First-order anharmonic correction to the free energy of a Coulomb crystal in periodic boundary conditions

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The free energy of the classical one-component plasma is calculated analytically in the crystalline phase for both fcc and bcc lattices to $O(T^2)$, where T is the temperature. By application of thermodynamic perturbation theory, we explicitly evaluate the effect of three- and four-phonon interactions on the partition function. Periodic boundary conditions are applied to make contact with previous numerical work, in which the $O(T^2)$ term was assumed to be negligible. We find that it is much larger than previously thought. This increases the thermodynamic stability of the crystal phase over previous estimates.

I. INTRODUCTION

The infinite homogeneous one-component plasma (OCP) is a system of like charges immersed in a uniform neutralizing background that ensures overall electrical neutrality. The OCP is of interest both from the standpoint of the statistical mechanics of strongly interacting systems and as a simple model of ionized matter, useful in describing several systems of astrophysical importance (such as the outer crust of neutron stars), as well as magnetically confined non-neutral plasmas, liquid metals, etc.[1] Particular theoretical emphasis has been placed on the classical regime of strong correlation, in which the correlation parameter $\Gamma \equiv e^2/akT$—the ratio of the kinetic to potential energy per charge—is larger than unity (here e is the charge, T the temperature, and a the Wigner-Seitz radius; $\frac{4}{3}\pi a^3 n = 1$ where n is the density). In this regime theory predicts that for $\Gamma \gtrsim 2$ the system exhibits short-range order characteristic of a liquid, and that for $\Gamma = \Gamma_{\rm crit}$ a first-order phase transition to a body-centered-cubic (bcc) crystal occurs.[2-4] The current prediction for $\Gamma_{\rm crit}$, based on the results of Monte Carlo (MC) computer simulations, is $\Gamma_{\rm crit} = 178-180$.[3,4]

This paper presents an analytic calculation of the free energy of the solid phase, asymptotically valid to $O(T^2)$ in the classical regime. The calculation is motivated by the fact that the MC-based estimates of $\Gamma_{\rm crit}$ rely on the assumption that the $O(T^2)$ term is very small. Indeed, several authors have assumed that it is identically zero.[2-4] We find that this term is in fact much larger than previously thought. At the phase transition this term contributes over half of the anharmonic internal energy. When our calculated values for this term are added to the simulation results for the internal energy of the solid phase, the thermodynamic stability of the solid phase is increased over previous estimates, leading to a decrease in $\Gamma_{\rm crit}$ to $\Gamma_{\rm crit} \sim 172$.

In order to make contact with the simulation results, our calculation is performed for a finite number of charges, N, in periodic boundary conditions. (The simulations use periodic boundary conditions in order to approximate the infinite OCP.) The N dependence of each term in the internal energy expansion is evaluated exactly, and the $N \to \infty$ limit is also determined.

Studies of N dependence in OCP MC simulations have previously involved semiempirical estimates based on the numerical data.[2-4] Our calculation attempts to set the theory of the N dependence on a more solid footing, and also provides exact results for this N dependence in the crystalline phase at large Γ. Results are presented for both bcc and face-centered-cubic (fcc) lattices.

The $O(T^2)$ term in the free energy gives the lowest-order correction due to anharmonicities in the lattice vibrations. Such anharmonic corrections have been the subject of several interesting theoretical studies. While most involve rather severe approximations in order to obtain a tractable theory,[5-8] a paper by Albers and Gubernatis[9] is of particular interest since it also presents an exact calculation of the $N \to \infty$ limit of the $O(T^2)$ term for a bcc lattice. The authors also obtain a nonzero value for this term; however, their result is approximately a factor of 3 smaller than ours. We have carefully checked their calculation, but the origin of the error is unknown. As we will later argue, both results are consistent with present MC data and more MC data are needed in order to differentiate between the two results.

Anharmonic corrections to the free energy have also been studied extensively through the previously mentioned MC computer simulations. These simulations determine the free energy by first calculating numerical values for the internal energy per charge, U/N, in both the solid and liquid phases at various values of Γ. An interpolation formula is then applied to connect these points and the free energy F is obtained by numerical integration via the equation

$$\frac{F(\Gamma)}{NkT} = \int_{\Gamma_0}^{\Gamma} d\Gamma' \frac{1}{\Gamma'} \frac{U(\Gamma')}{NkT} + \frac{F^0}{NkT} . \tag{1}$$

For the case of the solid phase Γ_0 is chosen sufficiently large so that F_0 is given by the results of harmonic lattice theory. The interpolation formula used for the internal energy in the solid phase is based on an asymptotic ex-

pansion of U in the small parameter $1/\Gamma$:[10]

$$\frac{U}{NkT}=A_{-1}\Gamma+A_0+\frac{A_1}{\Gamma}+\frac{A_2}{\Gamma^2}+\cdots , \tag{2}$$

where A_{-1} is one-half of the Madelung energy per ion of the equilibrium lattice and $A_0=3-3/(2N)$ is the contribution of harmonic lattice vibrations (i.e., phonons in the ideal gas limit). Higher-order terms represent anharmonic corrections to the energy ; A_1 is the lowest-order anharmonic correction. Numerical values for these anharmonic corrections are obtained by fitting to the MC data. However, the values are based entirely on MC data in the range of $160\leq\Gamma\leq 300$, and for $N\leq 686$. Within this limited range of Γ it is found that the MC data can be well fitted by keeping only A_1 and A_2, and in fact it is found that $A_1=0$ is consistent with the MC data.[11] However, we will argue that our nonzero A_1 values are also consistent with present MC data and that more data at higher Γ values are needed to obtain an accurate internal energy interpolation formula for the OCP solid phase.

The first part of this paper presents an analytic calculation of the first-order anharmonic coefficient A_1 for bcc and fcc lattices, as well as a discussion of the N dependence of the harmonic and anharmonic terms. In order to make contact with the MC results, the calculation is performed for N charges in a cubic cell of side L with periodic boundary conditions. For the bcc lattice, this limits N values to $N=2M^3$ where M is any positive integer; for the fcc lattice, $N=4M^3$ (these values of N allow the lattice to fit into a cube without inducing dislocations). The charges are assumed to be in equilibrium with a heat bath at temperature T. N-dependent terms are evaluated exactly without recourse to the $N\rightarrow\infty$ limit, so that results for the free energy per charge in the finite-N system are exact (for instance, the results hold for the $M=1$ case, a system of only four periodically repeating charges in the fcc case or two charges in the bcc case). We also determine the $N\rightarrow\infty$ limit for A_1, finding that for the bcc lattice, $\lim_{N\rightarrow\infty}A_1=10.84$, and for the fcc lattice, $\lim_{N\rightarrow\infty}A_1=12.35$.

In the second part of the paper we investigate the effect of our new values for A_1 on $\Gamma_{\rm crit}$. We find that a simple interpolation model for the free energy based on the MC results of Ref. 3 and our analytic values for A_1 shifts the liquid–bcc-lattice phase transition to $\Gamma_{\rm crit}\sim 172$ from the previous values[3,4] of 178–180. A similar analysis for the fcc lattice using published MC data for the fcc internal energy[12] along with our analytic points implies that the fcc phase becomes more stable than the liquid phase at $\Gamma\sim 182$, as opposed to the previously published value of 196. However, these values are only estimates since, as we will see, more MC data are required at large Γ in order to obtain an accurate interpolation model for the solid-phase internal energy.

Section II describes details of the perturbation calculation. Section III explores the liquid-solid phase transition. In Appendix A intermediate results involving lattice sums are derived. In Appendix B we consider $O(1/N)$ corrections to our expression for A_1, and in Appendix C we employ the Ewald method to obtain expressions for fast convergence of sums over the Coulomb interaction.

II. PERTURBATION EXPANSION OF THE CRYSTALLINE OCP FREE ENERGY

In this section we apply the well-known formalism of thermodynamic perturbation theory[10] in order to determine a power-series expansion of the free energy F in the inverse correlation parameter Γ^{-1}. However, unlike past treatments, we do not take the $N\rightarrow\infty$ limit of the expansion. The free energy may be found from the partition function Z through the equation $F=-kT\ln Z$. The partition function is determined as a sum over a complete set of quantum states of the density operator

$$Z={\rm Tr}(e^{-H/kT}) , \tag{3}$$

where

$$H(\mathbf{x}_1,\mathbf{p}_1,\ldots,\mathbf{x}_N,\mathbf{p}_N)=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\Phi(\mathbf{x}_1,\ldots,\mathbf{x}_N) , \tag{4a}$$

and where Φ is the potential energy of the ions (including the effect of the uniform neutralizing background) and $\mathbf{x}_i$ and $\mathbf{p}_i$ are the position and momentum of the ith ion. The potential can be decomposed into a sum over two-particle interactions:

$$\Phi=\sum_{i=1}^{N}\sum_{j>i}^{N}\phi(\mathbf{x}_i-\mathbf{x}_j)+\frac{N}{2}U_c , \tag{4b}$$

where ϕ is given by

$$\phi(\mathbf{x})=\frac{4\pi e^2}{v}{\sum_{\mathbf{f}}}'\frac{e^{i\mathbf{f}\cdot\mathbf{x}}}{f^2} , \tag{5}$$

and where $v=L^3$ and the vectors $\mathbf{f}=2\pi(l,m,n)/L\,\forall$ integers l,m,n are the reciprocal-lattice vectors for the cubic cell. (The prime on the sum indicates that the $\mathbf{f}=\mathbf{0}$ term is absent due to the effect of the neutralizing background charge.) The term U_c is the Madelung "self-energy" of the charge due to its own periodically repeating images in other cubic cells;[2] $U_c=-1.761\,19e^2/(N^{1/3}a)$.

In order to expand F/NkT in an asymptotic series in Γ^{-1}, we follow the usual approach by first assuming charges are confined to small excursions $\mathbf{u}_i$ about equilibrium positions $\mathbf{x}_i^0$. We then expand H in the change in positions, using $\mathbf{x}_i=\mathbf{x}_i^0+\mathbf{u}_i$. The result is

$$H=H^0+\Delta V . \tag{6}$$

Here H^0 is the Hamiltonian in the "harmonic approximation":

$$H^0(\mathbf{u}_1,\mathbf{p}_1,\ldots,\mathbf{u}_N,\mathbf{p}_N)$$

$$=\Phi^0+\sum_i\left[\frac{p_i^2}{2m}+\tfrac{1}{2}\sum_j\nabla_i\nabla_j\Phi^0\cdot\mathbf{u}_i\mathbf{u}_j\right] , \tag{7}$$

where $\Phi^0=\Phi(\mathbf{x}_1^0\cdots\mathbf{x}_N^0)$, ∇_i denotes $\partial/\partial\mathbf{x}_i^0$, and ΔV contains anharmonic corrections:

$$\Delta V=\sum_{n=3}^{\infty}\frac{1}{n!}U_n \ , \tag{8a}$$

where

$$U_n=\sum_{i,j,\ldots}\nabla_i\nabla_j\cdots\Phi^0\cdot\mathbf{u}_i\mathbf{u}_j\cdots \ , \tag{8b}$$

where the ∇ and $\mathbf{u}$ terms are repeated n times each. Substitution of Eq. (6) into Eq. (3) and expansion in powers of ΔV yields, after some work,[10]

$$F=F^0+\langle\Delta V\rangle-\frac{1}{2kT}(\langle\Delta V^2\rangle-\langle\Delta V\rangle^2)+O(\Delta V^3) \ , \tag{9}$$

where F^0 is the free energy of the phonon ideal gas,

$$F^0=-kT\ln[\mathrm{Tr}(e^{-H^0/kT})] \ , \tag{10}$$

and the averages are over the variables $(\mathbf{u}_1,\ldots,\mathbf{u}_N)$, weighted by the unperturbed equilibrium distribution. For instance,

$$\langle\Delta V\rangle=\frac{\left[\int\Delta V e^{-H^0/kT}d^3\mathbf{u}_1\cdots d^3\mathbf{u}_N\right]}{\left[\int e^{-H^0/kT}d^3\mathbf{u}_1\cdots d^3\mathbf{u}_N\right]} \ . \tag{11}$$

Here we have assumed that $kT\gg\hbar\omega_p$, where ω_p is the plasma frequency, in order that averages are performed in the classical limit (the vibrations are assumed to be classical). This assumption is compatible with our assumption that $kT\ll e^2/a$ (i.e., $\Gamma\gg1$) provided that $a\gg a_B$ where $a_B=\hbar^2/m^2e^4$ is the Bohr radius for the ions.

If one now substitutes Eq. (8) into Eq. (9) and compares the resulting expression for F to the series obtained by integrating Eq. (2) via Eq. (1), one obtains the following form for A_1:[13]

$$A_1=\Gamma\left[\frac{\langle U_3^2\rangle}{72N(kT)^2}-\frac{\langle U_4\rangle}{24NkT}\right] \ . \tag{12}$$

In deriving this expression one also uses the fact that averages over odd powers of $\mathbf{u}$ are zero (by symmetry) and that $\langle u^2\rangle\sim O(T)$.

A. Phonon coordinates and the zeroth-order free energy

In order to perform the averages in Eq. (12), it is useful to transform to phonon coordinates.[13] We assume that the equilibrium positions $\{\mathbf{x}^0\}$ form a lattice with one charge per unit cell, this cell repeating via lattice vectors $\mathbf{p}$. Then H^0 can be put in a standard form through transformation to phonon coordinates $q_{\mathbf{f},s}(t)$:

$$\mathbf{u}_p(t)=\sum_{\mathbf{f}}\sum_{s=1}^{3}q_{f,s}(t)e^{i\mathbf{f}\cdot\mathbf{p}}\mathbf{v}(\mathbf{f},s) \ . \tag{13}$$

Here, again, the vectors $\mathbf{f}$ are reciprocal-lattice vectors for the cubic cell, as in Eq. (5). However, here only N of these vectors fall within the basic reciprocal cell (the first Brillouin zone) formed with respect to the lattice $\{\mathbf{p}\}$; these N vectors form the only possible $\mathbf{f}$ vectors for the lattice phonons in periodic boundary conditions. Here and in the following formulas the sum runs only over these N vectors [as opposed to the sum in Eq. (5)]. The subscript s runs over three possible polarizations for each $\mathbf{f}$. The unit vectors $\mathbf{v}$ give the direction of each polarization; they are determined by the matrix $\nabla_i\nabla_j\Phi^0$. There are therefore a total of $3N$ phonon modes; of these there are three $\mathbf{f}=\mathbf{0}$ modes corresponding to translation of the system center of mass.

Substitution of Eq. (13) into Eq. (7) yields, after some work, the standard form[13] for H^0 in phonon coordinates:

$$H^0=\Phi^0+\tfrac{1}{2}Nm\sum_{\mathbf{f},s}\{|\dot{q}_{\mathbf{f},s}|^2+[\omega(\mathbf{f},s)]^2|q_{\mathbf{f},s}|^2\} \ , \tag{14}$$

where $m[\omega(\mathbf{f},s)]^2$ are the eigenvalues of the matrix $\underline{A}(\mathbf{f})$, defined as

$$\underline{A}(\mathbf{f})=N^{-1}\sum_{i,j}\nabla_i\nabla_j\Phi^0e^{i\mathbf{f}\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)} \ . \tag{15}$$

The unit vectors $\mathbf{v}(\mathbf{f},s)$ are the corresponding eigenvectors of $\underline{A}$.

The matrix $\underline{A}(\mathbf{f})$ can be written in terms of the two-particle interaction ϕ by substituting Eq. (4b) for Φ. After some algebra (see Appendix A) one obtains[14]

$$\underline{A}(\mathbf{f})=\sum_{\mathbf{p}}{}'[1-\cos(\mathbf{f}\cdot\mathbf{p})]\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\phi(\mathbf{p}) \ . \tag{16}$$

In Eq. (16), and in all following equations, the sum over $\mathbf{p}$ runs over the N ions in the cube, and the prime denotes a sum neglecting the $\mathbf{p}=\mathbf{0}$ term. This matrix may be evaluated using the Ewald sum method (see Appendix C).

Equations (10) and (14) then lead to the classical limit of the free energy of the lattice in the harmonic approximation:

$$\frac{F^0}{NkT}=\frac{\Phi^0}{NkT}+\frac{3(N-1)}{N}\ln\left[\frac{\hbar\omega_p}{kT}\right]+N^{-1}\sum_{\mathbf{f},s}{}'\ln\left[\frac{\omega(\mathbf{f},s)}{\omega_p}\right]+N^{-1}\ln\left[\frac{\lambda_D^3}{v}\right] \ , \tag{17}$$

where $\lambda_D^2=2\pi\hbar^2/(NmkT)$ is the thermal DeBroglie wavelength of the system center of mass, ω_p is the plasma frequency, and the prime on the sum denotes a sum neglecting the three zero-frequency translational modes. This form for F^0 is correct for finite N in periodic boundary conditions, and approaches the standard form[2] as $N\to\infty$. The average energy U^0 in the harmonic approximation is then given by $U^0=\partial(\beta F^0)/\partial\beta$, or

$$U^0=3(N-\tfrac{1}{2})kT+\Phi^0 \ , \tag{18}$$

which also follows from the equipartition theorem.

In the limit as $N\to\infty$, the sum over $\ln[\omega(\mathbf{f},s)/\omega_p]$ becomes an average over the first Brillouin zone, denoted as $\langle\ln(\omega/\omega_p)\rangle$. This average has been evaluated correctly for the bcc lattice,[2] but the published fcc value[12] is slight-

ly incorrect due to numerical roundoffs. We have calculated more accurate values for both lattices, which are displayed in Table I.

TABLE I. Values of $\langle \ln(\omega/\omega_p) \rangle$ for fcc and bcc lattices.

Lattice	$\langle \ln(\omega/\omega_p) \rangle$
bcc	−2.493 89(1)
fcc	−2.453 73(1)

B. Evaluation of the anharmonic terms

Because the distribution $e^{-\beta H^0}$ is a multivariate Gaussian, the averages in Eq. (12) can all be written in terms of products of $\langle |q_{\mathbf{f},s}|^2 \rangle$. This cumulant is easily evaluated using Eqs. (11) and (14), yielding

$$\langle |q_{\mathbf{f},s}|^2 \rangle = kT/\{Nm[\omega(\mathbf{f},s)]^2\} . \tag{19}$$

We first determine $\langle U_4 \rangle$. After substituting Eq. (13) into Eq. (8b) and averaging, one obtains

$$\langle U_4 \rangle = \sum_{\substack{f_1,f_2,f_3,f_4 \\ s_1,s_2,s_3,s_4}} c(\mathbf{f}_1,s_1;\mathbf{f}_2,s_2;\mathbf{f}_3,s_3;\mathbf{f}_4,s_4)\langle q_{\mathbf{f}_1,s_1} q_{\mathbf{f}_2,s_2} q_{\mathbf{f}_3,s_3} q_{\mathbf{f}_4,s_4} \rangle , \tag{20}$$

where

$$c(\mathbf{f}_1,s_1;\mathbf{f}_2,s_2;\mathbf{f}_3,s_3;\mathbf{f}_4,s_4) = N\underline{C}(\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3,\mathbf{f}_4)\cdot\mathbf{v}(\mathbf{f}_1,s_1)\mathbf{v}(\mathbf{f}_2,s_2)\mathbf{v}(\mathbf{f}_3,s_3)\mathbf{v}(\mathbf{f}_4,s_4) \tag{21}$$

and the tensor $\underline{C}$ is defined as

$$\underline{C}(\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3,\mathbf{f}_4) = N^{-1} \sum_{\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3,\mathbf{p}_4} e^{i(\mathbf{f}_1\cdot\mathbf{p}_1+\mathbf{f}_2\cdot\mathbf{p}_2+\mathbf{f}_3\cdot\mathbf{p}_3+\mathbf{f}_4\cdot\mathbf{p}_4)} \frac{\partial}{\partial\mathbf{p}_1}\frac{\partial}{\partial\mathbf{p}_2}\frac{\partial}{\partial\mathbf{p}_3}\frac{\partial}{\partial\mathbf{p}_4}\Phi^0 . \tag{22}$$

Because of statistical independence of the q's, only those terms in Eq. (20) contribute for which the indices are equal in pairs, for instance, $\mathbf{f}_1=-\mathbf{f}_2$, $s_1=s_2$; $\mathbf{f}_3=-\mathbf{f}_4, s_3=s_4$. There are three permutations of the indices which leads to the same result; so using Eq. (19) one obtains

$$\frac{\langle U_4 \rangle}{NkT} = \frac{3kT}{N^3} \sum_{\substack{\mathbf{f}_1,s_1 \\ \mathbf{f}_2,s_2}} \frac{c(\mathbf{f}_1,s_1;-\mathbf{f}_1,s_1;\mathbf{f}_2,s_2;-\mathbf{f}_2,s_2)}{m^2[\omega(\mathbf{f}_1,s_1)]^2[\omega(\mathbf{f}_2,s_2)]^2} . \tag{23}$$

There is an apparent singularity in this expression due to the three $\mathbf{f}=\mathbf{0}$ translational modes for which $\omega(\mathbf{f},s)=0$. However, translational invariance also implies $c=0$ for these modes so the sum converges and the $\mathbf{f}=\mathbf{0}$ modes make no contribution.

We have neglected an $O(1/N)$ term in Eq. (23) which occurs when all four modes are equal in Eq. (20)—the average of the four q's is then a fourth-order cumulant, which is not the same as the product of two second-order cumulants. However, we show in Appendix B that this correction in fact vanishes, so Eq. (23) is exact even for finite N.

We evaluate $\underline{C}$ in terms of the two-particle interaction ϕ in Appendix A; this yields the expression

$$\underline{C}(\mathbf{f}_1,-\mathbf{f}_1,\mathbf{f}_2,-\mathbf{f}_2) = 2\sum_{\mathbf{p}}{}' \{1-\cos(\mathbf{f}_1\cdot\mathbf{p})-\cos(\mathbf{f}_2\cdot\mathbf{p})+\tfrac{1}{2}[\cos(\mathbf{f}_1+\mathbf{f}_2)\cdot\mathbf{p}+\cos(\mathbf{f}_1-\mathbf{f}_2)\cdot\mathbf{p}]\} \frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\phi(\mathbf{p}) . \tag{24}$$

Since Eqs. (21) and (24) show explicitly that c is of $O(N)$, Eq. (23) then implies $\langle U_4 \rangle$ is $O(N)$, as it should be, and provides an $O(T^2)$ correction to the internal energy.

Turning now to $\langle U_3^2 \rangle$, a similar analysis yields the expression

$$\langle U_3^2 \rangle = \sum b(\mathbf{f}_1,s_1;\mathbf{f}_2,s_2;\mathbf{f}_3,s_3)b(\mathbf{f}_4,s_4;\mathbf{f}_5,s_5;\mathbf{f}_6,s_6)\langle q_{\mathbf{f}_1,s_1} q_{\mathbf{f}_2,s_2} q_{\mathbf{f}_3,s_3} q_{\mathbf{f}_4,s_4} q_{\mathbf{f}_5,s_5} q_{\mathbf{f}_6,s_6} \rangle , \tag{25}$$

where

$$b(\mathbf{f}_1,s_1;\mathbf{f}_2,s_2;\mathbf{f}_3,s_3) = N\underline{B}(\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3)\cdot\mathbf{v}(\mathbf{f}_1,s_1)\mathbf{v}(\mathbf{f}_2,s_2)\mathbf{v}(\mathbf{f}_3,s_3) \tag{26}$$

and

$$\underline{B}(\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3) = \frac{1}{N} \sum_{\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3} e^{i(\mathbf{f}_1\cdot\mathbf{p}_1+\mathbf{f}_2\cdot\mathbf{p}_2+\mathbf{f}_3\cdot\mathbf{p}_3)} \times \frac{\partial}{\partial\mathbf{p}_1}\frac{\partial}{\partial\mathbf{p}_2}\frac{\partial}{\partial\mathbf{p}_3}\Phi^0 . \tag{27}$$

Now the statistical independence of the q's leads to two types of terms.

Case (1).

$$\mathbf{f}_1=-\mathbf{f}_2, \quad s_1=s_2; \quad \mathbf{f}_3=-\mathbf{f}_4, \quad s_3=s_4 ;$$
$$\mathbf{f}_5=-\mathbf{f}_6, \quad s_5=s_6 .$$

Case (2).

$$\mathbf{f}_1=-\mathbf{f}_4, \quad s_1=s_4; \quad \mathbf{f}_2=-\mathbf{f}_5, s_2=s_5 ;$$
$$\mathbf{f}_3=-\mathbf{f}_6, \quad s_3=s_6 .$$

In case (1) there are nine possible permutations which give the same result; in case (2) there are six. However, since there is only one charge per basic cell, case (1) does not contribute.[13] This is because when Eq. (27) is written in terms of ϕ (see Appendix A), one obtains

$$\underline{B}(\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3) = i\Delta(\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3)\sum_{\mathbf{p}}{}'[\sin(\mathbf{f}_1\cdot\mathbf{p})+\sin(\mathbf{f}_2\cdot\mathbf{p}) +\sin(\mathbf{f}_3\cdot\mathbf{p})]\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\phi(\mathbf{p}) , \tag{28}$$

where the function $\Delta(\mathbf{f})$ is defined as

$$\Delta(\mathbf{f})=\begin{cases}1, & \mathbf{f}=\mathbf{g}\\ 0 & \text{otherwise},\end{cases} \tag{29}$$

and the vectors $\mathbf{g}$ form the reciprocal lattice to the vectors $\mathbf{p}$. For case (1), the Δ function in $\underline{B}$ then implies that when $\mathbf{f}_1=-\mathbf{f}_2$, then $\mathbf{f}_3=0$, which causes $\underline{B}$ to vanish by Eq. (28). Thus, only case (2) contributes and Eq. (25) becomes

$$\frac{\langle U_3^2\rangle}{N(kT)^2}=\frac{6kT}{N^4}\sum_{\substack{\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3\\ s_1,s_2,s_3}}\frac{|b(\mathbf{f}_1,s_1;\mathbf{f}_2,s_2;\mathbf{f}_3,s_3)|^2}{m^3\omega(\mathbf{f}_1,s_1)^2\omega(\mathbf{f}_2,s_2)^2\omega(\mathbf{f}_3,s_3)^2} , \tag{30}$$

where we have used the fact that

$$\underline{B}(-\mathbf{f}_1,-\mathbf{f}_2,-\mathbf{f}_3)=\underline{B}^*(\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3) .$$

We have again neglected an $O(1/N)$ term in Eq. (25) which enters when four or more of the modes are equal. However, this correction also vanishes (see Appendix B), so Eq. (30) is correct for finite N in periodic boundary conditions.

In order to evaluate the sums over normal modes appearing in Eqs. (23) and (30), we first require a simple form for the N possible values of $\mathbf{f}$ for bcc and fcc symmetry. For bcc symmetry we choose the primitive lattice vectors to be

$$\{a_0(1,0,0),a_0(0,1,0),a_0(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})\} ,$$

where $a_0=L/M$ is the lattice constant and m is any positive integer. This implies that primitive reciprocal-lattice vectors are $\mathbf{g}_1=2\pi(1,0,-1)/a_0$, $\mathbf{g}_2=2\pi(0,1,-1)/a_0$, $\mathbf{g}_3=4\pi(0,0,1)/a_0$, and the cell volume is $v_c=a_0^3/2$. Then some simple algebra implies that the N possible $\mathbf{f}$ vectors are

$$\mathbf{f}=(l\mathbf{g}_1+m\mathbf{g}_2+n\mathbf{g}_3/2)/M , \tag{31}$$

where l and m rum from 0 to $M-1$, and n runs from 0 to $2M-1$, for a total of $N=2M^3$ vectors.

In the fcc case, we take the primitive lattice vectors to be

$$\{a_0(1,0,0),a_0(\tfrac{1}{2},\tfrac{1}{2},0),a_0(0,\tfrac{1}{2},\tfrac{1}{2})\} .$$

The cell volume is $v_c=a_0^3/4$ and now $\mathbf{g}_1=2\pi(1,-1,1)/a_0$, $\mathbf{g}_2=4\pi(0,1,-1)/a_0$, and $\mathbf{g}_3=4\pi(0,0,1)/a_0$. Now the N possible $\mathbf{f}$'s are

$$\mathbf{f}=[l\mathbf{g}_1+\frac{m}{2}\mathbf{g}_2+\frac{n}{2}\mathbf{g}_3]/M , \tag{32}$$

where l runs from 0 to $M-1$, and m and n run between 0 and $2M-1$, for a total of $N=4M^3$ vectors. Note that the sum of any two vectors $\mathbf{f}$ gives another vector in the set, upon suitable translation by a reciprocal-lattice vector $\mathbf{g}$ back to the first Brillouin zone.

In order to determine $\langle U_3^2\rangle$ and $\langle U_4\rangle$, we first compute and store the normal mode frequencies $\omega^2(\mathbf{f},s)$ and polarizations $v(\mathbf{f},s)$ at the $3N$ values of $(\mathbf{f},s)$ by solving for the eigenvectors and values of $\underline{A}(\mathbf{f})$ at each $\mathbf{f}$ value of Eqs. (31) or (32).

We next determine and store the tensors $\underline{\beta}(\mathbf{f})$ and $\underline{\chi}(\mathbf{f})$, for the N values of $\mathbf{f}$, where

$$\underline{\beta}(\mathbf{f})\equiv\sum_{\mathbf{p}}{}'\sin(\mathbf{f}\cdot\mathbf{p})\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\phi(\mathbf{p}) \tag{33a}$$

and

$$\underline{\chi}(\mathbf{f})\equiv\sum_{\mathbf{p}}{}'\cos(\mathbf{f}\cdot\mathbf{p})\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\phi(\mathbf{p}) . \tag{33b}$$

In terms of these two tensors, Eqs. (24) and (28) become

$$\underline{B}(\mathbf{f}_1,\mathbf{f}_2,\mathbf{f}_3) = i[\underline{\beta}(\mathbf{f}_1)+\underline{\beta}(\mathbf{f}_2)+\underline{\beta}(\mathbf{f}_3)]\Delta(\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3) , \tag{34a}$$

$$\underline{C}(\mathbf{f}_1,-\mathbf{f}_1,\mathbf{f}_2,-\mathbf{f}_2) =2\{\underline{\chi}(0)-\underline{\chi}(\mathbf{f}_1)-\underline{\chi}(\mathbf{f}_2) +\tfrac{1}{2}[\underline{\chi}(\mathbf{f}_1+\mathbf{f}_2)+\underline{\chi}(\mathbf{f}_1-\mathbf{f}_2)]\} . \tag{34b}$$

Since a sum of any two vectors in the set of N $\mathbf{f}$'s gives another vector in the set, we can now perform the required double sums over $\mathbf{f}_1$ and $\mathbf{f}_2$ (and the sums over polarization) in Eqs. (23) and (30) using Eqs. (21), (26), and (34) and the stored values of ω^2, $\mathbf{v}$, $\underline{\beta}$, and $\underline{\chi}$; the total computation time scales like N^2. Ewald sums (see Appendix C) are used to evaluate $\underline{\chi}$ and $\underline{\beta}$. The final results for $\langle U_4\rangle$, $\langle U_3^2\rangle$, and A_1 are summarized in Table II for both fcc and bcc lattices for various N values.

We have determined that the result for A_1 asymptotes to $A_1=10.84$ for the bcc lattice and $A_1=12.35$ for the fcc case. This calculation was performed by noting that in the large N limit, the sums over $\mathbf{f}$ in Eqs. (23) and (30) convert to integrals. These integrals are then performed by using the third-order "midpoint-rule" method, in which the basic reciprocal cell formed by $\mathbf{g}_1$, $\mathbf{g}_2$, and $\mathbf{g}_3$, describable as a parallelepiped whose sides are determined by the planes formed between $\mathbf{g}_1$, $\mathbf{g}_2$, and $\mathbf{g}_3$, is chopped into $N_1\times N_2\times N_3$ geometrically similar parallelepipeds. The vectors $\mathbf{f}$ are then chosen at the centers of these cells. It is not difficult to show that for N_1, N_2, and N_3 odd, any two vectors $\mathbf{f}$ add to another $\mathbf{f}$ in the set, provided that the basic reciprocal cell is chosen so that $\mathbf{f}=0$ is a member of the set. The midpoint-rule method converges more quickly to the $N\to\infty$ result than if one simply takes M large using the $\mathbf{f}$ values of Eqs. (31)

TABLE II. Analytic values for anharmonic terms in periodic boundary conditions.

N	$\frac{\langle U_3^2\rangle\Gamma}{72N(kT)^2}$	$\frac{\langle U_4\rangle\Gamma}{24NkT}$	A_1
	bcc		
2	0	0	0
16	12.297	39.001	−26.704
54	27.145	23.090	4.055
128	25.243	16.426	8.817
250	23.661	13.625	10.036
432	22.794	12.331	10.463
686	22.319	11.675	10.645
	fcc		
4	0	0.832	−0.832
32	15.837	5.853	9.983
108	18.227	6.259	11.968
256	18.515	6.166	12.349
500	18.447	6.026	12.421
864	18.339	5.915	12.424
1372	18.248	5.836	12.412

or (32). Table III shows the results for various values of N_1, N_2, and N_3. The primitive lattice vectors used to determine $\mathbf{g}_1$, $\mathbf{g}_2$, and $\mathbf{g}_3$ are also shown in Table III.

III. THE LIQUID-SOLID PHASE TRANSITION

In this section we consider the effect of our value for A_1 on the phase transition to a bcc lattice. In order to determine the free energy of the solid phase, we use the MC data of Slattery, Doolen, and DeWitt[3] for the configurational internal energy of the solid phase at various values of Γ. They have corrected their data for center-of-mass motion, which means that the listed data, which we call $U^{\rm SDD}/NkT$, are related to their actual MC results by[4]

$$\frac{U^{\rm MC}}{NkT}=\frac{U^{\rm SDD}}{NkT}\frac{N-1}{N}+\frac{A_{-1}\Gamma}{N}\ .$$

The contribution to $U^{\rm MC}$ due to anharmonic effects is

TABLE III. Analytic values for anharmonic terms in limit as $N\to\infty$.

$N_1\times N_2\times N_3$	$\frac{\langle U_3^2\rangle\Gamma}{72N(kT)^2}$	$\frac{\langle U_4\rangle\Gamma}{24NkT}$	A_1
bcc: Primitive vectors $\{(1,1,-1),(-1,1,1),(1,-1,1)\}$			
11×11×11	22.631	11.894	10.737
15×15×15	21.909	11.086	10.823
21×21×21	21.633	10.792	10.841
25×25×25	21.572	10.730	10.842
31×31×31	21.530	10.687	10.843
fcc: Primitive vectors $\{(1,1,0),(0,1,1),(1,0,1)\}$			
11×11×11	18.199	5.805	12.394
15×15×15	18.095	5.717	12.378
21×21×21	18.021	5.661	12.360
25×25×25	17.997	5.644	12.353
31×31×31	17.978	5.630	12.348

$$\frac{U_a}{NkT}=\frac{U^{\rm MC}}{NkT}+\frac{3}{2}-\frac{U^0}{NkT}$$
$$=\left[\frac{U^{\rm SDD}}{NkT}-A_{-1}\Gamma-\frac{3}{2}\right]\left[\frac{N-1}{N}\right],\qquad(35)$$

where we note that the average kinetic energy per charge is $3kT/2$ and we have substituted Eq. (18) for U^0. This definition of U_a differs from that of previous authors in that we remove from $U^{\rm MC}/N$ the harmonic energy per ion for the N ion system, *not* the $N\to\infty$ limit of the harmonic energy. This is an important distinction for small N or large Γ which removes spurious N dependence in U_a. The anharmonic contribution F_a to the free energy F then follows from Eq. (1):

$$\frac{F_a}{NkT}=-\int_0^{1/\Gamma}d\left[\frac{1}{\Gamma'}\right]\Gamma'\frac{U_a(\Gamma')}{NkT}\ .\qquad(36)$$

It is therefore useful to plot $(\Gamma U_a)/(NkT)$ as a function of $1/\Gamma$ for the values of Γ at which $U^{\rm MC}$ was determined in Ref. 3 (see Fig. 1). From Eq. (2) this function should be expressable as

$$\frac{\Gamma U_a}{NkT}=A_1+A_2/\Gamma+\cdots\ .$$

Previous authors[2–4] used a straight-line fit through the origin (i.e., only A_2 was assumed to be nonzero). Instead we have used a three-parameter polynomial fit to the $N=432$ data, including the analytically determined $T=0$ point from Table II. This $T=0$ point fixes A_1 to be $A_1=10.463$. The other two parameters are then determined by the fit to be $A_2=352.8$, $A_3=1.794\times10^5$, with an error of $\chi^2=7$. The fit is shown in Fig. 1; it is not an unreasonable looking curve given the present MC data set. Indeed, any number of reasonable curves could be drawn through the MC data; our $\Gamma=\infty$ point is quite useful in pinning down the large Γ behavior of U. Furthermore, the MC data for the anharmonic energy show a

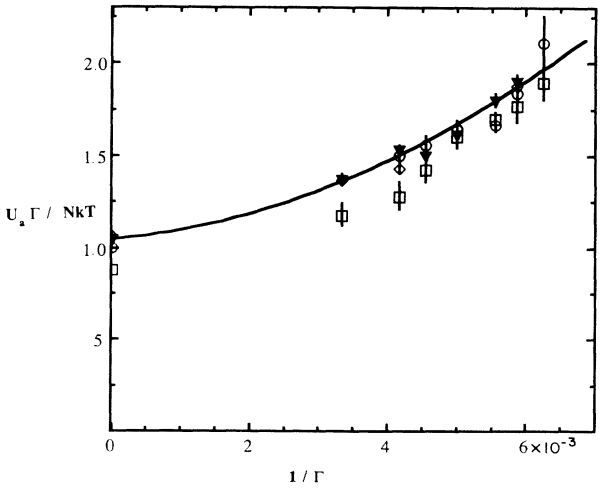

FIG. 1. Anharmonic energy of the bcc lattice from MC data of Ref. 3. $T=0$ points are analytic results. Squares, $N=128$; circles, $N=250$; solid triangles, $N=432$; diamonds, $N=686$. Solid line is the fit discussed in the text.

general increase in $U_a\Gamma/NkT$ as N increases, consistent with the analytic results of Table II for the bcc case. A relatively simple model for this N dependence is a shift upward in the entire curve as $N\to\infty$, until $A_1=10.84$ in the limit. Using Eq. (1), one then obtains the following expression for the anharmonic free energy:

$$\lim_{N\to\infty}\frac{F_a}{NkT}=-\left[\frac{10.84}{\Gamma}+\frac{176.4}{\Gamma^2}+\frac{5.980\times10^4}{\Gamma^3}\right]. \quad (37)$$

Comparison of this result for the free energy to that of Ref. 3 for the liquid free energy implies that the liquid-solid phase transition is shifted to $\Gamma_{\rm crit}\sim172$. However, it is clear from the data shown in Fig. 1 that more MC data (particularly at large Γ) would be extremely useful in improving this estimate for $\Gamma_{\rm crit}$. Such higher Γ data would also be useful as an independent check of the value of A_1.

It should also be noted that one could determine A_2 and A_3 using the same perturbation techniques as were employed in determining A_1. However, the values obtained probably would bear little resemblance to those used in Eq. (37). This is because our values for A_2 and A_3 are based on a numerical fit over a broad range of Γ, whereas values calculated from perturbation theory are rigorously valid only in the limit $\Gamma\to\infty$, and the range of convergence of Eq. (2) has not been established.

Some fcc data have also been generated for $N=108$.[12] A similar three-parameter fit to this data is shown in Fig. 2, using the exact $N=108$ value of $A_1=11.968$. The fit gives $A_2=-36.46$, $A_3=3.051\times10^5$, with an error of $\chi^2=2$. Comparison of the resulting fcc free energy to the fluid free energy of Ref. 3 then implies that the fcc lattice has lower free energy than the liquid at $\Gamma\sim182$. Again, however, this value is only a rough estimate, particularly since the available fcc data have rather large errors. More high-accuracy MC data are required for both the fcc and bcc cases in order to obtain sufficiently accurate interplation curves for the solid free energy.

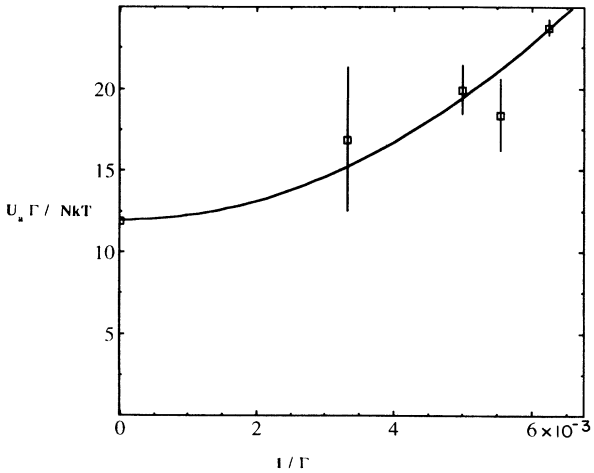

FIG. 2. Anharmonic energy of the fcc lattice from MC data of Ref. 12 for $N=108$. The $T=0$ point is the analytic result for $N=108$. Solid line is the fit discussed in text.

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APPENDIX A

Here we derive formulas for sums over $\nabla_i\nabla_j\Phi$, $\nabla_i\nabla_j\nabla_k\Phi$, and $\nabla_i\nabla_j\nabla_k\nabla_l\Phi$ in terms of the two-particle interaction $\phi_{ij}=\phi(\mathbf{x}_i^0-\mathbf{x}_j^0)$. We require sums of the form

$$\underline{S}_n=\sum_{i,j,k,\ldots}(\nabla_i\nabla_j\nabla_k\cdots\Phi^0)e^{i(\mathbf{f}_1\cdot\mathbf{x}_i^0+\mathbf{f}_2\cdot\mathbf{x}_j^0+\cdots)},$$

where the index n refers to the number of gradients and $\mathbf{f}$ vectors.

From Eq. (4b),

$$\nabla_i\Phi^0=\sum_{\bar{k}\,(\neq i)}\nabla_i\phi_{i\bar{k}},$$

$$\nabla_i\nabla_j\Phi^0=\delta_{ij}\sum_{\bar{k}\,(\neq i)}\nabla_i\nabla_i\phi_{i\bar{k}}+\delta'_{ij}\nabla_i\nabla_j\phi_{ij},$$

$$\nabla_i\nabla_j\nabla_k\Phi^0=\delta_{ij}\delta_{jk}\sum_{\bar{k}\,(\neq i)}\nabla_i\nabla_i\nabla_i\phi_{i\bar{k}}+\delta_{ij}\delta'_{jk}\nabla_i\nabla_i\nabla_k\phi_{ik}+\delta_{ik}\delta'_{ij}\nabla_i\nabla_i\nabla_j\phi_{ij}+\delta_{jk}\delta'_{ij}\nabla_i\nabla_j\nabla_j\phi_{ij},$$

$$\begin{aligned}\nabla_i\nabla_j\nabla_k\nabla_l\Phi^0=&\,\delta_{ij}\delta_{jk}\delta_{kl}\sum_{\bar{k}\,(\neq i)}\nabla_i\nabla_i\nabla_i\nabla_i\phi_{i\bar{k}}+\delta_{ij}\delta_{jk}\delta'_{il}\nabla_i\nabla_i\nabla_i\nabla_l\phi_{il}\\&+\delta_{ij}\delta_{jl}\delta'_{jk}\nabla_i\nabla_i\nabla_i\nabla_k\phi_{ik}+\delta_{kl}\delta_{ij}\delta'_{jk}\nabla_i\nabla_i\nabla_k\nabla_k\phi_{ik}+\delta_{il}\delta_{ik}\delta'_{ij}\nabla_i\nabla_i\nabla_i\nabla_j\phi_{ij}\\&+\delta_{jl}\delta_{ik}\delta'_{ij}\nabla_i\nabla_i\nabla_j\nabla_j\phi_{ij}+\delta_{il}\delta_{jk}\delta'_{ij}\nabla_i\nabla_i\nabla_j\nabla_j\phi_{ij}+\delta_{jl}\delta_{jk}\delta'_{ij}\nabla_i\nabla_j\nabla_j\nabla_j\phi_{ij},\end{aligned}$$

where $\delta'_{ij}\equiv1-\delta_{ij}$. Then using the symmetry of ϕ_{ij} upon interchange of indices, we obtain

$$\underline{S}_2=\sum_i e^{i(\mathbf{f}_1+\mathbf{f}_2)\cdot\mathbf{x}_i^0}\sum_{j(\neq i)}\nabla_i\nabla_i\phi_{ij}(1-e^{i\mathbf{f}_2\cdot(\mathbf{x}_j^0-\mathbf{x}_i^0)})$$
$$=N\Delta(\mathbf{f}_1+\mathbf{f}_2)\sum_{\mathbf{p}}{}'(1-\cos\mathbf{f}_2\cdot\mathbf{p})\frac{\partial}{\partial\mathbf{p}}\frac{\partial\phi}{\partial\mathbf{p}}(\mathbf{p}) ,$$

where we have again used the symmetry of ϕ, and we have performed the sum over i via the identity

$$\sum_{\mathbf{p}} e^{i\mathbf{f}\cdot\mathbf{p}}=N\Delta(\mathbf{f}) ,$$

true for all vectors $\mathbf{f}$ reciprocal to the cubic cell. Use of this form for $\underline{S}_2$ in Eq. (15) then leads to Eq. (16) for $\underline{A}$.

Similarly,

$$\underline{S}_3=\sum_i e^{i(\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3)\cdot\mathbf{x}_i^0}\sum_{j(\neq i)}\nabla_i\nabla_i\nabla_i\phi_{ij}[1-e^{i(\mathbf{f}_1+\mathbf{f}_2)\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}-e^{i(\mathbf{f}_1+\mathbf{f}_3)\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}+e^{-i(\mathbf{f}_2+\mathbf{f}_3)\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}]$$

or

$$\underline{S}_3=Ni\sum_{\mathbf{p}}{}'[\sin\mathbf{f}_1\cdot\mathbf{p}+\sin\mathbf{f}_2\cdot\mathbf{p}+\sin\mathbf{f}_3\cdot\mathbf{p}]\Delta(\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3)\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\phi(\mathbf{p}) ,$$

which leads to Eq. (28) for $\underline{B}$. Finally,

$$\underline{S}_4=\sum_i e^{i(\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3+\mathbf{f}_4)\cdot\mathbf{x}_i}\sum_{j(\neq i)}\nabla_i\nabla_i\nabla_i\nabla_i\phi_{ij}[1-e^{-i\mathbf{f}_4\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}-e^{-i\mathbf{f}_3\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}+e^{-i(\mathbf{f}_3+\mathbf{f}_4)\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}-e^{-i\mathbf{f}_2\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}$$
$$+e^{-i(\mathbf{f}_2+\mathbf{f}_3)\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}-e^{i\mathbf{f}_1\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}+e^{-i(\mathbf{f}_2+\mathbf{f}_4)\cdot(\mathbf{x}_i^0-\mathbf{x}_j^0)}]$$

or

$$\underline{S}_4=N\Delta(\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3+\mathbf{f}_4)\sum_{\mathbf{p}}{}'[1-\cos\mathbf{f}_1\cdot\mathbf{p}-\cos\mathbf{f}_2\cdot\mathbf{p}-\cos\mathbf{f}_3\cdot\mathbf{p}-\cos\mathbf{f}_4\cdot\mathbf{p}+\cos(\mathbf{f}_3+\mathbf{f}_4)\cdot\mathbf{p}+\cos(\mathbf{f}_2+\mathbf{f}_3)\cdot\mathbf{p}$$
$$+\cos(\mathbf{f}_2+\mathbf{f}_4)\cdot\mathbf{p}]\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\frac{\partial}{\partial\mathbf{p}}\phi(\mathbf{p}) .$$

Substitution of $\underline{S}_4$ into Eq. (22) leads, after some simple algebra, to Eq. (24).

APPENDIX B

In this appendix we consider the corrections to $\langle U_3^2\rangle$ and $\langle U_4\rangle$ due to the appearance of fourth-order and sixth-order cumulants in the expressions for average powers of q in Eqs. (20) and (25). To evaluate these cumulants it is easiest to break q into real and imaginary parts: $q_{\mathbf{f},s}=Q_R+iQ_I$. Then it follows that

$$\langle q_{\mathbf{f},s}^n q^{*\,n}_{\mathbf{f},s}\rangle=\langle(Q_R^2+Q_I^2)^n\rangle . \tag{B1}$$

This moment may be written in terms of $\langle|q_{\mathbf{f},s}|^2\rangle^n$ by observing that Eq. (14) implies that Q_R and Q_I are independent variables with equal Gaussian distributions so that, for instance,

$$\langle Q_R^4\rangle=\langle Q_I^4\rangle=3\langle Q_R^2\rangle^2$$

and

$$\langle Q_R^6\rangle=\langle Q_I^6\rangle=15\langle Q_R^2\rangle^3 .$$

However, there is an exceptional case, which occurs when $2\mathbf{f}=\mathbf{g}$ (or $\mathbf{f}=-\mathbf{f}+\mathbf{g}$) for some reciprocal vector $\mathbf{g}$. By Eq. (13) the reality of $\mathbf{u}$ implies that $q_{\mathbf{f},s}=q^*_{-\mathbf{f},s}$, so this implies that $Q_I=0$ for these special modes which lie on the surface of the Brillouin zone, and thus averages involving Q_I are zero. [Note, however, that Eq. (19) is still true for these modes.] Expansion of the polynomial on the right-hand side of Eq. (B1) then leads to the following results for the $n=2$ and 3 cases of Eq. (B1):

$$\langle q_{\mathbf{f},s}^2 q^{*\,2}_{\mathbf{f},s}\rangle=\langle|q_{\mathbf{f},s}|^2\rangle^2[2+\Delta(2\mathbf{f})] \tag{B2a}$$

and

$$\langle q_{\mathbf{f},s}^3 q^{*3}_{\mathbf{f},s}\rangle=\langle|q_{\mathbf{f},s}|^2\rangle^3[6+9\Delta(2\mathbf{f})] , \tag{B2b}$$

where the Δ function takes into account the special case of modes on the surface of the Brillouin zone.

Turning now to Eq. (20), we will count up permutations of mode indices which lead to the same contribution to the

sum over modes. We write Eq. (20) schematically as

$$\langle U_4\rangle=\sum_{1,2,3,4} c(1,2,3,4)\langle q_1q_2q_3q_4\rangle \ . \tag{B3}$$

As discussed in the text, nonzero contributions occur when $2=-1$ and $4=-3$, where the shorthand $2=-1$ means $(\mathbf{f}_2,s_2)=(-\mathbf{f}_1+\mathbf{g},s_1)$, for some $\mathbf{g}$. There are three permutations of the indices of c which lead to the same result provided that $1\neq\pm2$; these are $(1,-1,2,-2)$, $(1,2,-1-2)$, $(1,2,-2,-1)$. If $1=\pm2$ and $1\neq-1$ (i.e., $\mathbf{f}_1\neq-\mathbf{f}_1+\mathbf{g}\forall\mathbf{g}$), there are again three permutations: $(1,-1,1,-1)$, $(1,1,-1,-1)$, $(1,-1,-1,1)$. Finally, if $1=\pm2$ and $1=-1$, there is only one permutation, $(1,1,1,1)$. Thus Eq. (B3) may be written as

$$\langle U_4\rangle=3\sum_{\substack{1,2\\1\neq\pm2}} c(1,-1,2,-2)\langle|q_1|^2\rangle\langle|q_2|^2\rangle+3\sum_l c(1,-1,1,-1)\langle|q_1|^4\rangle[1-\Delta(2\mathbf{f})]$$
$$+\sum_l c(1,-1,1,-1)\langle|q_1|^4\rangle\Delta(2\mathbf{f}) \ .$$

To the first sum of this equation we add and subtract the missing cross terms to give

$$\langle U_4\rangle=3\sum_{1,2} c(1,-1,2,-2)\langle|q_1|^2\rangle\langle|q_2|^2\rangle-3\sum_1 c(1,-1,1,-1)[2-\Delta(2\mathbf{f}_1)]\langle|q_1|^2\rangle^2$$
$$+3\sum_1 c(1,-1,1,-1)2\langle|q_1|^2\rangle^2[1-\Delta(2\mathbf{f})]+\sum_1 c(1,-1,1,-1)3\langle|q_1|^2\rangle^2\Delta(2\mathbf{f}) \ ,$$

where use has been made of Eq. (B2a) in the last two sums. Finally, the last three sums in this equation cancel, leaving only the first sum in accordance with Eq. (23).

A similar argument may be put forward for $\langle U_3^2\rangle$. Writing Eq. (25) schematically as

$$\langle U_3^2\rangle=\sum_{\substack{1,2,3\\4,5,6}} b(1,2,3)b(4,5,6)\langle q_1q_2q_3q_4q_5q_6\rangle \ , \tag{B4}$$

one finds that only terms of the form $(1,2,3,-1,-2,-3)$ contribute, where $\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3=\mathbf{g}$ for some reciprocal lattice vector $\mathbf{g}$. If $1\neq2$, $2\neq3$, and $3\neq1$, then there are six possible permutations leading to the same result, as discussed in the text. If any two of the three modes are the same (e.g., $3=1$), the indices take on the form $(1,2,1,-1,-2,-1)$ and there are nine permutations which give the same result. [Note that $3=-1$ is disallowed since the condition $\mathbf{f}_1+\mathbf{f}_2+\mathbf{f}_3=\mathbf{g}$ then implies $\mathbf{f}_2=\mathbf{g}$ in this case, so by Eq. (28) b vanishes.] Finally, if all three modes are equal, there is only one possibility, $(1,1,1,-1,-1,-1)$. Thus, Eq. (B4) becomes

$$\langle U_3^2\rangle=6\sum_{\substack{1,2,3,\\1\neq2,2\neq3,3\neq1}}|b(1,2,3)|^2\langle|q_1|^2\rangle\langle|q_2|^2\rangle\langle|q_3|^2\rangle+9\sum_{1\neq2}|b(1,2,1)|^2\langle|q_1|^4\rangle\langle|q_2|^2\rangle+\sum_1|b(1,1,1)|^2\langle|q_1|^6\rangle \ . \tag{B5}$$

Note that in the last two sums no terms survive if $1=-1$, so we need not worry about this special case. Adding and subtracting the cross terms to the first sum and using Eqs. (B2) then leads to

$$\langle U_3^2\rangle=6\sum_{1,2,3}|b(1,2,3)|^2\langle q_1^2\rangle\langle q_2^2\rangle\langle q_3^2\rangle-6\left[3\sum_{1\neq2}|b(1,2,1)|^2\langle|q_1|^2\rangle^2\langle|q_2|^2\rangle+\sum_1|b(1,1,1)|^2\langle|q_1|^2\rangle^3\right]$$
$$+9\sum_{1\neq2}|b(1,2,1)|^2 2\langle|q_1|^2\rangle^2\langle|q_2|^2\rangle+\sum_1|b(1,1,1)|^2 6\langle|q_1|^2\rangle^3 \ .$$

Again, all sums cancel but the first, leaving Eq. (30) as the exact form for $\langle U_3^2\rangle$ for finite N.

APPENDIX C

In this appendix we consider the Ewald sum method, useful in summing series involving the Coulomb interaction. Since the sums we require are not standard, we go into some detail. Consider the following sum:

$$S(\mathbf{f},\mathbf{x})=\sum_{\mathbf{p}}{}'\,\phi(\mathbf{p}+\mathbf{x})e^{i\mathbf{f}\cdot\mathbf{p}}=\sum_{\mathbf{p}}\phi(\mathbf{p}+\mathbf{x})e^{i\mathbf{f}\cdot\mathbf{p}}-\phi(\mathbf{x}) \ . \tag{C1}$$

Note that the sum over $\mathbf{p}$ runs only over N ions, as discussed in the text. Then we can obtain $\underline{A}$, $\underline{\beta}$, and $\underline{\chi}$ as derivatives of S. For example, from Eq. (33a),

$$\underline{\beta}=\frac{\partial}{\partial\mathbf{x}}\frac{\partial}{\partial\mathbf{x}}\frac{\partial}{\partial\mathbf{x}}S\bigg|_{\mathbf{x}=0} \ .$$

This sum may be carried out by substitution of Eq. (5) for ϕ:

$$S(\mathbf{f},\mathbf{x})=\frac{4\pi e^2}{v}\sum_{\mathbf{p}}\sum_{\mathbf{k}}{}'\frac{e^{i\mathbf{k}\cdot(\mathbf{p}+\mathbf{x})+i\mathbf{f}\cdot\mathbf{p}}}{k^2}-\phi(\mathbf{x}) \ ,$$

where the $\mathbf{k}$'s run over a cubic lattice as in Eq. (5). The first term may be written as

$$\frac{4\pi e^2}{v}\sum_{\mathbf{p}}\sum_{\mathbf{k}}{}' \int_0^\infty dt\, e^{-k^2 t} e^{i\mathbf{k}\cdot(\mathbf{p}+\mathbf{x})+i\mathbf{f}\cdot\mathbf{p}} ,$$

which we break up into two terms:

$$I_1=\frac{4\pi e^2}{v}\sum_{\mathbf{p}}\sum_{\mathbf{k}}{}' \int_0^{R^2} dt e^{-k^2 t+i\mathbf{k}\cdot(\mathbf{p}+\mathbf{x})+i\mathbf{f}\cdot\mathbf{p}}$$

and

$$I_2=\frac{4\pi e^2}{v}\sum_{\mathbf{p}}\sum_{\mathbf{k}}{}' \int_{R^2}^\infty dt\, e^{-k^2 t+i\mathbf{k}\cdot(\mathbf{p}+\mathbf{x})+i\mathbf{f}\cdot\mathbf{p}} .$$

In the expression for I_1 we add and subtract the $\mathbf{k}=\mathbf{0}$ term; after performing the t integral for this term, we obtain

$$I_1=\frac{-4\pi e^2 N\Delta(\mathbf{f})}{v}R^2 + \frac{4\pi e^2}{v}\sum_{\mathbf{p}}\sum_{\mathbf{k}}{}' \int_0^{R^2} e^{-k^2 t+i\mathbf{k}\cdot(\mathbf{p}+\mathbf{x})+i\mathbf{f}\cdot\mathbf{p}} dt .$$

In order to perform the sum over $\mathbf{k}$ in the second term, we use a trick, noting that

$$\frac{1}{v}\sum_{\mathbf{k}}{}' f(\mathbf{k})=\sum_{\mathbf{a}}\int d^3\bar{k}\frac{1}{(2\pi)^3}f(\bar{k})e^{i\mathbf{a}\cdot\bar{\mathbf{k}}} ,$$

where the vectors $\mathbf{a}$ form a cubic lattice; $\mathbf{a}=(l,m,n)L$ for all integers (l,m,n). Then we complete the squares in I_1 and perform the integral over $\bar{\mathbf{k}}$, obtaining

$$I_1=-4\pi e^2 nR^2\Delta(f) + \frac{4\pi e^2}{(2\pi)^3}(\pi)^{3/2}\sum_{\mathbf{p}}\sum_{\mathbf{a}}\int_0^{R^2} dt\frac{e^{-|\mathbf{p}+\mathbf{a}+\mathbf{x}|^2/4t^2}}{t^{3/2}}e^{i\mathbf{f}\cdot\mathbf{p}} .$$

The integral can be written as a complementary error function, so we obtain

$$I_1=-4\pi e^2 nR^2\Delta(\mathbf{f})+e^2\sum_{\mathbf{a}}\sum_{\mathbf{p}}\frac{\operatorname{erfc}\left[\frac{|\mathbf{p}+\mathbf{a}+\mathbf{x}|}{2R}\right]}{|\mathbf{p}+\mathbf{a}+\mathbf{x}|}e^{i\mathbf{f}\cdot\mathbf{p}} .$$

Note that for the choices of N used in the text, the lattices formed by $\mathbf{p}$ and $\mathbf{a}$ are compatible and the sum $\sum_{\mathbf{p}}\sum_{\mathbf{a}}$ may be replaced by a sum over $\mathbf{p}$ extending through all the cubic cells.

Turning to I_2, we first perform the t integral:

$$I_2=\sum_{\mathbf{k}}{}'\sum_{\mathbf{p}}\frac{4\pi e^2}{v}\frac{e^{-k^2R^2+i\mathbf{k}\cdot(\mathbf{p}+\mathbf{x})+i\mathbf{f}\cdot\mathbf{p}}}{k^2} .$$

We then perform the sum over $\mathbf{p}$, obtaining

$$I_2=\sum_{\mathbf{k}}{}' 4\pi e^2 n\Delta(\mathbf{f}+\mathbf{k})\frac{e^{-k^2R+i\mathbf{k}\cdot\mathbf{x}}}{k^2} .$$

Thus, $S(\mathbf{f},\mathbf{x})$ becomes

$$S(\mathbf{f},\mathbf{x})=e^2\sum_{\mathbf{p};\mathbf{a}}\frac{\operatorname{erfc}\left[\frac{|\mathbf{p}+\mathbf{a}+\mathbf{x}|}{2R}\right]}{|\mathbf{p}+\mathbf{a}+\mathbf{x}|}e^{i\mathbf{f}\cdot\mathbf{p}}-4\pi e^2 nR^2\Delta(\mathbf{f}) -\phi(\mathbf{x})+4\pi e^2 n\sum_{\mathbf{k}}{}'\Delta(\mathbf{k}+\mathbf{f})\frac{e^{-k^2R^2+i\mathbf{k}\cdot\mathbf{x}}}{k^2} . \quad \text{(C2)}$$

In order to remove the singular term as $\mathbf{x}\to\mathbf{0}$, at $\mathbf{p}=\mathbf{a}=\mathbf{0}$, we will add and subtract e^2/x, noting that as $\mathbf{x}\to\mathbf{0}$, $\phi(\mathbf{x})\to e^2/x$. (Recall, however, that ϕ includes interactions with all ions on a cubic lattice.) The results for $\underline{A}$, $\underline{\beta}$, and $\underline{\chi}$ follow from derivatives of Eq. (C2) with respect to $\underline{x}$:

$$\underline{A}(\mathbf{f})=\overline{\underline{A}}(0)-\overline{\underline{A}}(\mathbf{f}) , \quad \text{(C3a)}$$

where

$$\overline{A}_{12}(\mathbf{f})=e^2\sum_{\mathbf{p},\mathbf{a}}{}'\left[\frac{\delta_{12}}{v}F'+\frac{v_1v_2}{v^2}\left[F''-\frac{F'}{v}\right]\right]\cos\mathbf{f}\cdot\mathbf{p}+\frac{e^2\delta_{12}}{6\sqrt{\pi}R^3} -4\pi e^2 n\sum_{\mathbf{k}}{}'\Delta(\mathbf{k}+\mathbf{f})\frac{k_1k_2}{k^2}e^{-k^2R^2}-\frac{\partial^2}{\partial x_1\partial x_2}\left[\phi(x)-\frac{e^2}{x}\right]\Bigg|_{x=0} , \quad \text{(C3b)}$$

$$\beta_{123}(\mathbf{f})=e^2\sum_{\mathbf{p},\mathbf{a}}{}'\left[\left[\frac{\delta_{12}v_3+\delta_{13}v_2+\delta_{23}v_1}{v^2}-\frac{3v_1v_2v_3}{v^4}\right]\left[F''-\frac{F'}{v}\right]+\frac{v_1v_2v_3}{v^3}F'''\right]\sin\mathbf{f}\cdot\mathbf{p} -4\pi e^2 n\sum_{\mathbf{k}}{}'\Delta(\mathbf{k}+\mathbf{f})\frac{k_1k_2k_3}{k^2}e^{-k^2R^2} , \quad \text{(C4)}$$

and

$$\chi_{1234}(\mathbf{f})=e^2\sum_{\mathbf{p}\cdot\mathbf{a}}{}' \left\{ \frac{\delta_{12}\delta_{34}+\delta_{13}\delta_{24}+\delta_{14}\delta_{23}}{v^2}\left[F''-\frac{F'}{v}\right]+\frac{(\delta_{12}v_3+\delta_{13}v_2+\delta_{23}v_1)v_4+\delta_{14}v_2v_3+\delta_{24}v_1v_3+\delta_{34}v_1v_2}{v^3} \right.$$
$$\left. \times\left[F'''-\frac{3}{v}\left[F''-\frac{F'}{v}\right]\right]+\frac{v_1v_2v_3v_4}{v^4}\left[F^{iv}-\frac{6}{v}F'''+\frac{15}{v^2}\left[F''-\frac{F'}{v}\right]\right]\right\}\cos\mathbf{f}\cdot\mathbf{p}$$
$$-\frac{e^2}{20\sqrt{\pi}R^5}(\delta_{12}\delta_{34}+\delta_{13}\delta_{24}+\delta_{14}\delta_{23})$$
$$+4\pi e^2 n\sum_{\mathbf{k}}{}'\frac{k_1k_2k_3k_4}{k^2}e^{-k^2R^2}\Delta(\mathbf{k}+\mathbf{f})-\frac{\partial^4}{\partial x_1\partial x_2\partial x_3\partial x_4}\left[\phi(x)-\frac{e^2}{x}\right]\Bigg|_{x=0}, \tag{C5}$$

where $\mathbf{v}=\mathbf{p}+\mathbf{a}$, each subscript runs over the three components (x,y,z), and

$$F'=\frac{-\operatorname{erfc}(v/2R)}{v^2}-\frac{e^{-v^2/4R^2}}{\sqrt{\pi}Rv},$$
$$F''-\frac{F'}{v}=\frac{3}{v^3}\operatorname{erfc}\left[\frac{v}{2R}\right]+\frac{e^{-v^2/4R^2}}{\sqrt{\pi}R}\left[\frac{3}{v^2}+\frac{1}{2R^2}\right],$$
$$F'''=\frac{-6\operatorname{erfc}(v/2R)}{v^4}-\frac{e^{-v^2/4R^2}}{\sqrt{\pi}R}\left[\frac{6}{v^3}+\frac{1}{vR^2}+\frac{v}{4R^4}\right],$$
$$F^{iv}=\frac{24}{v^5}\operatorname{erfc}\left[\frac{v}{2R}\right]+\frac{e^{-v^2/4R^2}}{\sqrt{\pi}R}\left[\frac{24}{v^4}+\frac{4}{v^2R^2}+\frac{1}{4R^4}+\frac{v^2}{8R^6}\right].$$

Note that terms involving $(\phi-e^2/x)$ cancel in Eq. (C3a) and Eq. (34b) and do not enter in Eq. (C4) for β by symmetry.

These forms for $\underline{\beta}$ and $\underline{\chi}$ have been checked by comparing them to the result obtained by performing a sum over gradients of the Coulomb interaction e^2/p (i.e., the $R\to\infty$ limit of the expressions). Equations (C3)–(C5) were evaluated on a Cray X-MP computer and enough terms were kept in the sums to keep accuracy to a few times 10^{-7}. The values of R chosen for fast convergence typically fell between $0.2a$ and $0.5a$ for both the fcc and bcc lattices.

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