Quantum Corrections for Lattice Gases

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Classical lattice gases consisting of structureless particles (with spin) have been quantized by introducing a kinetic energy operator that produces nearest-neighbor hops. Systematic quantum corrections for the partition function and the particle distribution functions appear naturally as power series in $X = \beta \hbar^2 / 2ml^2$ ($\beta^{-1} = k_B T$, m is the mass, l is a distance related to lattice spacing). These corrections require knowledge of certain particle displacement probabilities in the corresponding classical lattice gases. Leading-order corrections have been derived in forms that should facilitate their use in computer simulation studies of lattice gases by the standard Monte Carlo method.

KEY WORDS: Quantum corrections; lattice gases; equation of state; distribution functions; high-temperature series; Monte Carlo simulation.

1. INTRODUCTION

Classical lattice gas models were originally devised to clarify the nature of phase transitions.[1,2] They offered several attractive advantages. Since a general isomorphism had been established between Ising models and lattice gases,[2,3] it was possible to draw upon exact results available for the two-dimensional Ising model.[4,5] Even in three dimensions, where closed-form results for Ising models are not yet known, lattice gas models admit a wider range of approximate partition function evaluations than exist for the underlying "continuum" models.[6] Recently, lattice gases have also provided computational advantages in digital computer simulation of cooperative phenomena.[7]

The last few years have witnessed a trend toward use of classical lattice gas models to study relatively complicated molecular fluids, most notably water.[8,9] It seems likely that other hydrogen-bonding substances (ammonia,

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hydrogen halides, the alcohols, hydrogen cyanide, malononitrile, etc.) might also be similarly modeled. But with light hydrogen atoms present, quantum corrections to the classical partition function doubtless become significant.

It is the aim of the present paper to develop a systematic formal procedure for generating lattice gas quantum corrections. In the interests of simplicity and clarity, attention will be confined to models with structureless particles, for which the quantum corrections refer to translational motion. Having done this, the procedure for incorporating other molecular degrees of freedom (such as rotation) is straightforward. We intend to devote a subsequent publication to lattice gas quantum corrections for water.[10]

Fully quantized lattice gases have been examined before, as models for liquid helium.[11–13] There, of course, the emphasis lay on the ground state and low-lying excited states. No effort was made to generate the high-temperature expansions derived here.

2. BASIC DEFINITIONS

Let α index the Ω sites forming the regular lattice. A fixed number $N < \Omega$ of particles inhabit these sites, and can jump from site to site. The single-occupancy constraint applies: At most one particle can occupy any given site. The particles have spin S, but are otherwise structureless.

A localized state for particle j to be on site α_j with spin component σ_j will be denoted by the symbol

$$|j; \alpha_j, \sigma_j\rangle \tag{1}$$

These states are assumed to be normalized:

$$\langle j; \alpha_j, \sigma_j \,|\, j; \alpha_k, \sigma_k\rangle = \delta(\alpha_j, \alpha_k)\,\delta(\sigma_j, \sigma_k) \tag{2}$$

By employing the permutation operator P for the particles $1,...,N$, we can construct a suitable complete set of N-particle basis functions ($\alpha_1,..., \alpha_N$ distinct):

$$|\alpha, \sigma_1,..., \alpha_N, \sigma_N\rangle = (N!)^{-1/2} \sum_P (\pm 1)^P \prod_{j=1}^{N} |j; \alpha_{Pj}, \sigma_{Pj}\rangle \tag{3}$$

with bosons using the upper sign, fermions the lower sign.

It will be convenient to introduce creation and annihilation operators for each site, $a^+(\alpha, \sigma)$ and $a(\alpha, \sigma)$, along with the associated number operator:

$$n(\alpha) = \sum_{\sigma=-S}^{+S} a^+(\alpha, \sigma)a(\alpha, \sigma), \qquad n^2(\alpha) = n(\alpha) \tag{4}$$

for the space of single-occupancy states (3). The basic commutation relations are[13]

$$[a(\alpha_j, \sigma_j), a(\alpha_k, \sigma_k)] = 0$$

$$[a(\alpha_j, \sigma_j), a^+(\alpha_k, \sigma_k)] = [1 - 2n(\alpha_j)] \, \delta(\alpha_j, \alpha_k) \, \delta(\sigma_j, \sigma_k) \qquad (5)$$

The single-occupancy constraint also requires

$$a(\alpha_j, \sigma_j)a(\alpha_j, \sigma_k) = 0 \qquad (6)$$

Using these relations, one sees that $a^+(\alpha_j, \sigma_j)a(\alpha_k, \sigma_k)$ acting on a given state (3) gives zero unless site α_j is empty and site α_k contains a particle with spin σ_k; in that event the particle is shifted to α_j and has its spin changed to σ_j.

Following established convention, the lattice gas Hamiltonian operator will be written

$$\mathbf{H} = \mathbf{T} + \mathbf{V} \qquad (7)$$

where **T** and **V** represent kinetic and potential energies, respectively. The kinetic energy operator **T** will have the following form [defined *only* on the space of states (3)]:

$$\mathbf{T} = \sum_{\alpha=1}^{\Omega} \mathbf{T}_\alpha \qquad (8)$$

$$\mathbf{T}_\alpha = \frac{\hbar^2}{2ml^2} \left[zn(\alpha) - \sum_{\alpha'}^{(nn\ \alpha)} \sum_{\sigma} a^+(\alpha, \sigma)a(\alpha', \sigma) \right] \qquad (9)$$

This provides a finite-difference version of the usual Laplace operator. Here m stands for particle mass, z is the lattice coordination number, and l is an appropriate length comparable to the lattice spacing b.[2] The α' summation in Eq. (9) covers the z nearest neighbors of site α.

In the following development, the potential energy operator **V** will be an arbitrary function of the site occupation numbers $n(\alpha)$, but we will require that it be independent of particle spins. Contributions both from intermolecular forces and from external fields (such as gravity) can be present in **V** simultaneously.

The lattice gas partition function is

$$Z = \text{Tr}[\exp(-\beta\mathbf{H})], \qquad \beta = (k_B T)^{-1} \qquad (10)$$

where the trace is calculated over the complete set of N-particle states (3). Quantum corrections to Z arise due to particle identity and to the fact that **T** and **V** do not commute. We shall define the "classical limit" partition function Z_0 to be

$$Z_0 = \lim_{m \to \infty} Z \qquad (11)$$

[2] For the linear, square, and simple cubic lattices, l equals the nearest-neighbor spacing b. For the body-centered cubic lattice, $l = 2b/3^{1/2}$. The cubic and hexagonal close-packed lattices in three dimensions and the planar hexagonal lattice require $l = 2b$.

This limit obviously removes **T** from the problem altogether. Aside from trivial spin factors, Z_0 adopts the familiar classical lattice gas form

$$Z_0 = (2S + 1)^N \sum{}' \exp\{-\beta V[n(1),..., n(\Omega)]\} \tag{12}$$

wherein the interaction can be treated as a c-number. The primed summation in Eq. (12) includes all sets of numbers $n(\alpha) = 0, 1$ subject to

$$\sum_{\alpha=1}^{\Omega} n(\alpha) = N \tag{13}$$

Distribution functions $P^{(n)}(\alpha_1,..., \alpha_n)$ may also be introduced.

$$P^{(n)}(\alpha_1,..., \alpha_n) = Z^{-1} \operatorname{Tr}\left[\exp(-\beta \mathbf{H}) \prod_{j=1}^{n} n(\alpha_j)\right] \tag{14}$$

These quantities give the probabilities that all sites $\alpha_1,..., \alpha_n$ in a given set are simultaneously occupied. Following Eq. (11),

$$\lim_{m \to \infty} P^{(n)} = P_0^{(n)} \tag{15}$$

will represent the classical limit distribution functions. The corresponding analog of Eq. (12) will be

$$P_0^{(n)}(\alpha_1,..., \alpha_n) = Z_0^{-1}(2S + 1)^N \sum{}' \exp(-\beta V) \prod_{j=1}^{n} n(\alpha_j) \tag{16}$$

It is our task to derive corrections to Z_0 and the $P_0^{(n)}$ in the form of series in ascending orders in m^{-1}.

3. ELEMENTARY EXAMPLE

Before examining the full problem with N interacting particles, it will be profitable to study a simple case in detail. Specifically we shall now consider a single particle moving on a linear lattice (Ω sites with separation $b = l$; see footnote 2), with periodic boundary conditions.

The energy spectrum is easy to determine:

$$\varepsilon(k) = (\hbar^2/ml^2)[1 - \cos(kl)] \tag{17}$$

where the wave vectors k are

$$k = 2\pi s/\Omega l \tag{18}$$

$$s = 0, \pm 1, \pm 2,..., \pm \left[\operatorname{int}\left(\frac{\Omega + 1}{2}\right) - 1\right] \tag{19}$$

(plus $\Omega/2$ if Ω is even)

Due to particle spin, each k value should be reckoned as occurring $2S + 1$ times.

The partition function is

$$Z = (2S + 1) \sum_{k} \exp\{-(\beta\hbar^2/ml^2)[1 - \cos(kl)]\} \qquad (20)$$

Of course we have

$$Z_0 = (2S + 1) \sum_{k} 1 = (2S + 1)\Omega \qquad (21)$$

If the number of sites Ω is large, the k values (18) become sufficiently closely spaced that the k sum in Eq. (20) passes into an integral:

$$Z = (2S + 1)(\Omega l/2\pi) \int_{-\pi/l}^{\pi/l} dk \exp\{(\beta\hbar^2/ml^2)[\cos(kl) - 1]\}$$

$$= (2S + 1)\Omega \exp\left(-\frac{\beta\hbar^2}{ml^2}\right) I_0\left(\frac{\beta\hbar^2}{ml^2}\right) \qquad (22)$$

where I_0 is the modified Bessel function[14]:

$$I_0(x) = 1 + \frac{x^2}{2^2(1!)^2} + \frac{x^4}{2^4(2!)^2} + \frac{x^6}{2^6(3!)^2} + \cdots \qquad (23)$$

Thus we can also write

$$\ln Z = \ln Z_0 - 2X + X^2 - \tfrac{1}{4}X^4 + \tfrac{1}{9}X^6 - (11/192)X^8 + \cdots \qquad (24)$$

with

$$X = \beta\hbar^2/2ml^2 \qquad (25)$$

serving as the natural dimensionless expansion parameter for corrections to the leading "classical" term $\ln Z_0$.

Since

$$I_0(x) \sim (2\pi x)^{-1/2} \exp(x) \qquad (26)$$

as $x \to \infty$, we find that in the low-temperature limit, expression (22) reduces to

$$Z \sim (2S + 1)\Omega l(2\pi m/\beta\hbar^2)^{1/2} \qquad (27)$$

This agrees precisely with the partition function for a particle able to move *continuously* along a line of length Ωl. The agreement is hardly surprising, since low temperature entails wavelengths in the eigenfunctions which span many lattice spacings.

The fact that spectrum (17) is bounded above, whereas that for the continuum problem is not leads to qualitative disparity between the two in the high-temperature limit. The same situation applies in the more general

multidimensional N-particle lattice gas. However, our main interest lies in the way that density variations (at a given temperature) cause varying quantum corrections in the equation of state and distribution functions, and for this purpose the boundedness of the spectrum is largely irrelevant.

4. BULK THERMODYNAMIC PROPERTIES

We return now to the general N-particle lattice gas. Its partition function Z provides the free energy F:

$$Z = \exp(-\beta F) \tag{28}$$

and F in turn can be used to calculate other bulk thermodynamic properties by standard manipulations. For this reason it is desirable to develop $\ln Z$ in a series in the dimensionless parameter X defined in Eq. (25).

We shall employ the following operator expansion[15]:

$$
\begin{aligned}
\exp[-\beta(\mathbf{T} + \mathbf{V})] &= \mathbf{G}_0 - X \int_0^1 d\lambda_1 \; G_0(\lambda_1)\mathbf{t}G_0(1 - \lambda_1) + \cdots \\
&+ (-X)^n \int_0^1 d\lambda_1 \int_0^{1-\lambda_1} d\lambda_2 \cdots \int_0^{1-\lambda_1-\cdots-\lambda_{n-1}} d\lambda_n \; G_0(\lambda_1)\mathbf{t} \\
&\times \; \mathbf{G}_0(\lambda_2)\mathbf{t} \cdots \mathbf{G}_0(\lambda_n)\mathbf{t}G_0(1 - \lambda_1 - \cdots - \lambda_n) \\
&+ \cdots
\end{aligned} \tag{29}
$$

where again X stands for $\beta\hbar^2/2ml^2$, and

$$G_0(\lambda) = \exp(-\lambda\beta\mathbf{V}), \qquad \mathbf{t} = (\beta/X)\mathbf{T} \tag{30}$$

Reference to Eqs. (8) and (9) shows that $\mathbf{t}$ is independent of X and β, so Eq. (29) is properly arranged in ascending orders in X.

Define

$$
\begin{aligned}
D_n(\beta) &= (-1)^n Z_0^{-1} \, \mathrm{Tr}\bigg\{ \int_0^1 d\lambda_1 \int_0^{1-\lambda_1} d\lambda_2 \cdots \int_0^{1-\lambda_1-\cdots-\lambda_{n-1}} d\lambda_n \\
&\times \; \mathbf{G}_0(\lambda_1)\mathbf{t}G_0(\lambda_2) \cdots G_0(\lambda_n)\mathbf{t}G_0(1 - \lambda_1 - \cdots - \lambda_n) \bigg\}
\end{aligned} \tag{31}
$$

Then by inserting expansion (29) into Eq. (10) we have

$$Z = Z_0 \left[1 + \sum_{j=1}^{\infty} D_j(\beta)X^j \right] \tag{32}$$

For the usual technical reasons connected with N dependence of the terms generated, it is advisable to transform Eq. (32) into an expansion for $\ln Z = -\beta F$:

$$\ln Z = \ln Z_0 + \sum_{n=1}^{\infty} \Lambda_n(\beta)X^n \tag{33}$$

The leading-order cumulants Λ_n are related to the D_n thus:

$$
\begin{aligned}
\Lambda_1 &= D_1 \\
\Lambda_2 &= D_2 - \tfrac{1}{2}(D_1)^2 \\
\Lambda_3 &= D_3 - D_2 D_1 + \tfrac{1}{3}(D_1)^3 \\
\Lambda_4 &= D_4 - D_3 D_1 - \tfrac{1}{2}(D_2)^2 + D_2(D_1)^2 - \tfrac{1}{4}(D_1)^4
\end{aligned}
\tag{34}
$$

The structure of the general cumulant may be written as follows:

$$
\Lambda_n = \sum_{\{n_j\}}^{(\sum j n_j = n)} (-1)^{\sum n_j - 1} \left(\sum n_j - 1 \right)! \prod_{j=1}^{\infty} [(D_j)^{n_j}/n_j!]
\tag{35}
$$

Having formally generated series (33), we consider its leading terms in detail. The quantity $\Lambda_1 = D_1$ is trivial to evaluate. Using the cyclic invariance property of the trace, one has

$$
\Lambda_1 = -Z_0^{-1} \operatorname{Tr}[\mathbf{t} \exp(-\beta \mathbf{V})]
\tag{36}
$$

Since $\mathbf{V}$ is diagonal in the basis (3), only the diagonal parts of $\mathbf{t}$ in that basis can contribute to Λ_1. One has

$$
\mathbf{t} = \sum_{\alpha=1}^{\Omega} \left[zn(\alpha) - \sum_{\alpha'}^{(nn\,\alpha)} \sum_{\sigma} a^+(\alpha, \sigma) a(\alpha', \sigma) \right]
\tag{37}
$$

Hence [the $zn(\alpha)$ terms are the diagonal parts]

$$
D_1 = \Lambda_1 = -Nz
\tag{38}
$$

In evaluating the second-order quantity D_2 (as part of Λ_2), diagonal processes are important again, but with two $\mathbf{t}$'s present it is also possible to step a particle into an empty neighbor site and back again. The specific expression to be evaluated is

$$
\begin{aligned}
D_2 &= Z_0^{-1} \operatorname{Tr}\left\{ \int_0^1 d\lambda_1 \int_0^{1-\lambda_1} d\lambda_2 \, \mathbf{t} \mathbf{G}_0(\lambda_2) \mathbf{t} \mathbf{G}_0(1 - \lambda_2) \right\} \\
&= Z_0^{-1} \operatorname{Tr}\left\{ \int_0^1 d\lambda_1 \, \lambda_1 \mathbf{t} \mathbf{G}_0(1 - \lambda_1) \mathbf{t} \mathbf{G}_0(\lambda_1) \right\}
\end{aligned}
\tag{39}
$$

where again we have used cyclic invariance of the trace, then integrated by parts. One readily verifies that the diagonal contributions give

$$
Z_0^{-1}(Nz)^2 \operatorname{Tr}\left[\int_0^1 d\lambda_1 \, \lambda_1 \mathbf{G}_0(1) \right] = \tfrac{1}{2}(D_1)^2
\tag{40}
$$

which will cancel a corresponding term in Λ_2 [see Eq. (34)].

The more significant second-order contribution, involving particle hop and return, requires detailed consideration of the local particle arrangements.
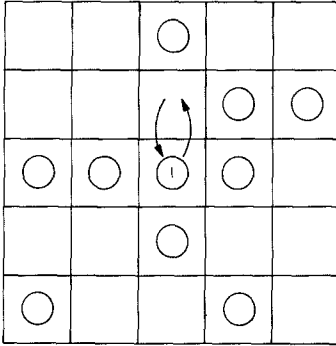
Fig. 1. Particle motion incorporated in the second-order quantum correction D_2 [Eq. (39)].

Figure 1 should aid in clarifying the situation. It shows a portion of a square lattice gas, with particle 1 the one whose transfer is of interest. Obviously a neighboring vacancy must be present to receive this particle, which will not always be the case. Even if it is, a change ΔV in the system potential energy can be involved. For the shift illustrated in Fig. 1, particle 1 has three nearest neighbors to begin with, but only two after the shift. If nearest-neighbor interactions alone were present in $\mathbf{V}$, this clearly would suffice to determine ΔV, but with more general interactions greater detail about local structure would be required.

In order to analyze these second-order nondiagonal contributions properly, it is advisable to carry out the full trace summation indicated in Eq. (39) in several stages. Specifically, we distinguish terms according to which pair α_1, α_2 of sites is involved, and according to what ΔV magnitude occurs in the intermediate (i.e., displaced) state. Thus, accounting for result (40), we write

$$
\begin{aligned}
\Lambda_2 &= Z_0^{-1} \sum_{\alpha_1, \alpha_2, \sigma} \int_0^1 d\lambda_1 \, \lambda_1 \, \mathrm{Tr}\{a^+(\alpha_1, \sigma)a(\alpha_2, \sigma)\mathbf{G}_0(1 - \lambda_1) \\
&\quad \times a^+(\alpha_2, \sigma)a(\alpha_1, \sigma)\mathbf{G}_0(\lambda_1)\} \\
&= Z_0^{-1} \sum_{\alpha_1, \alpha_2} \sum_{\Delta V} \int_0^1 d\lambda_1 \, \lambda_1 \exp[-(1 - \lambda_1)\beta \, \Delta V] \, \mathrm{Tr}\Big\{\exp(-\beta \mathbf{V}) \\
&\quad \times n(\alpha_1)[1 - n(\alpha_2)] \, \delta\Big[\Delta V, \sum_\sigma a^+(\alpha_1, \sigma)a(\alpha_2, \sigma)\mathbf{V}a^+(\alpha_2, \sigma) \\
&\quad \times a(\alpha_1, \sigma) - \mathbf{V}\Big]\Big\}
\end{aligned}
$$
(41)

wherein δ stands for the Kronecker delta function. Here we have assumed that only a finite, discrete set of ΔV values can arise (this will be the case if interparticle interactions have strictly finite range, and if the external field potential is linear in position coordinates).

Let $Q_0^{(2)}(\alpha_1, \alpha_2; \Delta V \mid \alpha_2, \alpha_1)$ denote, for the classical limit ensemble, the probability that simultaneously (a) site α_1 is occupied, (b) a specific nearest-neighbor site α_2 is unoccupied, and (c) that shift of the particle from α_1 to α_2 causes the total potential energy to change by ΔV. A formal expression for $Q_0^{(2)}$ is the following.

$$
\begin{aligned}
Q_0^{(2)}&(\alpha_1, \alpha_2; \Delta V \mid \alpha_2, \alpha_1) \\
&= Z_0^{-1} \, \mathrm{Tr}\Big\{ \exp(-\beta \mathbf{V}) \, n(\alpha_1)[1 - n(\alpha_2)] \\
&\quad \times \delta\Big[\Delta V, \sum_\sigma a^+(\alpha_1, \sigma) a(\alpha_2, \sigma) \mathbf{V} a^+(\alpha_2, \sigma) a(\alpha_1, \sigma) - \mathbf{V} \Big] \Big\}
\end{aligned} \quad (42)
$$

In the event that external forces are absent and periodic boundary conditions are applicable, $Q_0^{(2)}$ is independent of the specific location of the site pair α_1, α_2 within the system.

Upon comparing definition (42) with the preceding Λ_2 expression (41), one sees that the latter can be written compactly in terms of $Q_0^{(2)}$. One finds

$$
\begin{aligned}
\Lambda_2 &= \sum_{\alpha_1, \alpha_2, \Delta V} Q_0^{(2)}(\alpha_1, \alpha_2; \Delta V \mid \alpha_2, \alpha_1) \int_0^1 d\lambda_1 \, \lambda_1 \exp[-(1 - \lambda_1)\beta \, \Delta V] \\
&= \sum_{\alpha_1, \alpha_2, \Delta V} Q_0^{(2)}(\alpha_1, \alpha_2; \Delta V \mid \alpha_2, \alpha_1) f(\beta \, \Delta V)
\end{aligned} \quad (43)
$$

where

$$
f(x) = \frac{1}{x}\left(1 + \frac{e^x - 1}{x}\right) = \frac{1}{2} - \frac{1}{6}x + \frac{1}{24}x^2 - \cdots \quad (44)
$$

Since $f(x)$ is a monotonically decreasing function of x, its presence in Eq. (43) biases the particle excursions toward regions of lower potential energy.

Notice that Λ_2 is never negative. Consequently it will have the effect of reducing the free energy F in comparison with the classical-limit value F_0. This reduction is associated with the tendency of $\mathbf{T}$ to broaden the distribution of energy states in the system.

The types of contributions that can be present in third order (i.e., in D_3) depend on the topology of the lattice. The smallest polygons of nearest-neighbor links present on the square, simple cubic, and body-centered cubic lattices are quadrilaterals. Three successive shifts cannot circumnavigate such paths. For these lattices only a combination of diagonal contributions and one-particle, two-step excursions (as in D_2) is possible. In fact, one can show that the third-order semiinvariant Λ_3 appearing in Eq. (34) will vanish for these lattices.

In contrast, the planar, cubic, and hexagonal close-packed lattices include triangular circuits. For them it is necessary to examine the two

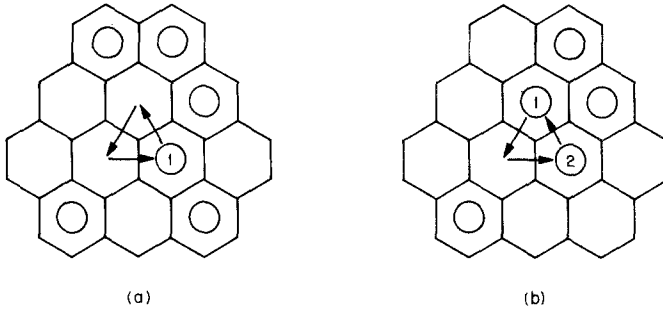(a)   (b)

Fig. 2. Third-order processes possible on lattices with triangular circuits of nearest-neighbor shifts. (a) The single particle 1 completes the triangular circuit and returns to its starting point. (b) Particles 1 and 2 change places after three shifts (of 1, 2, then 1 again).

processes illustrated in Fig. 2. Figure 2a represents a triangular circum-navigation by a single particle, which returns in three successive steps to its starting point. Figure 2b illustrates an exchange process for which the three successive steps (by 1, then 2, then 1 again) result in a permutation of the positions of 1 and 2. In order for this exchange to occur, the spins σ_1 and σ_2 must be identical.

To evaluate the contributions of these third-order processes to $\ln Z$, as well as to examine more complex higher order processes, it is advisable to generalize $Q_0^{(2)}$, Eq. (42), to the set of s-step quantities

$$Q_0^{(s)}(\alpha_1, \alpha_1'; \Delta V_1| \cdots |\alpha_j, \alpha_j'; \Delta V_j| \cdots |\alpha_s, \alpha_s') \tag{45}$$

As before, these are shift probabilities to be evaluated for the classical-limit ensemble (subscript zero). The requirements mandated by (45) are that: (1) site α_1 be filled, α_1' neighboring it be empty, and that when the $\alpha_1 \to \alpha_1'$ particle shift is carried out the potential energy changes by ΔV_1; (2)...; (j) after the preceding $j - 1$ steps, α_j should be filled and its neighbor α_j' empty, and the subsequent $\alpha_j \to \alpha_j'$ shift should change the potential by ΔV_j; $(j + 1)$.... The $Q_0^{(s)}$ will only be defined for sets of shifts which restore the particles finally to the original sites or some permutation thereof. Consequently there is no need to indicate ΔV_s for the last shift, since it is automatically given by

$$\Delta V = - \sum_{j=1}^{s-1} \Delta V_j \tag{46}$$

For notational simplicity we can let $n^{(j)}(\alpha)$ stand for the number of particles at site α after j shifts specified above have been completed. A general

expression for $Q_0^{(s)}$ may then be introduced, as an average in the classical-limit ensemble:

$$Q_0^{(s)}(\alpha_1, \alpha_1'; \Delta V_1 | \cdots)$$

$$= (2S + 1)^N Z_0^{-1} \sum_{\{n\}}' \exp[-\beta V(\{n\})] \prod_{j=1}^{s} n^{(j)}(\alpha_j)[1 - n^{(j)}(\alpha_j')]$$

$$\times \delta[\Delta V_j, V(\{n^{(j)}\}) - V(\{n^{(j-1)}\})] \tag{47}$$

One easily verifies that the prior equation (42) is equivalent to a special case of Eq. (47).

We are now in a position to state the $\ln Z$ contributions (for the planar close-packed and the fcc and hcp lattices) symbolized in Fig. 2. One obtains for Fig. 2a the result

$$I_a = \sum_{\alpha_1, \alpha_2, \alpha_3} \sum_{\Delta V_1, \Delta V_2} Q_0^{(3)}(\alpha_1, \alpha_2; \Delta V_1 | \alpha_2, \alpha_3; \Delta V_2 | \alpha_3, \alpha_1) F(\beta \Delta V_1, \beta \Delta V_2) \tag{48}$$

where

$$F(x, y) = \int_0^1 d\lambda_1 \int_0^{1-\lambda_1} d\lambda_2 \int_0^{1-\lambda_1-\lambda_2} d\lambda_3 \exp[-\lambda_2(x + y) - \lambda_3 x]$$

$$= \frac{1}{x} \left[\frac{1}{x + y} + \left(\frac{1}{y} - \frac{1}{x + y} \right) \frac{1 - \exp(-x - y)}{x + y} - \frac{1 - \exp(-x)}{xy} \right] \tag{49}$$

In a similar way, the third-order exchange contribution illustrated in Fig. 2b is found to be (upper sign for bosons, lower for fermions)

$$I_b = \pm (2S + 1)^{-1} \sum_{\alpha_1, \alpha_2, \alpha_3} \sum_{\Delta V_1, \Delta V_2} Q_0^{(3)}(\alpha_1, \alpha_2; \Delta V_1 | \alpha_3, \alpha_1; \Delta V_2 | \alpha_2, \alpha_3)$$

$$\times F(\beta \Delta V_1, \beta \Delta V_2) \tag{50}$$

Therefore the total third-order cumulant for two- and three-dimensional close packed lattices will be

$$\Lambda_3 = I_a + I_b = \sum_{\alpha_1, \alpha_2, \alpha_3} \sum_{\Delta V_1, \Delta V_2} F(\beta \Delta V_1, \beta \Delta V_2)$$

$$\times [Q_0^{(3)}(\alpha_1, \alpha_2; \Delta V_1 | \alpha_2, \alpha_3; \Delta V_2 | \alpha_3, \alpha_1)$$

$$\pm (2S + 1)^{-1} Q_0^{(3)}(\alpha_1, \alpha_2; \Delta V_1 | \alpha_3, \alpha_1; \Delta V_2 | \alpha_2, \alpha_3)] \tag{51}$$

The one-particle excursion quantity I_a will never be negative and (as was the case with Λ_2) it tends to reduce the free energy. The exchange quantity I_b reduces free energy for bosons, but raises it for fermions.

Fourth-order corrections for the $\ln Z$ could be calculated along the lines already established, using the classical-ensemble quantities $Q_0^{(4)}$. However,

the calculations begin to become rather tedious, and we do not reproduce them here. In addition to the types of terms thus far encountered, one must consider pairs of distinct particles which, by virtue of closeness, have separate but correlated hop-and-return motions.

5. DISTRIBUTION FUNCTIONS

We now have the task of generating corrections in ascending orders in X for the distribution functions defined in Eq. (14). The operator expansion (29) is again the proper starting point. Having inserted it in both numerator and denominator (Z) in expression (14), we have symbolically

$$
\begin{aligned}
P^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n) &= P_0^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n) \frac{1 + \sum_{j=1}^{\infty} E_j^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n)X^j}{1 + \sum_{j=1}^{\infty} D_j X^j} \\
&= P_0^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n)\{1 + [E_1^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n) - D_1]X \\
&\quad + [E_2^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n) - D_1 E_1^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n) - D_2 + (D_1)^2]X^2 \\
&\quad + [E_3^{(n)} - D_1 E_2^{(n)} + (-D_2 + \tfrac{1}{2}(D_1)^2)E_1^{(n)} - D_3 \\
&\quad + 2D_2 D_1 - (D_1)^3]X^3 + \cdots\}
\end{aligned} \tag{52}
$$

For emphasis, bars have been placed over labels referring to the n fixed sites. Just as Eq. (31) serves to define the D_j, the quantities $E_j^{(n)}$ have the form

$$
\begin{aligned}
E_j^{(n)}(\bar{\alpha}_1,..., \bar{\alpha}_n) &= (-1)^n Z_0^{-1}\, \mathrm{Tr}\Big\{ \int_0^1 d\lambda_1 \cdots \int_0^{1-\lambda_1-\cdots-\lambda_{j-1}} d\lambda_j \\
&\quad \times \mathbf{G}_0(\lambda_1)\mathbf{t} \cdots \mathbf{G}_0(\lambda_j)\mathbf{t}\mathbf{G}_0(1 - \lambda_1 \cdots - \lambda_j) \prod_{k=1}^{n} n(\bar{\alpha}_k) \Big\}
\end{aligned} \tag{53}
$$

Since it is normally the case that Ω is very much larger than the distribution function order n, we can expect wholesale cancellation between D's and E's in each term of the expansion (52).

It is easy to see that in the absence of external fields every $E_1^{(n)}$ is identical to D_1. Consequently the $O(X)$ correction terms vanish identically for each distribution function.

Nontrivial corrections begin to arise in the next order. To evaluate partition-function corrections in second order, it was necessary that the quantities $Q_0^{(2)}$ be defined; now a generalization must be sought which includes the requirement that sites $\bar{\alpha}_1,..., \bar{\alpha}_n$ be occupied. Anticipating a corresponding demand for higher orders, we shall write the following symbol for the most general case:

$$
Q_0^{(s,n)}(\{\bar{\alpha}_1,..., \bar{\alpha}_n\}|\alpha_1, \alpha_1'; \Delta V| \cdots |\alpha_s, \alpha_s') \tag{54}
$$

to denote the classical-limit probability for existence of the specified s-step transformation, under the restriction that sites $\bar{\alpha}_1,..., \bar{\alpha}_n$ are initially occupied.

As before, the same set of sites must be occupied throughout the lattice at the end of the s steps as at the beginning (though possibly with particle exchanges). It should be borne in mind that particles on $\bar{\alpha}_1, ..., \bar{\alpha}_n$ might themselves be moved about. A formal definition of the quantity (54) follows that shown in Eq. (47), except for an insertion of $\prod n(\bar{\alpha}_i)$:

$$Q_0^{(s,n)}(\{\bar{\alpha}_1, ..., \bar{\alpha}_n\}|\alpha_1, \alpha_1'; \Delta V_1| \cdots |\alpha_s, \alpha_s')$$

$$= (2S + 1)^N Z_0^{-1} \sum_{\{n\}}' \exp[-\beta V(\{n\})] \left[\prod_{l=1}^n n(\bar{\alpha}_i)\right] \prod_{j=1}^s n^{(j)}(\alpha_j)$$

$$\times [1 - n^{(j)}(\alpha_j')] \, \delta[\Delta V_j, V(\{n^{(j)}\}) - V(\{n^{(j-1)}\})] \tag{55}$$

By straightforward calculation one establishes that $O(X^2)$ corrections to the $P_0^{(n)}$ can be expressed in terms of $Q_0^{(2)}$ and $Q_0^{(2,n)}$. The result is

$$E_2^{(n)}(\bar{\alpha}_1, ..., \bar{\alpha}_n) - D_2 = \sum_{\alpha_1, \alpha_2, \Delta V} f(\beta \, \Delta V)[Q_0^{(2,n)}(\{\bar{\alpha}_1, ..., \bar{\alpha}_n\}|\alpha_1, \alpha_2; \Delta V|\alpha_2, \alpha_1)$$

$$- Q_0^{(2)}(\alpha_1, \alpha_2; \Delta V|\alpha_2, \alpha_1)] \tag{56}$$

The function f is the same one encountered earlier, Eq. (44).

As was the case for bulk thermodynamic properties, the existence of $O(X^3)$ corrections for the $P_0^{(n)}$ is contingent upon presence of triangular paths on the lattice. Square, simple cubic, and body-centered cubic lattices, being devoid of such paths, permit no third-order corrections. However, the close-packed planar and three-dimensional lattices do generate third-order $P^{(n)}$ corrections, which one finds to have the following form:

$$E_3^{(n)}(\bar{\alpha}_1, ..., \bar{\alpha}_n) - D_1 E_2^{(n)}(\bar{\alpha}_1, ..., \bar{\alpha}_n) - D_3 + D_2 D_1 - \tfrac{1}{2}(D_1)^3$$

$$= \sum_{\alpha_1, \alpha_2, \alpha_3} \sum_{\Delta V_1, \Delta V_2} F(\beta \, \Delta V_1, \beta \, \Delta V_2)$$

$$\times \{[Q_0^{(3,n)}(\{\bar{\alpha}_1, ..., \bar{\alpha}_n\}|\alpha_1, \alpha_2; \Delta V_1|\alpha_2, \alpha_3; \Delta V_2|\alpha_3, \alpha_1)$$

$$- Q_0^{(3)}(\alpha_1, \alpha_2; \Delta V_1|\alpha_2, \alpha_3; \Delta V_2|\alpha_3, \alpha_1)]$$

$$\pm (2S + 1)^{-1}[Q_0^{(3,n)}(\{\bar{\alpha}_1, ..., \bar{\alpha}_n\}|\alpha_1, \alpha_2; \Delta V_1|\alpha_3, \alpha_1; \Delta V_2|\alpha_2, \alpha_3)$$

$$- Q_0^{(3)}(\alpha_1, \alpha_2; \Delta V_1|\alpha_3, \alpha_1; \Delta V_2|\alpha_2, \alpha_3)]\} \tag{57}$$

6. DISCUSSION

The preceding development has shown that quantum corrections to lattice-gas thermodynamic properties and distribution functions require knowledge of the s-step probability functions $Q_0^{(s)}$ and $Q_0^{(s,n)}$. In the event that only short-range intermolecular forces are present, each of these functions can always be expressed in terms of a finite set of classical-limit distribution functions $P_0^{(n)}$, the maximum order of which equals the number of sites influenced by the s-step excursion. In most cases of interest the required $P_0^{(n)}$ will not be known precisely, though it is not inconceivable that suitable approximations might be constructed.

The present results likely will find their most fruitful application in connection with computer studies of lattice gases by the Monte Carlo method.[7,16,17] The requisite excursion probabilities could be evaluated numerically during the course of such Monte Carlo studies, and the computation of low-order quantum corrections could then become a routine appendage to the conventional classical simulation.

Even without implementing a full-scale numerical program, it is possible to draw some qualitative conclusions about lattice-gas quantum corrections. The two-step process required for Λ_2 [Eq. (43)], whose probability is determined by $Q_0^{(2)}$, will be quenched as the system is compressed toward complete filling of the lattice with particles. This compression removes vacant sites which are required for the hop and return. Recall that Λ_2 reduces free energy F; since the reduction will thus be less at high density than at low density, Λ_2 will tend to produce faster increase in the system pressure with compression than would be the case with the classical lattice gas alone.

Similarly, $Q_0^{(2,n)}$ will vanish in the high-compression limit, in the analogous correction (56) for the distribution functions. Partial quenching of the hop-and-return motion obviously also occurs if the n particles in $P^{(n)}$ must reside on n tightly packed sites $\bar{\alpha}_1,..., \bar{\alpha}_n$. Thus second-order quantum corrections destabilize tight particle clusters.

The exchange processes involved in Λ_3 [Eq. (51)], and the corresponding third-order correction [Eq. (57)] for the $P_0^{(n)}$, will likewise be quenched by compression to the close-packed limit. But in addition, exchanges will be inhibited at low density as well since most particles will be isolated. We also remark that the existence of large, repulsive intermolecular forces (hard cores spanning many lattice sites) can suppress exchange since many successive steps would be required to interchange particle locations. It is this last situation essentially which causes quantum exchange corrections to the *continuum* hard-sphere virial coefficients to vanish exponentially at high temperature.[18,19]

Finally we point out that at the critical point for the classical lattice gas with short-range interactions, the quantum corrections Λ_2 for F_0 should manifest the same critical singularity type that is exhibited by the (classical) energy per particle. Such a correction is symptomatic of a simple shift in the critical point temperature and density, rather than of exponent renormalization.[20]

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