \omega_0 \left[ \bar{D} + (1-\rho) \left\{ \bar{D} - \frac{1}{2} [D(0) + D(\pi)] \right\} + O((1-\rho)^2) \right] \end{aligned} \quad (5.16)$$

Here

$$\bar{D} = \frac{1}{\pi} \int_0^{\pi} D(x) dx$$

which like (5.11) give the energy when  $\rho = 1$ . We may again expand in  $\varepsilon$  to find

$$\bar{D} - \frac{1}{2} [D(0) + D(\pi)] = \frac{1}{16} \varepsilon^2 + \frac{25}{1024} \varepsilon^4 + \dots \quad (5.17)$$

The MSA solution may also be found more explicitly when  $\rho$  is close to 1 ( $T=0$ ). As concluded before the exact result  $u = \frac{1}{2} \hbar \omega_0 \bar{D}$  is obtained when  $\rho = 1$ . When  $1 - \rho$  is small the  $\hat{g}(q)$  of (4.23) changes like the factor  $1/\rho$  when  $q$  is away from the end points of the interval. At the end points the changes will be peaked and can be regarded as two  $\delta$  functions of equal magnitude (due to symmetry). Thus for small  $(1 - \rho)$

$$\hat{g}(q) = \frac{1}{q} \hat{g}(q) \Big|_{\rho=1} + a[\delta(q-1) + \delta(q+1)] \quad (5.18)$$

where  $a$  is determined by the normalization (4.19) together with (4.22),

$$1 = \frac{1}{\rho} + 2a \quad (5.19)$$

$$a = \frac{1}{2} \left( 1 - \frac{1}{\rho} \right) \approx -\frac{1}{2} (1 - \rho)$$

Inserted in (5.15) we thus find

$$u = \frac{1}{2} \hbar \omega_0 \left\{ \frac{1}{\rho} \bar{D} + a[D(0) + D(\pi)] \right\}$$

$$= \frac{1}{2} \hbar \omega_0 \left( \bar{D} + (1 - \rho) \left\{ \bar{D} - \frac{1}{2} [D(0) + D(\pi)] \right\} \right) \quad (5.20)$$

which coincides with the exact result (5.16).

In summary, we can conclude that the MSA internal energy approximates the exact result well at  $T=0$ . (When  $T$  increases the difference becomes even smaller.) To  $O(\varepsilon^2)$  the results actually coincide. This also follows from the results (5.4) and (5.6). To this order in  $\varepsilon$ ,  $u$  varies linearly with  $\rho$ . However, to  $O(\varepsilon^4)$  the MSA result will differ somewhat from the exact result (except at  $\rho = 0$  and  $\rho = 1$ ). As a function of  $\rho$  the two results have slightly different slopes at  $\rho = 0$  [cf. Eqs. (5.9) and (5.10)], while at  $\rho = 1$  the slopes are the same.

For the extreme case  $|\varepsilon| = 1$ , the  $u$  has been computed numerically for arbitrary  $\rho$  ( $T=0$ ), and the results are plotted in Figs. 1 and 2. Clearly the results differ little, and the difference has roughly a parabolic shape, with



maximum near  $\rho = 0.5$ . When  $\varepsilon$  becomes smaller this difference vanishes rapidly, and double precision computations will be needed. In view of the parabolic shape and the analytic results at the end points this difference can be estimated easily. The maximum difference is thus roughly half the difference between (5.9) and (5.10) at  $\rho = \frac{1}{2}$ . This maximum is thus

$$\begin{aligned} \Delta u_{\max} = u_{\text{MSA}} - u_{\varepsilon x} &\approx u_0 \frac{1}{2} \frac{1}{16} \frac{5}{64} \frac{1}{2} \varepsilon^4 \\ &\approx 1.2 \times 10^{-3} u_0 \varepsilon^4 \end{aligned} \quad (5.21)$$

Relative to the ground state energy  $u_0$  of a single oscillator the error is very small, since  $|\varepsilon| \leq 1$ . However, relative to the change in  $u$  when  $\rho$  varies from 0 to 1, the error is somewhat larger. With (5.14) this becomes roughly

$$\Delta u_{\max} \left/ \left( \frac{1}{16} \varepsilon^2 u_0 \right) \right. = \frac{5}{256} \varepsilon^2 \quad (5.22)$$

which still is small.

## ACKNOWLEDGMENT

One of us (R.H.) wants to thank Norges Tekniske Høgskole for a student exchange stipend, by which part of this work was done.

## REFERENCES

1. J. S. Høye and G. Stell, *J. Chem. Phys.* **75**:5133 (1981).
2. M. J. Thompson, K. Schweizer, and D. Chandler, *J. Chem. Phys.* **76**:1128 (1982).
3. E. H. Lieb and D. C. Mattis, *Mathematical Physics in One Dimension* (Academic Press, New York, 1966).
4. J. S. Høye and K. Olaussen, *J. Chem. Phys.* **77**:2583 (1982).
5. D. Chandler, K. Schweizer, and P. G. Wolynes, *Phys. Rev. Lett.* **49**:1100 (1982).
6. J. H. van Vleck, *J. Chem. Phys.* **5**:556 (1937).
7. P. Henrici, *Applied and Computational Complex Analysis* (Wiley, New York, 1977).