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Melting of the Wigner crystal at finite temperature

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Melting of the Wigner crystal is studied in a new expansion scheme which is much more powerful than the Wigner-Kirkwood expansion of the quantum correction. The theory does not include the symmetry effect. The free energy including the quantum correction is evaluated with full use of the recent Monte Carlo results obtained for the classical one-component plasma. The melting entropy as well as the melting curve is obtained as a result of various extrapolations of properties for the liquid phase, in the approximation up to the sixth "reduced moment" of our expansion.

I. INTRODUCTION

The phases of the electron gas have attracted a great deal of interest[1] since the pioneering work of Wigner.[2] He pointed out that the electron gas would crystallize at sufficiently low density and temperature. The melting curve of the Wigner crystal is still unknown, though the melting density at zero temperature has approximately been determined by the recent Monte Carlo studies.[3-5] Even at zero temperature, determination of the melting point is very difficult because a high accuracy is needed for estimation of the free energies of both the crystal and the fluid.

The electron gas is a one-component plasma, the system of charged particles in a uniform neutralizing background. The properties of the classical one-component plasma are known very accurately, owing to the Monte Carlo studies.[6-8] It is then conceivable to take account of the quantum correction in order to get the quantum plasma, with the classical one as a starting point. There exists some attempts along the above line of thought,[9] in the Wigner-Kirkwood (WK) expansion.[10,11]

The WK expansion is a power series of $\hbar^2$, with $2\pi\hbar$ denoting the Planck constant. This expansion is awkward to handle in obtaining the higher-order terms; the coefficient of $\hbar^6$ consists of thirteen terms according to Hill,[12] where all of the terms are not so simple. When applied to the Coulomb system the WK expansion gives a power series of $(\beta\hbar\omega_p)^2$, where $\beta=1/k_BT$ with k_B the Boltzmann constant and with T the absolute temperature, and ω_p denotes the plasma frequency. The series is divergent at low temperature where $\beta\hbar\omega_p \gtrsim 1$. Thus the validity region of the WK expansion is confined to the high-temperature region.

In this paper we adopt the quantum-correction approach to the electron gas in a new formalism. Our formalism is based on an expansion obtained by resumming the partial series in the WK expansion for our particular system. In deriving it we observe that the WK expansion is a moment expansion of the free energy, as apparent when applied to a harmonic lattice. Accordingly, we shall get the quantum correction to the free energy by starting with the moment expansion for the harmonic lattice. For our harmonic Coulomb lattice,[13] the moment is a polynomial of ω_p^2, where each coefficient is the reduced moment apart from a numerical factor. Then we obtain a new expansion by summing up all of the terms for a particular reduced moment in the moment expansion.

The reduced moment is generalized to the anharmonic Coulomb lattice. By examining the free-energy correction due to the anharmonic term, we get the general expansion, apart from additional contributions. Here the reduced moments are expressed in terms of the configuration average of products of the derivative of the forces between particles. The resultant expressions are independent of whether the system is the solid or the liquid, and accordingly must be valid in the liquid phase as well. In actuality the present result in the expanded form reproduces completely the WK expansion up to $(\beta\hbar\omega_p)^6$, irrespective of the phases of our Coulomb system.

The reduced-moment expansion is effective even at low temperature in contradiction to the WK expansion, though the validity is confined to the low-density region of particles. In treating the electron gas by the new formalism, we utilize the Monte Carlo results for the classical one-component plasma. The reduced moments can be evaluated from the classical distribution function of charged particles, provided also by the Monte Carlo simulation.[6-8]

Using the free energies with the quantum correction, we treat the melting of the Wigner crystal. The symmetry effect will be disregarded throughout the present paper, though it is an important quantum effect.

The melting occurs at the crossing point of two free-energy curves for the liquid and solid phases. Generally, the quantum effect works to lower the free energy for the liquid relative to that for the solid, with depression of the melting temperature. By extrapolation we estimate the free energy for the liquid phase below the classical melting temperature. For our system the quantum correction is small with fractional contribution less than ~10% in the whole region of interest, where the primary term of the quantum corrections vanishes in the free-energy difference responsible for the relative stability of liquid and solid phases. It is a very small quantum correction that shifts the melting point remarkably. We note here that the free-energy difference is generally small between the two phases of interest.

This paper is organized as follows. In Sec. II we describe the moment expansion of the free energy for a harmonic lattice. The result is applied to the harmonic Coulomb lattice in Sec. III, where the moments are represented in the configuration space, followed by description of the reduced-moment expansion. In Sec. IV we consider modification of the reduced moments for the anharmonic lattice to obtain the general form of it. Then we evaluate the reduced moment in Sec. V and describe the result in Sec. VI. The summary will be given in Sec. VII with some discussion.

II. QUANTUM CORRECTION IN A HARMONIC LATTICE

The harmonic oscillator model is very useful in obtaining the quantum correction. By relying on this model, Feynman and Hibbs[14] have given the primary quantum correction to the classical distribution of a particle in an external potential. Thus we first consider the quantum correction to the free energy of a harmonic lattice.

Let Z_h be the partition function for the harmonic lattice, whose normal-mode frequencies are denoted by ω_i. Then we have

$$Z_h(\beta)=\prod_i [2\sinh(\beta\hbar\omega_i/2)]^{-1} \ . \tag{2.1}$$

The free energy of the system is then given by the known formula

$$F_h=k_BT\sum_i \ln[2\sinh(\beta\hbar\omega_i/2)] \ . \tag{2.2}$$

Let us begin with writing the free energy F_{hc} for the classical harmonic lattice,

$$F_{hc}=k_BT\sum_i \ln(\beta\hbar\omega_i) \ . \tag{2.3}$$

Then the difference (F_h-F_{hc}) stands for the quantum correction, which will be denoted by F_{hq}. That is,

$$F_h=F_{hc}+F_{hq} \ . \tag{2.4}$$

The expression for F_{hq} can easily be obtained by utilizing the following expansion formula:

$$\ln\sinh x=\ln x+\sum_{k=1}^{\infty}(-1)^{k-1}\frac{2^{2k-1}B_k}{(2k)!k}x^{2k} \tag{2.5}$$

valid for $0<|x|<\pi$, where B_k is the Bernoulli number given by

$$B_1=\tfrac{1}{6},\ B_2=B_4=\tfrac{1}{30},\ B_3=\tfrac{1}{42},\ldots \ . \tag{2.6}$$

The result becomes

$$F_{hq}=3Nk_BT\sum_{k=1}^{\infty}a_{2k}M_{2k}(\beta\hbar)^{2k} \ , \tag{2.7}$$

where

$$a_{2k}=(-1)^{k-1}\frac{B_k}{(2k)!(2k)} \ , \tag{2.8}$$

and M_{2k} is the $2k$th moment of the normal-mode frequencies given by

$$M_{2k}=(3N)^{-1}\sum_i \omega_i^{2k} \ , \tag{2.9}$$

with N denoting the number of particles for the system of unit volume.

The expansion coefficients a_{2k}'s are given numerically in Table I. For later use we also note a known formula

$$x\coth x=1+2\sum_{k=1}^{\infty}ka_{2k}(2x)^{2k} \ , \tag{2.10}$$

which is obtained from Eq. (2.5) by differentiation.

Now we have the quantum correction in the moment expansion, Eq. (2.7), for the harmonic lattice. This expansion is a power series with respect to the Planck constant $2\pi\hbar$, and hence may seem appropriate for treating the correction. For the Coulomb lattice, however, the convergence of the expansion series is limited to a very small value of β because our characteristic plasmon frequency ω_p is quite high. We shall obtain an improved expansion series, by decomposing the moment M_{2k} in the configuration space and by resumming the resulting partial series.

III. REDUCED-MOMENT EXPANSION FOR THE COULOMB LATTICE

A. Expression for the moments in the configuration space

For the Coulomb lattice, the moments have been evaluated by Coldwell-Horsfall and Maradudin (CHM).[13] Let us describe their procedure, since it is very important in deriving our expansion formula. Let $D_{\alpha\beta}(\mathbf{q})$ be the dynamical matrix for phonons with wave vector $\mathbf{q}$, such that

$$D_{\alpha\beta}(\mathbf{q})e_\beta(\mathbf{q},j)=\omega_j^2(\mathbf{q})e_\alpha(\mathbf{q},j) \tag{3.1}$$

with $\mathbf{e}(\mathbf{q},j)$ denoting the polarization vector for a normal mode $(\mathbf{q},j)$. On the left-hand side of Eq. (3.1) the summation over repeated Greek suffixes is implied. Then the moments are given easily by

$$\begin{aligned} M_2&=(3N)^{-1}\sum_q D_{\alpha\alpha}(\mathbf{q}) \ , \\ M_4&=(3N)^{-1}\sum_q D_{\alpha\beta}(\mathbf{q})D_{\beta\alpha}(\mathbf{q}),\ldots \ . \end{aligned} \tag{3.2}$$

Let us below consider the Coulomb lattice, for which we have[13]

TABLE I. Numerical values for the coefficients a_{2k}.

k	a_{2k}
1	$\frac{1}{24}$
2	$-\frac{1}{2880}$
3	$\frac{1}{181\,440}$
4	$-\frac{1}{9\,676\,800}$

$$D_{\alpha\beta}(\mathbf{q})=\tfrac{1}{3}\omega_p^2\delta_{\alpha\beta}+\frac{1}{m}\sum_n{}'[1-\cos(\mathbf{q}\cdot\mathbf{R}_n)]\phi_{\alpha\beta}(\mathbf{R}_n)\ , \tag{3.3}$$

where ω_p is the plasma frequency given by

$$\omega_p^2=\frac{4\pi Ne^2}{m}\ , \tag{3.4}$$

with m denoting the particle mass, and with e the electronic charge. $\phi_{\alpha\beta}(\mathbf{R})$ is defined by

$$\phi_{\alpha\beta}(\mathbf{R})=\nabla_\alpha\nabla_\beta\frac{e^2}{R}\ . \tag{3.5}$$

In the second term on the right-hand side of Eq. (3.3) the summation is taken over lattice points $\mathbf{R}_n$ with origin at $\mathbf{R}_0$ $(=\mathbf{0})$, where the prime on the summation sign indicates the sum to be taken over $\mathbf{R}_n$ except $\mathbf{R}_n=\mathbf{0}$.

Using Eq. (3.3) we evaluate Eq. (3.2). In the evaluation we note

$$\phi_{\alpha\alpha}(\mathbf{R})=-4\pi e^2\delta(\mathbf{R})\ . \tag{3.6}$$

We note also

$$\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_n}=N\delta(\mathbf{R}_n) \tag{3.7}$$

for the system of unit volume.

By this way we obtain CHM's expressions[13]

$$\begin{aligned}&M_2=\tfrac{1}{3}\omega_p^2,\quad M_4=\tfrac{1}{9}\omega_p^4+\mu_4\ ,\\ &M_6=\tfrac{1}{27}\omega_p^6+\omega_p^2\mu_4+\mu_6\ ,\\ &M_8=\tfrac{1}{81}\omega_p^8+\tfrac{2}{3}\omega_p^4\mu_4+\tfrac{4}{3}\omega_p^2\mu_6+\mu_8\ ,\end{aligned} \tag{3.8}$$

where we put

$$\begin{aligned}\mu_4={}&\frac{1}{3m^2}\left[\sum_n\sum_{n'}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\alpha}(\mathbf{R}_{n'})+\sum_n\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\alpha}(\mathbf{R}_n)\right]\ ,\\ \mu_6={}&\frac{1}{3m^3}\left[\sum_n\sum_{n'}\sum_{n''}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\alpha}(\mathbf{R}_{n''})+3\left[\sum_n\phi_{\alpha\beta}(\mathbf{R}_n)\right]\sum_{n'}\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\alpha}(\mathbf{R}_{n'})\right.\\ &\left.-\sum_n\sum_{n'}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\alpha}(\mathbf{R}_n-\mathbf{R}_{n'})\right]\ ,\\ \mu_8={}&\frac{1}{3m^4}\left[\sum_n\sum_{n'}\sum_{n''}\sum_{n'''}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\delta}(\mathbf{R}_{n''})\phi_{\delta\alpha}(\mathbf{R}_{n'''})+4\sum_n\sum_{n'}\sum_{n''}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\delta}(\mathbf{R}_{n''})\phi_{\delta\alpha}(\mathbf{R}_{n''})\right.\\ &+2\sum_n\sum_{n'}\sum_{n''}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\delta}(\mathbf{R}_{n''})\phi_{\delta\alpha}(\mathbf{R}_{n'})-4\sum_n\sum_{n'}\sum_{n''}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\delta}(\mathbf{R}_{n''})\phi_{\delta\alpha}(\mathbf{R}_{n'}-\mathbf{R}_{n''})\\ &\left.+\sum_n\sum_{n'}\sum_{n''}\phi_{\alpha\beta}(\mathbf{R}_n)\phi_{\beta\gamma}(\mathbf{R}_{n'})\phi_{\gamma\delta}(\mathbf{R}_{n''})\phi_{\delta\alpha}(\mathbf{R}_n-\mathbf{R}_{n'}-\mathbf{R}_{n''})\right]\ .\end{aligned} \tag{3.9}$$

The quantities $\mu_4, \mu_6, \ldots$ will below be called the *reduced moment.*

B. Resummation of the partial series

In Eq. (3.8) the moment M_{2k} is a polynomial of ω_p^2 with coefficients including the reduced moment, whose order becomes higher with decreasing power of ω_p^2. Here the term of the highest power of ω_p^2 is the most important and the subsequent terms become less important with decreasing power of ω_p^2, since ω_p^2 is very large.

The moment expansion (2.7) consists of the partial series, each for a particular reduced moment apart from the most important one. In summing up each partial series we note

$$\begin{aligned}M_{2k}={}&\left[\frac{\omega_p^2}{3}\right]^k+\binom{k}{2}\left[\frac{\omega_p^2}{3}\right]^{k-2}\mu_4\\ &+\binom{k}{3}\left[\frac{\omega_p^2}{3}\right]^{k-3}\mu_6+\cdots\ .\end{aligned} \tag{3.10}$$

Substituting Eq. (3.10) into Eq. (2.7) we get

$$(Nk_BT)^{-1}F_{hq}=3f_0(t)+3\sum_{l\geq 2}\left[\frac{3}{\omega_p^2}\right]^l\mu_{2l}f_{2l}(t)\ , \tag{3.11}$$

where f_{2l} is given by

$$f_{2l}(t)=\sum_{k=l}^{\infty}\binom{k}{l}a_{2k}(2t)^{2k} \tag{3.12}$$

as a function of our important parameter t defined by

$$t=\frac{\beta\hbar\omega_p}{2\sqrt{3}}\ . \tag{3.13}$$

Let us consider the series (3.12). For $l=0$ we have simply

$$f_0=\ln\left[\frac{\sinh t}{t}\right] \tag{3.14}$$

by recalling Eqs. (2.5) and (2.7) with Eq. (2.8). In the evaluation of f_{2l} for $l\geq 2$ we utilize an integral representation for the binomial coefficient

$$\left[\begin{matrix}k\\ l\end{matrix}\right]=\frac{1}{2\pi i}\oint\frac{(1+z)^k}{z^{l+1}}dz\ , \tag{3.15}$$

where the contour is taken to be a circle of radius $|z|<1$, with its center at the origin. Substituting Eq. (3.15) into Eq. (3.12) we get

$$f_{2l}=\frac{1}{2\pi i}\oint\ln\left[\frac{\sinh(t\sqrt{1+z})}{t\sqrt{1+z}}\right]\frac{dz}{z^{l+1}}\ . \tag{3.16}$$

Thus

$$f_{2l}=\frac{1}{l!}\left[\frac{\partial^l}{\partial z^l}\ln\left[\frac{\sinh(t\sqrt{1+z}\,)}{t\sqrt{1+z}}\right]\right]_{z=0}\ , \tag{3.17}$$

which gives us the following:

$$\begin{aligned} f_4&=\tfrac{1}{4}-\frac{t}{8}\coth t-\frac{t^2}{8}\mathrm{csch}^2 t\ ,\\ f_6&=-\tfrac{1}{6}+\frac{t}{16}\coth t+\frac{t^2}{16}\mathrm{csch}^2 t\\ &\quad+\frac{t^3}{24}\mathrm{csch}^2 t\coth t\ ,\\ f_8&=\tfrac{1}{8}-\frac{5t}{128}(\coth t+t\,\mathrm{csch}^2 t)-\frac{t^3}{32}\mathrm{csch}^2 t\coth t\\ &\quad-\frac{t^4}{192}\mathrm{csch}^2 t\,(2\coth^2 t+\mathrm{csch}^2 t)\ . \end{aligned} \tag{3.18}$$

The functions f_{2l}'s are plotted in Fig. 1. For large t these functions are linear in t,

$$f_4\cong-\frac{t}{8},\quad f_6\cong\frac{t}{16},\quad f_8\cong-\frac{5t}{128}\ . \tag{3.19}$$

Owing to the resummation our expansion series works much more effectively than the moment expansion. The latter expansion is no longer valid in the low-temperature region where $\beta\hbar\omega_p \gtrsim 2\pi$. On the other hand, the present expansion, Eq. (3.11), does not break down at low temperature, as manifested in Eq. (3.19) for large $\beta\hbar\omega_p$.

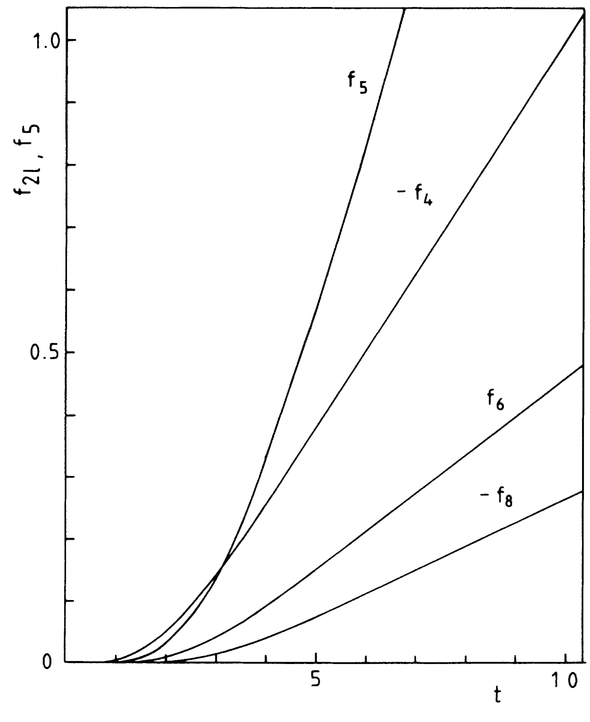

FIG. 1. Curves for f_{2l} and f_5 as functions of t. The functions $f_{2l}(t)$ and $f_5(t)$ are defined in the text.

IV. GENERALIZATION

A. Generalized expression for the reduced moments

For the quantum correction in the system of a harmonic Coulomb lattice the important quantities are the reduced moments, which are $\mu_4(\{\mathbf{R}_n\})$, $\mu_6(\{\mathbf{R}_n\}),\ldots$ as functions of $\mathbf{R}_1,\mathbf{R}_2,\ldots$, where $\mathbf{R}_i$ denotes the position vector of the ith particle relative to the 0th one at origin $\mathbf{R}_0=\mathbf{0}$ in the rigid lattice. We want to generalize our result to the liquid states as well, by replacing $\mu_4(\{\mathbf{R}_n\})$, $\mu_6(\{\mathbf{R}_n\}),\ldots$, respectively, by the averages $\langle\mu_4(\{\mathbf{r}_{i0}\})\rangle$, $\langle\mu_6(\{\mathbf{r}_{i0}\})\rangle\ldots$ of the corresponding quantities, where $\mathbf{r}_{i0}\equiv\mathbf{r}_i-\mathbf{r}_0$ denotes the position vector of the ith particle relative to the 0th one at $\mathbf{r}_0$. Here the average is taken over a canonical ensemble for the classical system such that

$$\langle A\rangle=\frac{1}{\Omega}\int\cdots\int Ae^{-\beta U}d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_N \tag{4.1}$$

with U denoting the potential energy of the system and with Ω the configurational part of the partition function.

The generalization above implies that the average value is different for different phases, whereas the quantities to be averaged must be independent of the phases as it is the case in the WK expansion. In proving the generalization we shall examine modification of the reduced-moment expansion in the anharmonic lattice. The modification will be shown to occur with the reduced moments averaged over the distribution of particles, as mentioned before. We note here that the resultant reduced moments are expressed in terms of the average of products of the derivative of interparticle forces which depend only on the relative position vectors of interacting particles. Accordingly these reduced moments depend upon phases of the system only through the average over the configuration of the particles. Therefore the generalized expansion must be valid in the liquid phase, because the liquid is different from the solid only by the absence of long-range order of particle density as far as the equilibrium properties are concerned.

The effect of the anharmonic terms also brings us additional terms to the reduced-moment expansion. With these terms taken into account our generalized expansion is in agreement with the WK expansion when expanded in power series of $\beta\hbar$. This agreement shows that the general expansion brought by our heuristic method should be correct.

Our expansion is basically a low-density approximation, where the Madelung energy or its equivalent in the liquid is assumed to be most dominant and its quantum corrections are taken into account successively. However, the mentioned nature of our expansion is appropriate to the study of melting of the Wigner crystal which occurs at sufficiently low density of particles.

Let us now consider the primary anharmonic contributions to the free energy. The first contribution is the diagonal part of the quartic terms in particle displacements $\mathbf{u}_i$. This term is given by[15]

$$F_4=\frac{\hbar^2}{32Nm^2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\frac{V(\mathbf{q},j;\mathbf{q}'j')}{\omega_j(\mathbf{q})\omega_{j'}(\mathbf{q}')}(2n_{\mathbf{q}j}+1)(2n_{\mathbf{q}'j'}+1)\ , \tag{4.2}$$

with

$$\begin{aligned}V(\mathbf{q},j;\mathbf{q}',j')=\sum_n e_\alpha(\mathbf{q},j)e_\beta(-\mathbf{q},j)e_\gamma(\mathbf{q}',j')e_\delta(-\mathbf{q}',j')\\ \times(2-2e^{i\mathbf{q}\cdot\mathbf{R}_n}-2e^{i\mathbf{q}'\cdot\mathbf{R}_n}+e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{R}_n}\\ +e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}_n})\phi_{\alpha\beta\gamma\delta}(\mathbf{R}_n)\ ,\end{aligned} \tag{4.3}$$

where $n_{\mathbf{q}j}$ is the occupation number of phonons in the normal mode $(\mathbf{q}\,j)$ and $\phi_{\alpha\beta\gamma\delta}(\mathbf{R})=\nabla_\alpha\nabla_\beta\nabla_\gamma\nabla_\delta(e^2/R)$.

In Eq. (4.2) we expand $(2n_1+1)=\coth(\beta\hbar\omega_1/2)$ with the use of Eq. (2.10) to get

$$\begin{aligned}\frac{1}{\omega_1\omega_2}\coth\left[\frac{\beta\hbar\omega_1}{2}\right]\coth\left[\frac{\beta\hbar\omega_2}{2}\right]\\ =\left[\frac{2}{\beta\hbar\omega_1\omega_2}\right]^2A_1(\omega_1,\omega_2)+(4\beta\hbar)^2A_2(\omega_1,\omega_2)\ ,\end{aligned} \tag{4.4}$$

where we put

$$\begin{aligned}A_1(\omega_1,\omega_2)=1+2a_2(\beta\hbar)^2(\omega_1^2+\omega_2^2)\\ +4a_4(\beta\hbar)^4(\omega_1^4+\omega_2^4)\\ +6a_6(\beta\hbar)^6(\omega_1^6+\omega_2^6)+\cdots\ ,\end{aligned} \tag{4.5}$$

$$A_2(\omega_1,\omega_2)=a_2^2+2a_2a_4(\beta\hbar)^2(\omega_1^2+\omega_2^2)+\cdots\ . \tag{4.6}$$

In Eq. (4.4) we divide the expanded terms into two parts: the singular part and the regular one, in ω_1 and ω_2. With the substitution of Eq. (4.6) into Eq. (4.2) we obtain the primary term of F_4 as

$$F_{4c}=\frac{1}{8Nm^2\beta^2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\frac{V(\mathbf{q},j;\mathbf{q}',j')}{[\omega_j(\mathbf{q})\omega_{j'}(\mathbf{q}')]^2}\ , \tag{4.7}$$

which is an anharmonic contribution for the classical lattice.

The remaining terms in F_4 are the quantum correction, and will be denoted by F_{4q}. We divide F_{4q} as

$$F_{4q}=F_{4q}^{(1)}+F_{4q}^{(2)} \tag{4.8}$$

in accordance with Eq. (4.4), where $F_{4q}^{(1)}$ is the free-energy contribution coming from $A_1(\omega_1,\omega_2)$ and $F_{4q}^{(2)}$ from $A_2(\omega_1,\omega_2)$. We shall consider $F_{4q}^{(1)}$ below. In dealing with $F_{4q}^{(1)}$ we utilize the following identities:

$$\begin{aligned}D_{\alpha\beta}(\mathbf{q})=\sum_j e_\alpha(\mathbf{q},j)\omega_j^2(\mathbf{q})e_\beta(\mathbf{q},j)\ ,\\ D_{\alpha\beta}(\mathbf{q})D_{\beta\gamma}(\mathbf{q})=\sum_j e_\alpha(\mathbf{q},j)\omega_j^4(\mathbf{q})e_\gamma(\mathbf{q},j),\ \ldots\ ,\end{aligned} \tag{4.9}$$

assuming $e_\alpha(-\mathbf{q},j)=e_\alpha(\mathbf{q},j)$. These identities can be derived from Eq. (3.1). We also utilize

$$\langle u_{\alpha i}u_{\beta k}\rangle_h=\frac{1}{N\beta m}\sum_{\mathbf{q}j}\frac{e_\alpha(\mathbf{q},j)e_\beta(\mathbf{q},j)}{\omega_j^2(\mathbf{q})}e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_k)}\ , \tag{4.10}$$

which implies the average of the product of displacements in the classical harmonic system, according to Eq. (4.1). In applying Eq. (4.10) we shall use the following abbreviation:

$$\Lambda_{nn'}^{\alpha\beta}=\langle(u_{\alpha n}-u_{\alpha 0})(u_{\beta n'}-u_{\beta 0})\rangle_h\ . \tag{4.11}$$

Then it follows that

$$(3Nk_BT)^{-1}F_{4q}^{(1)}=a_4M_4'(\beta\hbar)^4+a_6M_6'(\beta\hbar)^6 \tag{4.12}$$

in accordance with Eq. (2.7), where we set

$$M_4'=(3m^2)^{-1}\sum_n\Lambda_{nn}^{\gamma\delta}\phi_{\alpha\beta\gamma\delta}(\mathbf{R}_n)\left[\sum_{n'}\phi_{\beta\alpha}(\mathbf{R}_{n'})+\phi_{\beta\alpha}(\mathbf{R}_n)\right]\ , \tag{4.13}$$

$$\begin{aligned}M_6'=\omega_p^2M_4'+(2m^3)^{-1}\sum_n\Lambda_{nn}^{\gamma\delta}\phi_{\alpha\beta\gamma\delta}(\mathbf{R}_n)\left[\sum_{n'n''}\phi_{\alpha\kappa}(\mathbf{R}_{n'})\phi_{\kappa\beta}(\mathbf{R}_{n''})+2\phi_{\alpha\kappa}(\mathbf{R}_n)\sum_{n'}\phi_{\kappa\beta}(\mathbf{R}_{n'})\right.\\ \left.+\sum_{n'}\phi_{\alpha\kappa}(\mathbf{R}_{n'})[\phi_{\kappa\beta}(\mathbf{R}_{n'})-\phi_{\kappa\beta}(\mathbf{R}_n-\mathbf{R}_{n'})]\right]\ .\end{aligned} \tag{4.14}$$

The next contribution comes from the second-order perturbation of the cubic terms. It can be written as[15]

$$F_3=-\frac{\hbar^2}{48Nm^3}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{q}'',j''}\frac{|V(\mathbf{q},j;\mathbf{q}',j';\mathbf{q}'',j'')|^2}{\omega_j(\mathbf{q})\omega_{j'}(\mathbf{q}')\omega_{j''}(\mathbf{q}'')}h[\omega_j(\mathbf{q}),\omega_{j'}(\mathbf{q}'),\omega_{j''}(\mathbf{q}'')]\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'')\ . \tag{4.15}$$

In the above expression we set

$$V(\mathbf{q},j;\mathbf{q}',j';\mathbf{q}'',j'')=\sum_n e_\alpha(\mathbf{q},j)e_\beta(\mathbf{q}',j')e_\gamma(\mathbf{q}'',j'')(e^{i\mathbf{q}\cdot\mathbf{R}_n}+e^{i\mathbf{q}'\cdot\mathbf{R}_n}+e^{i\mathbf{q}''\cdot\mathbf{R}_n})\phi_{\alpha\beta\gamma}(\mathbf{R}_n) \tag{4.16}$$

with $\phi_{\alpha\beta\gamma}(\mathbf{R})$ defined similarly as before, and

$$h(\omega_1,\omega_2,\omega_3)$$
$$=\tfrac{1}{4}\operatorname{csch}\left[\frac{\beta\hbar\omega_1}{2}\right]\operatorname{csch}\left[\frac{\beta\hbar\omega_2}{2}\right]\operatorname{csch}\left[\frac{\beta\hbar\omega_3}{2}\right]$$
$$\times\left[\frac{\sinh[\beta\hbar(\omega_1+\omega_2+\omega_3)/2]}{\omega_1+\omega_2+\omega_3}+\sum_{\text{cycl}}\frac{\sinh[\beta\hbar(-\omega_1+\omega_2+\omega_3)/2]}{-\omega_1+\omega_2+\omega_3}\right], \tag{4.17}$$

where in the second term inside square brackets the sum is taken over terms obtained by cyclic permutations in ω_1, ω_2, and ω_3.[16] Also,

$$\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'')=\begin{cases}1 & \text{if } \mathbf{q}+\mathbf{q}'+\mathbf{q}''=0,\mathbf{G}\\ 0 & \text{otherwise}\end{cases} \tag{4.18}$$

for any reciprocal lattice vector **G**.

We expand $h(\omega_1,\omega_2,\omega_3)$ similarly as before,

$$\frac{h(\omega_1,\omega_2,\omega_3)}{\omega_1\omega_2\omega_3}=\left[\frac{2}{\beta\hbar}\right]^2\frac{1}{\omega_1^2\omega_2^2\omega_3^2}B_1(\omega_1,\omega_2,\omega_3)$$
$$+4(\beta\hbar)^4B_2(\omega_1,\omega_2,\omega_3), \tag{4.19}$$

where

$$B_1(\omega_1,\omega_2,\omega_3)=1-4a_4(\beta\hbar)^4\sum_{\text{cycl}}\omega_1^2\omega_2^2$$
$$-6a_6(\beta\hbar)^6\sum_{\text{cycl}}(\omega_1^4\omega_2^2+\omega_1^2\omega_2^4)+\cdots, \tag{4.20}$$

$$B_2(\omega_1,\omega_2,\omega_3)=6a_6+\cdots. \tag{4.21}$$

The primary term is the free energy of the classical system

$$F_{3c}=-\frac{1}{12Nm^3\beta^2}\sum_{\mathbf{q},j;\ldots;\mathbf{q}'',j''}\frac{|V(\mathbf{q},j;\mathbf{q}',j';\mathbf{q}'',j'')|^2}{[\omega_j(\mathbf{q})\omega_{j'}(\mathbf{q}')\omega_{j''}(\mathbf{q}'')]^2}$$
$$\times\Delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}''). \tag{4.22}$$

We divide the quantum correction F_{3q} as

$$F_{3q}=F_{3q}^{(1)}+F_{3q}^{(2)} \tag{4.23}$$

in accordance with the decomposition in Eq. (4.19).

Similarly as before we obtain $F_{3q}^{(1)}$ as follows:

$$(3Nk_BT)^{-1}F_{3q}^{(1)}=a_4M_4''(\beta\hbar)^4+a_6M_6''(\beta\hbar)^6, \tag{4.24}$$

where M_4'' and M_6'' are given respectively by

$$M_4''=(3m^2)^{-1}\left[\sum_{n,n'}\phi_{\alpha\beta\gamma}(\mathbf{R}_n)\Lambda_{nn'}^{\gamma\delta}\phi_{\delta\beta\alpha}(\mathbf{R}_{n'})+\sum_{n}\phi_{\alpha\beta\gamma}(\mathbf{R}_n)\Lambda_{nn}^{\gamma\delta}\phi_{\delta\beta\alpha}(\mathbf{R}_n)\right], \tag{4.25}$$

$$M_6''=\omega_p^2M_4''+m^{-3}\left[\sum_{n,n',n''}\phi_{\alpha\beta\gamma}(\mathbf{R}_n)\Lambda_{nn'}^{\gamma\delta}\phi_{\delta\beta\kappa}(\mathbf{R}_{n'})\phi_{\kappa\alpha}(\mathbf{R}_{n''})+\sum_{n,n'}\phi_{\alpha\beta\gamma}(\mathbf{R}_n)\Lambda_{nn}^{\gamma\delta}\phi_{\delta\beta\kappa}(\mathbf{R}_n)\phi_{\kappa\alpha}(\mathbf{R}_{n'})\right.$$
$$\left.+\sum_{n,n'}\phi_{\alpha\beta\gamma}(\mathbf{R}_n)\Lambda_{nn'}^{\gamma\delta}\phi_{\delta\beta\kappa}(\mathbf{R}_{n'})[2\phi_{\kappa\alpha}(\mathbf{R}_{n'})-\phi_{\kappa\alpha}(\mathbf{R}_n-\mathbf{R}_{n'})]\right]. \tag{4.26}$$

Now we substitute $\mathbf{R}_n+(\mathbf{u}_n-\mathbf{u}_0)$ for $\mathbf{R}_n$ in M_4, Eq. (3.8) with (3.9), and then average over the particle distribution. If we expand the substituted expression in powers of displacements, the quadratic parts of it are identified with $M_4'+M_4''$. Similarly the terms M_6' and M_6'' are absorbed in M_6 of Eq. (3.8) with the same substitution.

Thus we conclude that the quantum correction including $F_q^{(1)}=F_{4q}^{(1)}+F_{3q}^{(1)}+\cdots$ should generally be of the form

$$F_{hq}+F_q^{(1)}=3Nk_BT\sum_{k\geqq 1}a_{2k}M_{2k}(\beta\hbar)^{2k}, \tag{4.27}$$

with M_{2k}'s still given by Eq. (3.8) but now with the generalization of the reduced moments,

$$\mu_4=\frac{1}{3m^2}\left[\sum_i\sum_{i'}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\alpha}(\mathbf{r}_{i'0})\rangle+\sum_i\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\alpha}(\mathbf{r}_{i0})\rangle\right],$$

$$\mu_6=\frac{1}{3m^3}\left[\sum_i\sum_{i'}\sum_{i''}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\alpha}(\mathbf{r}_{i''0})\rangle+3\sum_i\sum_{i'}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\alpha}(\mathbf{r}_{i'0})\rangle-\sum_i\sum_{i'}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\alpha}(\mathbf{r}_{ii'})\rangle\right],$$

$$\mu_8=\frac{1}{3m^4}\left[\sum_i\sum_{i'}\sum_{i''}\sum_{i'''}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\delta}(\mathbf{r}_{i''0})\phi_{\delta\alpha}(\mathbf{r}_{i'''0})\rangle+4\sum_i\sum_{i'}\sum_{i''}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\delta}(\mathbf{r}_{i''0})\phi_{\delta\alpha}(\mathbf{r}_{i''0})\rangle\right.$$
$$+2\sum_i\sum_{i'}\sum_{i''}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\delta}(\mathbf{r}_{i''0})\phi_{\delta\alpha}(\mathbf{r}_{i'0})\rangle-4\sum_i\sum_{i'}\sum_{i''}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\delta}(\mathbf{r}_{i''0})\phi_{\delta\alpha}(\mathbf{r}_{i'i''})\rangle$$
$$\left.+\sum_i\sum_{i'}\sum_{i''}\langle\phi_{\alpha\beta}(\mathbf{r}_{i0})\phi_{\beta\gamma}(\mathbf{r}_{i'0})\phi_{\gamma\delta}(\mathbf{r}_{i''0})\phi_{\delta\alpha}(\mathbf{r}_{ii'}-\mathbf{r}_{i''0})\rangle\right]. \tag{4.28}$$

Here the average in the harmonic lattice may be replaced by that in the full classical system. With the reduced moments defined above we still have Eq. (3.11) for $F_{hq}+F_q^{(1)}$ which replaces F_{hq}.

B. Additional quantum corrections

In the foregoing analysis we left aside the free-energy contributions $F_{4q}^{(2)}$ and $F_{3q}^{(2)}$. These contributions come respectively from $A_2(\omega_1,\omega_2)$ and $B_2(\omega_1,\omega_2,\omega_3)$ which are given respectively by Eqs. (4.6) and (4.21). The neglected terms bring us corrections to the reduced-moment expansion which is related basically to the harmonic lattice.

Let us first consider $F_{4q}^{(2)}$. Since $A_2(\omega_1,\omega_2)$ is an integral function of ω_1 and ω_2, we put

$$(4\beta\hbar)^2 A_2(\omega,\omega')=\sum_{l,l'\geq 0} c_{ll'}\omega^{2l}(\omega')^{2l'} . \tag{4.29}$$

By Eq. (4.4) we obtain the coefficient $c_{ll'}$ as

$$c_{ll'}=\frac{1}{(2\pi i)^2}\oint d\omega \oint d\omega' \frac{\coth(\beta\hbar\omega/2)\coth(\beta\hbar\omega'/2)}{\omega^{2l+2}(\omega')^{2l'+2}} \tag{4.30}$$

with contour encircling the origin in the complex ω plane.

We substitute Eqs. (4.3) and (4.29) into Eq. (4.2) and then utilize Eq. (4.9) with the following result:

$$F_{4q}^{(2)}=\frac{\hbar^2}{32Nm^2}\sum_{l,l'\geq 0} c_{ll'}\sum_{n}{}'\sum_{\mathbf{q},\mathbf{q}'}(2-2e^{i\mathbf{q}\cdot\mathbf{R}_n}-2e^{i\mathbf{q}'\cdot\mathbf{R}_n}+e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{R}_n}+e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}_n})\phi_{\alpha\beta\gamma\delta}(\mathbf{R}_n)[D^{l}(\mathbf{q})]_{\alpha\beta}[D^{l'}(\mathbf{q}')]_{\gamma\delta} . \tag{4.31}$$

We expand $[D^{l}(\mathbf{q})]_{\alpha\beta}$ in a power series of $(3/\omega_p^2)$ by the substitution of Eq. (3.3), where the primary term $(\omega_p^2/3)^l\delta_{\alpha\beta}$ vanishes identically because of the identity $\phi_{\alpha\alpha\gamma\delta}(\mathbf{R}_n)=0$. Then the primary contribution to $F_{4q}^{(2)}$ proves to be of the higher order.

The other contribution $F_{3q}^{(2)}$ can be evaluated similarly. In the evaluation, we need to modify Eq. (4.16), referred to the lattice of inversion symmetry, in order to ensure relevancy of the resultant expression to the noncrystalline state. It is proved that the above modification corresponds to adding -1 to the terms inside parentheses on the right-hand side of Eq. (4.16). Thus we get

$$F_{3q}^{(2)}=-\frac{9N\hbar}{16}\left[\frac{3}{\omega_p^2}\right]^2 \mu_5 t^{-1} f_5(t) \tag{4.32}$$

as a primary term, where a "moment" μ_5 is given by

$$\mu_5=\frac{\hbar}{(3m)^3}\left[\sum_{i,i'}\langle\phi_{\alpha\beta\gamma}(\mathbf{r}_{i0})\phi_{\alpha\beta\gamma}(\mathbf{r}_{i'0})\rangle+3\sum_{i}\langle\phi_{\alpha\beta\gamma}(\mathbf{r}_{i0})\phi_{\alpha\beta\gamma}(\mathbf{r}_{i0})\rangle\right] , \tag{4.33}$$

with the average taken in the rigid lattice. And we put

$$f_5(t)=t\left[\tfrac{1}{3}\coth^2 t-\frac{3}{2t}\coth t+\frac{2}{t^2}-\tfrac{5}{6}\operatorname{csch}^2 t\right] , \tag{4.34}$$

which is shown in Fig. 1. The above expression follows from

$$\begin{aligned} t^{-1}f_5(t)&=\sum_{l,l',l''\geq 0} c_{ll'l''}\left[\frac{\omega_p^2}{3}\right]^{l+l'+l''+2} \\ &=\left[\frac{\omega_p^2}{3}\right]^2\frac{1}{(2\pi i)^3}\oint d\omega_1\oint d\omega_2\oint d\omega_3\frac{h(\omega_1,\omega_2,\omega_3)}{[\omega_1^2-(\omega_p^2/3)][\omega_2^2-(\omega_p^2/3)][\omega_3^2-(\omega_p^2/3)]} , \end{aligned} \tag{4.35}$$

where $c_{ll'l''}$ is defined by

$$4(\beta\hbar)^4 B_2(\omega_1,\omega_2,\omega_3)=\sum_{l,l',l''\geq 0} c_{ll'l''}\omega_1^{2l}\omega_2^{2l'}\omega_3^{2l''} . \tag{4.36}$$

The quantity μ_5, Eq. (4.33), is dimensionally the fifth moment and will hereafter be so called, where the rigid-lattice average will be replaced by the average over the particle distribution. This is a reasonable procedure in view of the generalization made before in Sec. IV A.

Another contribution ranked with the sixth moment comes from the second-order perturbation of the quartic terms. However, this contribution has been shown to be very small, and may be omitted.

C. Comparison with the WK expansion

We compare our expansion with the WK, which is a power series of the Planck constant $2\pi\hbar$. This series is known up to the term of $(2\pi\hbar)^6$ for the system of general force.[12] The series adapted to the Coulomb system can be identified as Eq. (3.11) with μ_{2l} given by Eq. (4.28), with additional contribution $F_{3q}^{(2)}$ given by Eq. (4.32). In the identification we use the following expansion for small t:

$$\begin{aligned} &f_0\cong\frac{t^2}{6}-\frac{t^4}{180}+\frac{t^6}{2835} , \\ &f_4\cong-\frac{t^4}{180}+\frac{t^6}{945} ,\quad f_6\cong\frac{t^6}{2835} , \end{aligned} \tag{4.37}$$

and

$$f_5 \cong \frac{6t^5}{2835} \ . \tag{4.38}$$

Note that the above identification is independent of the phases.

V. EVALUATION OF THE REDUCED MOMENTS

We shall use the parameter r_s which is defined by $4\pi N(r_s a_0)^3/3=1$ with a_0 the Bohr radius, and measure the distance r in units of $r_s a_0$. Define the dimensionless moment $\tilde{\mu}_{2l}$ by $m^l \mu_{2l}$ with substitution of

$$\tilde{\phi}_{\alpha\beta}(\mathbf{r})=\nabla_\alpha \nabla_\beta \frac{1}{r} \tag{5.1}$$

for $\phi_{\alpha\beta}$, in Eq. (4.28). Then Eq. (3.11) can be written as

$$(Nk_B T)^{-1}\Delta F=3\left[f_0(t)+\sum_{l\geqq 2}\tilde{\mu}_{2l}f_{2l}(t)\right] \tag{5.2}$$

with $t=\Gamma/(2\sqrt{r_s})$, where Γ is a current parameter

$$\Gamma=\frac{\beta e^2}{r_s a_0} \ . \tag{5.3}$$

The additional correction, Eq. (4.32), can similarly be written as

$$(Nk_B T)^{-1}F_{3q}^{(2)}=-\frac{9}{8}\frac{1}{\sqrt{r_s}}f_5\tilde{\mu}_5 \tag{5.4}$$

with μ_5 defined similarly as above ($m=\hbar=1$).

Below we shall evaluate the reduced moment $\tilde{\mu}_{2l}$ and the similar moment $\tilde{\mu}_5$ separately for solid and liquid states.

A. Reduced moments in solid state

In the body-centered cubic (bcc), which is the lowest-energy structure of the Coulomb lattices, numerical values of $\tilde{\mu}_{2l}$ can easily be obtained from CHM's moments for the harmonic lattice.[13] However, small error in the moments does produce considerable effects on the estimation of reduced moments.

In the rigid lattice, the expressions for the reduced moments become simpler, since the terms including $\sum_i \phi_{\alpha\beta}(\mathbf{R}_{i0})$ as a factor vanish identically due to the cubic symmetry of lattices. It is also the case for the other moment μ_5. The calculated results are shown in Table II for the rigid-lattice values of our reduced moments. We note that CHM's values,[13] $\tilde{\mu}_6=0.198\,56$ and $\tilde{\mu}_8=0.1347$, are considerably different from the tabulated ones due to their insufficient lattice summations.[17]

At zero temperature Eq. (5.2) gives us the zero-point energy

$$\frac{\Delta E}{N}=\frac{3}{r_s^{3/2}}\left(1-\tfrac{1}{8}\tilde{\mu}_4+\tfrac{1}{16}\tilde{\mu}_6-\tfrac{5}{125}\tilde{\mu}_8\right)\ \mathrm{Ry}\ , \tag{5.5}$$

which is estimated as $2.633r_s^{-3/2}$, in comparison with $2.657r_s^{-3/2}$, an accurate value based on the direct sum over 32 768 points in the first Brillouin zone. Equation (5.4) contributes to the same energy by

$$\frac{E_{3q}^{(2)}}{N}\cong-\frac{3}{8}\frac{1}{r_s^2}\tilde{\mu}_5\ \mathrm{Ry}\ , \tag{5.6}$$

which is estimated to be $-0.4243r_s^{-2}$. For comparison we note $-1.10r_s^{-2}$ for the total zero-point-energy contributions from Eq. (4.15), according to Kugler.[18]

TABLE II. Rigid-lattice values of the reduced moments (bcc).

$\tilde{\mu}_4$	$\tilde{\mu}_6$	$\tilde{\mu}_8$	$\tilde{\mu}_5$
0.827 702	0.550 45	1.3673	1.131

At finite temperature we first consider μ_4 in Eq. (4.28). The first term of μ_4 is divided into two parts. The part with $i\neq i'$ needs the three-particle distribution function for estimation, while the part with $i=i'$ can be estimated simply with the use of the two-particle one. It is noted that these parts cancel each other for the rigid lattice, as mentioned before. However, a small remainder is left owing to the distribution of particles around lattice point. It is also the case for the first and second term in μ_6, and for the similar term in μ_5.

We shall evaluate the distribution function in the harmonic approximation, following Kugler.[18] Consider a 6×6 correlation matrix

$$D=\begin{bmatrix}\lambda_0 I & \lambda_{ik}\\ \lambda_{ki} & \lambda_0 I\end{bmatrix} \ . \tag{5.7}$$

Here λ_{ik} is a 3×3 matrix whose $\alpha\beta$ component $\lambda_{\alpha i,\beta k}\equiv\langle u_{\alpha i}u_{\beta k}\rangle_h$ is given by Eq. (4.10), and $\lambda_0 I$ is a unit matrix multiplied by $\lambda_0=\langle u_{\alpha i}u_{\alpha i}\rangle/3$. [Note that the factor $(N\beta m)^{-1}$ in Eq. (4.10) changes to $(1/3N\Gamma)$ in our scaled coordinate and for $\omega_j(\mathbf{q})$ measured in units of ω_p.] The probability distribution of $(\mathbf{u}_i,\mathbf{u}_k)$ must be equal to the product of the Gaussian functions in a six-dimensional coordinate system where D reduces to a diagonal matrix. Thus we get for the two-particle distribution function

$$g_2(\mathbf{u}_i,\mathbf{u}_k)=[(2\pi)^6\det D]^{-1/2} \times\exp\left[-\tfrac{1}{2}\sum_{j,j'=i,k}u_{\alpha j}(D^{-1})_{\alpha j,\beta j'}u_{\beta j'}\right] \tag{5.8}$$

with D^{-1} implying the inverse matrix to D. Generalization of the above expression to the higher-order distribution function is straightforward and may be omitted.

By the use of the above distribution function, we estimate the temperature-dependent part by confining ourselves to the nearest neighboring pairs. The results thus obtained are shown in Fig. 2 for $\tilde{\mu}_4$, $\tilde{\mu}_6$, and $\tilde{\mu}_5$ in comparison with the rigid-lattice values. These reduced moments increase with increasing temperature. However, the temperature dependence is rather small.

B. Reduced moments in liquid state

The reduced moments, Eq. (4.28), can be treated as above. The moment $\tilde{\mu}_4$ consists of two kinds of terms, where the one is expressed in terms of the three-particle distribution function $g_3(1,2,3)$ and the other in terms of the two-particle one $g_2(1,2)\equiv g(r)$ with r denoting the distance between two particles. After angular average we obtain

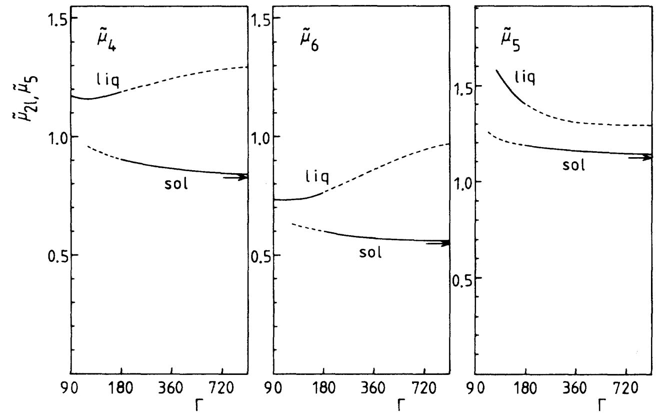

FIG. 2. Reduced moments $\tilde{\mu}_{2l}$ and $\tilde{\mu}_5$ as functions of Γ for solid and liquid phases. The dashed lines show the extrapolated curve. The rigid lattice values for bcc are indicated by arrows.

$$\tilde{\mu}_4=3(4I_2[4]+3I_3[1,1]) \tag{5.9}$$

with the integrals defined by

$$I_2[k]=\int_0^\infty \frac{dr}{r^k}g(r) , \tag{5.10}$$

$$I_3[k,l] =\tfrac{1}{2}\int_0^\infty dr_1 \int_0^\infty dr_2 \frac{1}{r_1^k r_2^l}\int_{-1}^1 dx(3x^2-1) \times g_3(r_1,r_2,x) , \tag{5.11}$$

where $x=\cos\theta$ with θ denoting the angle $\mathbf{r}_2$ makes with $\mathbf{r}_1$. The above result is by Hansen and Vieillefosse.[9]

For $\tilde{\mu}_6$ we similarly evaluate from Eq. (4.28),

$$\tilde{\mu}_6=3(8I_2[7]+18I_3[1,4]-3J_3^{(1)}+9J_4^{(1)}) . \tag{5.12}$$

The above expression includes the new integrals

$$J_3^{(1)}=\tfrac{1}{2}\int_0^\infty dr_1 \int_0^\infty dr_2 \frac{1}{r_1 r_2}\int_{-1}^1 dx \frac{2-3(x^2+u^2+v^2)-9uvx}{(r_1^2+r_2^2-2r_1r_2x)^{3/2}} g_3(r_1,r_2,x) , \tag{5.13}$$

$$J_4^{(1)}=\frac{1}{8\pi}\int_0^\infty dr_1 \int_0^\infty dr_2 \int_0^\infty dr_3 \frac{1}{r_1r_2r_3}\int_{-1}^1 dx_1 \int_{-1}^1 dx_2 \int_0^{2\pi} d\phi[2-3(x_1^2+x_2^2+\gamma^2)+9x_1x_2\gamma] \times g_4(r_1,r_2,r_3,x_1,x_2,\phi) . \tag{5.14}$$

In the first integral $J_3^{(1)}$, by x, u, and v we denote the cosines of the interior angles for a triangle with sides r_1, r_2, and $|\mathbf{r}_1-\mathbf{r}_2|$, respectively. The second integral $J_4^{(1)}$ includes the four-particle distribution function $g_4(1,2,3,4)\equiv g_4(r_1,r_2,r_3,x_1,x_2,\phi)$, where x_1 and x_2 are, respectively, the cosines of the angles $\mathbf{r}_1$ and $\mathbf{r}_2$ make with $\mathbf{r}_3$. In the same integral we also put $\gamma=x_1x_2+[(1-x_1^2)(1-x_2^2)]^{1/2}\cos\phi$.

The evaluation of $\tilde{\mu}_5$ can be done as above,

$$\tilde{\mu}_5=5(8I_2[6]+3J_3[2,2]) \tag{5.15}$$

with a new integral defined by

$$J_3[k,l]=\tfrac{1}{2}\int_0^\infty dr_1 \int_0^\infty dr_2 \frac{1}{r_1^k r_2^l}\int_{-1}^1 dx(5x^3-3x) \times g_3(r_1,r_2,x) . \tag{5.16}$$

No computer-simulation data are available for the higher-order distribution functions than g_2. There exist some methods for obtaining the many-particle distribution functions from the liquid-structure function.[19,20] However, the evaluation becomes formidable particularly for the integral including the four-particle distribution function, because the relevant integral is conditionally convergent (Appendix A). In computation we assume the superposition approximation:

$$g_3(1,2,3)=g(1,2)g(2,3)g(3,1) , \tag{5.17}$$

$$g_4(1,2,3,4)=g(1,2)g(2,3)g(3,4)g(4,1)g(1,3)g(2,4) . \tag{5.18}$$

With these approximations the integrations were performed by the Monte Carlo method, where the pair distribution function $g(r)$ is obtained from the available data for the structure functions,[21] through the Fourier transform. The estimates are given in Table III for our in-

TABLE III. Numerical values of the integrals.

Γ	$I_2[4]$	$I_2[6]$	$I_2[7]$	$I_3[1,1]$	$I_3[1,4]$	$J_3^{(1)}$	$J_3[2,2]$	$J_4^{(1)}$
80	0.1660	0.0552	0.0337	−0.0894	−0.0157	−0.0663	−0.0299	0.0064
120	0.1581	0.0499	0.0296	−0.0810	−0.0134	−0.0642	−0.0298	0.0061
140	0.1559	0.0485	0.0284	−0.0779	−0.0126	−0.0636	−0.0296	0.0061
150	0.1546	0.0477	0.0278	−0.0757	−0.0121	−0.0632	−0.0295	0.0059
160	0.1538	0.0471	0.0274	−0.0742	−0.0118	−0.0630	−0.0294	0.0060
170	0.1528	0.0465	0.0269	−0.0722	−0.0114	−0.0627	−0.0293	0.0060
180	0.1522	0.0461	0.0266	−0.0709	−0.0111	−0.0625	−0.0292	0.0060
∞[a]	0.1380	0.0377	0.0205	−0.0920	−0.0136	−0.0612	−0.0251	0.0091

[a] The rigid lattice values for bcc.

tegrals, at several values of Γ. We also estimated the same integrals by the use of Hansen's distribution function,[6] with results close to the tabulated ones. However, our estimate involves certain systematic errors due to the superposition approximation, which should be more significant for the integrals including g_4 than the others. Accuracy of the approximation is examined in Appendix B using Schofield's identity.[22]

The values of $\tilde{\mu}_4, \tilde{\mu}_6, \ldots$ thus obtained are shown in Fig. 2. The shown curves include extrapolation to the values of Γ higher than $\Gamma_m^{cl} = 178$ at which our classical liquid freezes.[8] In the extrapolation we assume the reduced moments to be of the form $A + B/\Gamma + C/\Gamma^2$ for Γ larger than Γ_m^{cl}, where the constants A, B, and C are chosen so as to fit the assumed form to the values computed for each moment in the region of $\Gamma \leqq \Gamma_m^{cl}$.

VI. MELTING OF THE WIGNER CRYSTAL

We shall now consider the melting of the Wigner crystal. Generally the solid phase is characterized by the order parameters which describe particle density of lattice periodicity. These order parameters vanish in the liquid phase. Thus we have two branches of the free energies, the one for liquid and the other for solid, which cross at the melting point. Such treatment has been done also for the classical Wigner crystal,[23] in fairly good agreement with the simulation results.

Instead of extending the above kind of theory to the quantum Wigner crystal, we utilize the Monte Carlo results consistently for both of the classical free energies and the quantum correction. Let us set

$$F_s = F_s^{cl} + \Delta F_s \ , \tag{6.1}$$

$$F_l = F_l^{cl} + \Delta F_l \ , \tag{6.2}$$

where F_s^{cl} is the classical part of the free energy in solid phase, and ΔF_s the quantum correction. Similar quantities are denoted by F_l^{cl} and ΔF_l for liquid phase.

For the classical part of the free energy the Monte Carlo data are available in Slattery, Doolen, and DeWitt (SDD),[8] whom we follow in our treatment but with some modifications. For the solid phase we use

$$\frac{F_s^{cl}}{Nk_BT} = -0.895\,929\Gamma + \tfrac{9}{2}\ln\Gamma - 1.8856 - \frac{10.9}{\Gamma} - \frac{h}{2\Gamma^2} \tag{6.3}$$

with $h = 1318$. On the right-hand side of the above formula the first three terms are the free energy of the classical harmonic lattice in accord with Pollock and Hansen,[24] who added the anharmonic term proportional to Γ^{-2} to the above three terms. However, the anharmonic corrections to the free energy are given primarily by Eqs. (4.7) and (4.22), which we estimate to be

$$\frac{F_{4c}}{Nk_BT} = \frac{11.51}{\Gamma} \ , \tag{6.4}$$

$$\frac{F_{3c}}{Nk_BT} = -\frac{22.37}{\Gamma} \ . \tag{6.5}$$

These contributions give the fourth term in Eq. (6.3). The internal energy U_s^{cl} is written as

$$\frac{U_s^{cl}}{Nk_BT} = -0.895\,929 + \tfrac{3}{2} + \frac{10.9}{\Gamma} + \frac{h}{\Gamma^2} \ . \tag{6.6}$$

In the second term on the right-hand side, a part $\frac{3}{2}$ is retained of $\frac{9}{2}$ in Eq. (6.3), since we drop out the remainder 3 of which a half stands for the kinetic energy part. The other half has been inserted in Eq. (6.3) for convenience, in accord with SDD. We fit U_s^{cl} to SDD's Monte Carlo data to get the estimate of h.

For the liquid phase SDD have given an interpolation formula covering a wide range of temperatures. On the other hand, our interest is in finding an extrapolation formula applicable to the liquid far below the melting temperature. We assume it to be of the form

$$\frac{F_l^{cl}}{Nk_BT} = a\Gamma + (b+3)\ln\Gamma - \frac{c}{\Gamma} - \frac{d}{2\Gamma^2} + \delta \ . \tag{6.7}$$

The above formula comes from the internal energy

$$\frac{U_l^{cl}}{Nk_BT} = a + b + \frac{c}{\Gamma} + \frac{d}{\Gamma^2} \ , \tag{6.8}$$

in conformity with Eq. (6.6).

In the solid phase we have $b = \frac{3}{2}$, a classical result in the harmonic approximation. For the liquid branch, which is characterized basically by vanishing of order parameters, one must get an amorphous solid at low temperatures.[25] This system is metastable in the sense that it has higher free energy than the solid. However, the motion of particles must still be harmonic in the potential of local minima at low temperatures. Thus classically we should have $b = \frac{3}{2}$ for the amorphous solid, in accordance with Itoh and Ichimaru.[26]

In Eq. (6.8) with the prescribed value of b, the coefficients are determined by least-squares fit to SDD's Monte Carlo data for $N = 1024$ and $\Gamma \geqq 120$,

$$\begin{aligned} &a = -0.892\,54, \quad b = 1.5000 \ , \\ &c = 77.94, \quad d = -5622 \ , \\ &\delta = -2.1963 \ . \end{aligned} \tag{6.9}$$

In the above the last value is a result of fitting our free energy to that of SDD at $\Gamma = 120$.

By adding the quantum correction to the classical free energies, Eqs. (6.3) and (6.7), we get the total free energy F/Nk_BT, respectively, for solid and liquid phases. It is a function of r_s as well as of Γ. The r_s dependence comes from the quantum corrections, Eqs. (5.2) and (5.4). We write them collectively as

$$\begin{aligned} \frac{\Delta F}{Nk_BT} &= 3f_0(t) + 3\tilde{\mu}_4 f_4(t) \\ &\quad - \frac{9}{8}\frac{1}{\sqrt{r_s}}\tilde{\mu}_5 f_5(t) + 3\tilde{\mu}_6 f_6(t) \ , \end{aligned} \tag{6.10}$$

where $f_l(t)$'s are shown in Fig. 1 and $\tilde{\mu}_l$'s in Fig. 2. In the treatment below we shall use the above expression, which has different values for different phases by virtue of the reduced moments $\tilde{\mu}_l$'s.

We first examine accuracy of our free energies for the worst case of zero-temperature limit.[27] For the ground-state energy in the liquid branch, the present extrapolation gives us

$$\frac{E_l}{N}=-\frac{1.7851}{r_s}+\frac{2.694}{r_s^{3/2}}-\frac{0.489}{r_s^2}\ , \tag{6.11}$$

which is compared with Ceperley and Alder's Monte Carlo one[5] in Fig. 3 in the low-density region.[28] We shall compare our E_l with the corresponding result for E_s, the ground-state energy in the solid branch,

$$\frac{E_s}{N}=-\frac{1.7919}{r_s}+\frac{2.793}{r_s^{3/2}}-\frac{0.424}{r_s^2}\ . \tag{6.12}$$

As can be seen in Fig. 3, our ground-state energies are very close to each other for the liquid and solid branches, while both of the energies deviate considerably from the simulation results. By this deviation one might suspect the validity of the present treatment.

However, the mentioned deviation is mainly due to neglect of the next term with a reduced-moment $\tilde{\mu}_8$. If we take it into account, the second term on the right-hand side of Eq. (6.12) for E_s changes to $2.633/r_s^{3/2}$. The resulting ground-state energy is very close to the simulation result, as shown in Fig. 3. In the same stage of the approximation, one would get the liquid ground-state energy in the close vicinity of the solid one. It is very important to recognize that the relevant quantity to the zero-temperature melting is the difference of ground-state energies. Therefore, the mentioned deviation of our sixth-moment results from the simulation ones does not negate the effectiveness of the present formalism. It is emphasized that the energy difference of the liquid and solid phases would be very small unless the system is very far from the melting point. We also emphasize that our result for the liquid branch is most unrelible at zero temperature, in view of our extrapolation.

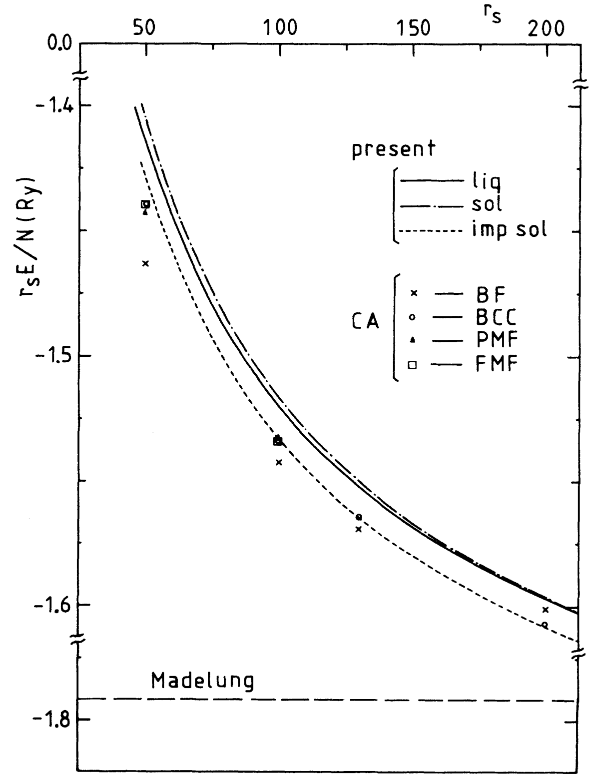

FIG. 3. Ground-state energy as a function of r_s. The solid line shows the ground-state energy, E_l/N, per particle for liquid. The Monte Carlo results of Alder and Ceperley's (Ref. 5) are indicated by ×'s for Bose liquid with spin 0, by Δ and □, respectively, for paramagnetic and ferromagnetic Fermi liquids, and by ○ for solid. The dash-dotted line shows the ground-state energy, E_s/N, for solid, and the dashed line shows the corresponding quantity in the higher approximation with the eighth reduced moment taken into account. The lowest horizontal line indicates the Madelung-energy term.

Our treatment works well when the Madelung energy or its equivalent in the liquid is the most important (Sec. IV). The Madelung energy corresponds to a horizontal line roughly at -1.8 in Fig. 3. The energy correction is surely small in the region of $r_s \gtrsim 100$.

The symmetry effect is more considerable at higher density (Fig. 3) where the present result is less effective. We shall consider the density region of $r_s \gtrsim 100$. At finite temperature the quantum correction is small by itself and less than $\sim 10\%$ of the total free energy. We note that the quantum correction comes mostly from the primary term $f_0(\Gamma/2\sqrt{r_s})$ with small contribution of the remaining terms. However, these remainders are very important in shaping the melting curve from the free-energy difference F_l-F_s, owing to cancellation of the primary term f_0.

In Fig. 4 we show curves for $(F_l-F_s)/Nk_BT$ as a function of Γ for several values of r_s. We note here that the effect of $\tilde{\mu}_6$ works in opposite direction to that of $\tilde{\mu}_4$ and $\tilde{\mu}_5$.

In the classical limit the melting point is located at $\Gamma_m^{\text{cl}}=172$, according to the present treatment. Our value of Γ_m^{cl} is slightly lower than 178, the location predicted by SDD.[8] The result including the quantum correction is shown in Fig. 5 for the melting curve in the $r_s^{-1}-k_BT$

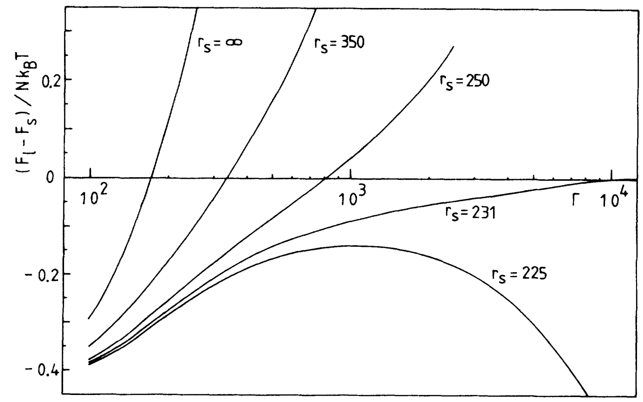

FIG. 4. Curves for $(F_l-F_s)/Nk_BT$ as a function of Γ for several values of r_s. These curves are the results including the sixth reduced moment.

plane. The melting curve continues to go up with descending melting temperature. This is similar to Imada and Takahashi's curve for the two-dimensional Wigner lattice,[29] but different from those by the Lindemann condition[24] and its modification,[30] which has a horizontal part on the low-temperature side.

At zero temperature the melting point is located at $r_s^0=230$. This value is fairly larger than Ceperley and Alder's ones:[5] $r_s^0=100\pm20$ for fermions with spin $\frac{1}{2}$ and $r_s^0=160\pm10$ for bosons with spin 0, with values still larger than the earlier ones for fermions.[3,4] On the other hand, our value is quite smaller than $r_s^0\cong1000$, a value predicted from the Lindemann condition.[24]

A modified Lindemann condition has been proposed by Mochkovitch and Hansen,[30] but with old values of r_s^0 (100 for boson, 75 for fermion) and $\Gamma_m^{\text{cl}}(155)$. Their formula is adapted now to Ceperley and Alder's r_s^0 above and $\Gamma_m^{\text{cl}}=172$.[31] The resultant melting curves are plotted in Fig. 5, with large deviation from ours and with sizable symmetry effect, even in the low-density region of $r_s \gtrsim 500$.

However, the present result should be correct at least in the mentioned region, where the symmetry effect is smaller than the diffraction effect taken up in the present study. It is noted for the Coulomb system that the quantum-mechanical parameter characteristic of the diffraction effect is $\Gamma/\sqrt{r_s}$, whereas the characteristic parameter of the symmetry effect is given by Γ/r_s, square of the ratio of the thermal de Broglie wavelength to the mean particle distance.

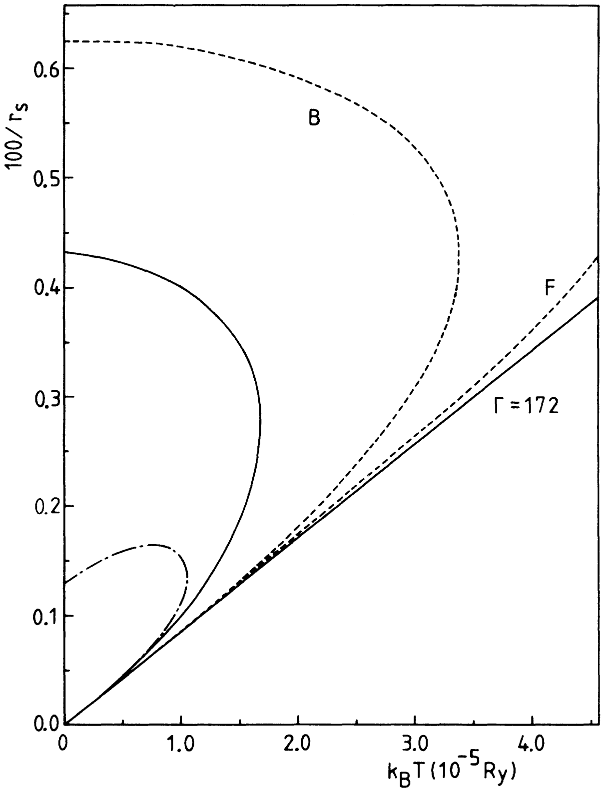

FIG. 5. Melting curves in the $r_s^{-1}-k_BT$ plane. The solid curve is the result up to the sixth reduced moment and the dot-dashed curve up to the fourth one. Straight lines are the classical melting curves, dashed curves are by the modified Lindemann condition of Mochkovitch and Hansen (Ref. 30) adapted to the one by Ceperley and Alder (Ref. 5) and our value of $\Gamma_m^{\text{cl}}=172$. Of the two dashed curves, F indicates the system of fermions and B that of bosons.

We finally consider the entropy change ΔS which appears in the solid-liquid transition. This quantity proves to be

$$\frac{\Delta S}{Nk_B}=\Gamma\frac{\partial}{\partial\Gamma}\left[\frac{F_l-F_s}{Nk_BT}\right], \qquad (6.13)$$

which is to be evaluated at the melting point. The entropy change ΔS is plotted in Fig. 6 as a function of r_s^0/r_s, with r_s the density parameter at the melting point. This result shows that the entropy change decreases with increasing quantum correction. It is mentioned that ΔS should go to zero in the limit of zero temperature, as a consequence of the third law of thermodynamics.

VII. SUMMARY AND DISCUSSIONS

We have studied the quantum effect on the melting of the Wigner crystal at finite temperature, where the symmetry effect has been neglected. The WK expansion of the quantum correction, which has proved to be a moment expansion, is inappropriate for the present study, because of the validity confined to a very small value of our quantum-mechanical parameter, $\Gamma/\sqrt{r_s}$.

A powerful expansion has been obtained by summing up the partial series in the WK expansion for the free energy of the Coulomb system, where each partial series is a power series of $(\hbar\omega_p/k_BT)^2$. The coefficients in the new expansion are the reduced moments for the classical system. Such an expansion is necessary for the present study, because the WK expansion series breaks down in the low-temperature region of $(\hbar\omega_p/k_BT)\gtrsim1$, or $(\Gamma/\sqrt{r_s})\gtrsim1$.

Since the WK expansion is awkward to handle, we study the harmonic Coulomb lattice as a starting point, in

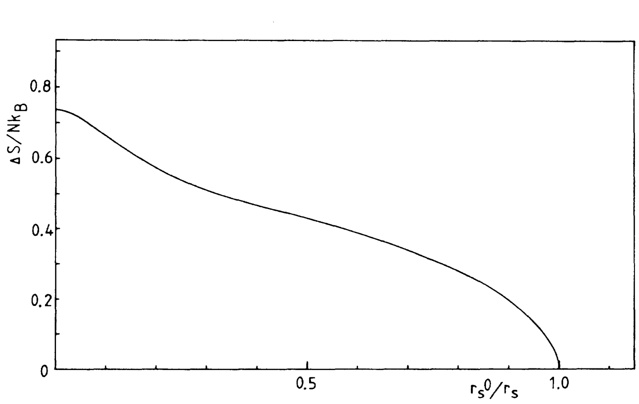

FIG. 6. Melting entropy $\Delta S/Nk_B$ as a function of (r_s^0/r_s). The curve is obtained in the approximation up to the sixth reduced moment. Here r_s denotes the r_s value for the melting point, and $r_s^0=230$ the corresponding value at 0 K.

order to find the form of the reduced-moment expansion. The expansion thus found out has proved applicable to the liquid phase as well, by generalizing the reduced moments in the rigid lattice to those in the nonrigid one. This point has been proved by examining the effects of the anharmonic terms. These anharmonic terms also brings us additional contribution to the free energy, contributions due to the reduced moments of odd order.

The free energy of the system can be obtained with full use of knowledge of the corresponding classical system. For the evaluation the existing Monte Carlo data have been utilized mainly for the liquid phase of our classical system. Since the quantum melting occurs at lower temperature than the classical one, some extrapolation procedures were needed in the classical liquid phase. This might give rise to certain errors in the resultant predictions when the melting temperature is highly depressed.

In the extrapolation of the free energy for the liquid phase, we for a moment look for the range of a parameter a fitting the simulation data by the same procedure as before. In Fig. 7 are shown the differences of the predicted energies from the corresponding SDD's, where the predicted ones are obtained from Eq. (6.8) with the least-squares fit of b, c, and d when we set $a=-0.8920$ and $a=-0.8940$, respectively. There is no appreciable difference between the two extrapolation formulas above, as seen in Fig. 7. The allowed band lies quite lower than $a=-0.88006$ for simple cubic and slightly higher than $a=-0.89587$ for face-centered cubic. In the parameter range of interest, the b value changes from 2.13 to 1.27 as the parameter a becomes higher. Our value $b=\frac{3}{2}$ lies between the two extremum ones.

The b value above is a result of applying the equipartition law to the supercooled classical liquid far below the freezing point. The prescribed value is necessary for the heat capacity of our liquid with quantum correction to vanish in the limit of zero temperature, according to the third law of thermodynamics. Note that the primary quantum correction, $3f_0(t)$ in Eq. (5.2), gives a contribution which just cancels the classical term due to the equipartition law of energy.

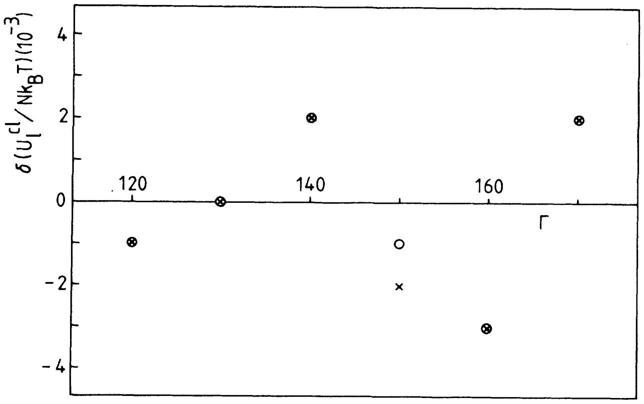

FIG. 7. Allowed range of the parameter a in fitting our extrapolation formula to the Monte Carlo data for liquid phase. For the internal energy (U_l^{cl}/Nk_BT) difference is plotted between the Monte Carlo datum and the interpolated value. The Monte Carlo data are taken from Ref. 8 for $N=1024$. Circles and crosses indicate the differences for the interpolated values, respectively, when $a=-0.8940$ (○) and $a=-0.8920$ (×) are assumed in the formula $(U_l^{cl}/Nk_BT)=a\Gamma+b+(c/\Gamma)+(d/\Gamma^2)$. Here b, c, and d are obtained by least-squares fit.

The melting curve has been studied in the approximation up to the sixth reduced moment. The melting point r_s^0 at zero temperature is fairly larger than the current ones.[3-5] Another result is the melting entropy which has proved to decrease with increasing quantum effect.

The fourth-moment result is rather miserable.[32] Slow convergence of the reduced-moment expansion may also be seen in the expansion of the zero-point energy for the harmonic lattice, Eq. (5.5). However, the essential quantity to the melting is the free-energy difference between two phases. The moment μ_6 works to widen the region of solid phase in opposite direction to the effect of μ_4. Accordingly, the effect of μ_8 possibly works in the same direction as that of μ_4, namely, to reduce the region of solid phase. It has, however, been confirmed that the seventh moment μ_7 arising from the expansion of $F_{4q}^{(2)}$ and $F_{3q}^{(2)}$ works to widen the solid-phase region, and accordingly to cancel the effect of μ_8. We note a large effect of μ_7 in comparison with that of μ_5.

These results are based on the estimation of the reduced moments in the superposition approximation. By this approximation, however, no sizable error comes in for the average values of the three-particle quantities (Appendix B), though for the four-particle quantities the accuracy remains unsettled.

Despite the slow convergence of the reduced-moment expansion, our sixth-moment results for melting are surely correct for the region of quantum-mechanical parameter $(\Gamma/\sqrt{r_s})\lesssim 10$, which is quite wide compared with the region of $(\Gamma/\sqrt{r_s})\lesssim 1$ validating the WK expansion. In the validity region of our result, the symmetry effect is of less importance in view of its characteristic parameter, to be given by Γ/r_s.

APPENDIX A: EVALUATION OF THE INTEGRALS IN THE SUPERPOSITION APPROXIMATION

Some of the integrals appearing in the moments are conditionally convergent. Let us consider, for example, the integral $I_3[1,1]$ which is given by Eq. (5.11). The integral does not converge absolutely for the large value of r_1 or r_2, as can be seen by setting $g_3(1,2,3)\cong 1$ for large separations between particles. In evaluating the integral in the superposition approximation, we set

$$g_3(1,2,3)=g(1,2)g(1,3)\{[g(2,3)-1]+1\} . \qquad (A1)$$

By substituting Eq. (A1) into Eq. (5.11) we divide the integral into two parts, where the integral corresponding to the second term in the braces of Eq. (A1) proves to vanish after angular integrations and the remaining part is absolutely convergent.

The most cumbersome integral is $J_4^{(1)}$ given by Eq. (5.14), which is slowly convergent with respect to radial coordinates. For the mentioned integral, we use the identity

$$\begin{aligned} g_4(1,2,3,4)=g(1,2)g(1,3)g(1,4)\{&[g(2,3)-1][g(3,4)-1][g(4,2)-1]\\ &+[g(2,3)-1][g(3,4)-1]+[g(3,4)-1][g(4,2)-1]\\ &+[g(4,2)-1][g(2,3)-1]+[g(2,3)-1]+[g(3,4)-1]\\ &+[g(4,2)-1]+1\}\ , \end{aligned} \tag{A2}$$

where the last four terms in braces bring no contribution after angular integrations. Of the decomposed integrals resulting from Eq. (A2), the most awkward one is brought by the first term inside braces. We evaluate it directly by the Monte Carlo method. The convergence of the six-dimensional integral becomes slower approaching the freezing point. The number of samplings amounts to 1.5×10^7 until the integral converges, in the case of the slowest convergence. The remaining three terms in the braces give the identical contribution, and can be collectively written as

$$\tfrac{3}{8}\int_0^\infty dr\frac{g(r)}{r}\left[\int_0^\infty dr'\int_{-1}^{1}dx\frac{g(r')}{r'}(3x^2-1)\{g([r^2+(r')^2-2rr'x]^{1/2})-1\}\right]^2 \tag{A3}$$

as a contribution to the integral. The integration can be performed in two steps. The first step is a double integration with respect to r' and x at a fixed value of r and the second one the integration with respect to r using the tabulated values for the integral obtained in the first step.

APPENDIX B: SUPERPOSITION APPROXIMATION AND SCHOFIELD'S IDENTITY

The validity of the superposition approximation (SA) has been a controversial problem. We examine it by using Schofield's identity,[22] which relates the s-particle distribution function $g_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)$ to the $(s+1)$-particle one $g_{s+1}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{s+1})$.

For the one-component plasma the structure factor vanishes identically in the long-wavelength limit. Namely, we have for the pair distribution function $g(r)$

$$N\int[g(r)-1]d\mathbf{r}=-1\ , \tag{B1}$$

where N is the particle density. Owing to the above property, Schofield's identity reduces to a simple form

$$sg_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)+N\int[g_{s+1}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{s+1})-g_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)]d\mathbf{r}_{s+1}=0\ . \tag{B2}$$

Let us consider a simple case, $s=2$. For liquid we may put $g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\equiv g_3(\mathbf{r},\mathbf{r}')$ where $\mathbf{r}$ and $\mathbf{r}'$ denote two vectors characterizing a triangle formed by three particles. By dividing both sides of Eq. (B2) for our particular case by $2g(r)$, we have

$$1+\frac{N}{2}\int\left[\frac{g_3(\mathbf{r},\mathbf{r}')}{g(r)}-1\right]d\mathbf{r}'=0\ . \tag{B3}$$

This equation may be an integral equation for the three-particle distribution function $g_3(\mathbf{r},\mathbf{r}')$ when the function $g(r)$ is given.

If the SA holds exactly, then

$$\Delta=\frac{N}{2}\int[g(|\mathbf{r}'-\mathbf{r}|)-1][g(r')-1]d\mathbf{r}' \tag{B4}$$

must vanish. This relation follows by substituting Eq. (5.17) into Eq. (B3), and by using Eq. (B1). In Fig. 8 we plot Δ as a function of r, using $g(r)$ obtained from Ref. 21. This curve demonstrates the failure of the SA.

Let us set the correct form of g_3 to be of the form

$$g_3(\mathbf{r},\mathbf{r}')=[1+C(\mathbf{r},\mathbf{r}')]g(r)g(r')g(|\mathbf{r}'-\mathbf{r}|)\ . \tag{B5}$$

By Eq. (B3) we then have

$$\frac{N}{2}\int g(r')g(|\mathbf{r}'-\mathbf{r}|)C(\mathbf{r},\mathbf{r}')d\mathbf{r}'=-\Delta\ , \tag{B6}$$

with Δ defined by Eq. (B4). Since $g_3(\mathbf{r},\mathbf{r}')$ is a symmetric function with respect to interchange of the position vectors of particles, the same symmetry must be kept also for $C(\mathbf{r},\mathbf{r}')$.

A tentative form with the required symmetry is assumed as

$$\begin{aligned} C(\mathbf{r},\mathbf{r}')&=\frac{A}{(r+r'+|\mathbf{r}'-\mathbf{r}|)^3}\sin\psi\ ,\\ \psi&=\frac{2\pi}{\lambda}(r+r'+|\mathbf{r}'-\mathbf{r}|)+\frac{\alpha}{1+rr'|\mathbf{r}'-\mathbf{r}|}-\delta\ , \end{aligned} \tag{B7}$$

where A, λ, α, and δ are adjustable parameters. In Fig. 8 we plot the left-hand side of Eq. (B6) with reverse of sign when $\lambda=1.4$, $\alpha=5\pi/8$, and $\delta=\pi/4$, for the distance in units of $r_s a_0$. In the shown curve we fix $A=37$

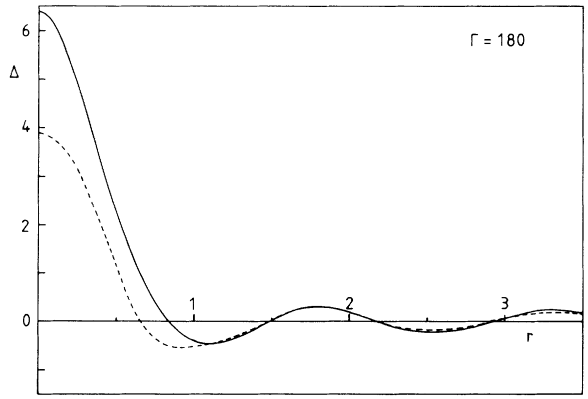

FIG. 8. Illustration showing failure of the superposition approximation. The solid line shows the curve for Δ as a function of r. The dashed line shows the curve for the correction term which cancels Δ, for tentatively chosen form of $C(r,r')$ (r in $r_s a_0$ units).

such that the plotted quantity coincides with $\Delta(r)$ at $r=1.8$. The Schofield's identity seems to fail still in the region of small r, where $g(r)$ is vanishingly small. We note that the quantity of real interest is the plotted one multiplied by $g(r)$.

For the three-particle integrals in Sec. V B, the correction due to $C(\mathbf{r},\mathbf{r}')$ has proved very small. It is less than 1% for $I_3[1,1]$ at $\Gamma=180$.

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[16] Our Eq. (4.15) corresponds to Cowley's Eq. (4.10) in Ref. 15, where Eq. (4.17) for the function $h(\omega_1,\omega_2,\omega_3)$ comes out from Cowley's by eliminating the occupation numbers n_i with the aid of $(2n_i+1)=\coth(\beta\hbar\omega_i/2)$. Note that his $V(\lambda_1,\lambda_2,\lambda_3)$ is different from ours by a certain factor.

[17] Our summation is taken over 608 lattice points per single sum, which are compared with CHM's number of lattice points, 150 for $\bar{\mu}_6$ and 26 for $\bar{\mu}_8$. In spite of large differences of the estimates, CHM's values of M_6 and M_8 differ from the correct ones merely by $\sim 10\%$; a demonstration that the most important contribution to M_{2k} comes from the term of ω_p^{2k}.

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[27] In the extrapolation we assume the classical liquid branch to be continued to the zero temperature. This assumption should be reasonable in view of our definition of liquids which are translationally disordered or without long-range order of particle density. In the purely classical system the liquid branch must go to an aggregation state of particles which are at rest at positions of local minima of the potential energy, namely, an amorphous state, at zero temperature.

[28] In principle, the ground-state wave function of a distinguishable particle system must be identical to that of a bosonic one, as proved, for instance, in R. P. Feynman, *Statistical Mechanics* (Benjamin, Massachusetts, 1972), p. 321. According to the present approach, however, the free energy of the distinguishable particle system would not tend to that of the bosonic one in the low-temperature limit even if the quantum correction were taken into account properly up to infinite power of $(2\pi\hbar)$. It is because the quantum correction results essentially from incommutable effects of the kinetic energy and the potential energy operators of the system, being averaged over states of the distinguishable particle system in accordance with the WK expansion. Since the number of these states is enormously larger than that of the bosonic ones, the lowest state must be buried under integration over the states under consideration. The symmetry effect results from the other contributions, as described in Ref. 11.

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[31] The formula of Mochkovitch and Hansen is really an interpolation between the classical and quantum limits, which includes the second parameter η besides the Lindemann one γ. For adapting it to the new values of r_s^0 and Γ_m^{cl}, the only modification comes out in Eq. (7) of Ref. 30. In place of it one now has

$$\gamma_B=0.2489-\frac{0.0926}{1+2.16\times10^{-2}\eta^2}\,,$$

$$\gamma_F=0.2799-\frac{0.1236}{1+1.62\times10^{-2}\eta^2}\,,$$

respectively, for bosons and fermions.

[32] In the fourth-moment result, the melting curve has a finite slope at zero temperature in violation of the third law of thermodynamics. It is because the zero-point entropy characteristic of the classical system is canceled very incompletely by the fourth-moment term. [The above term corresponds to the constant term in Eq. (6.3) or (6.7). The terms which cancel the above one come mostly from products of the constant terms in $f_{2l}(t)$, the next terms in the asymptotic expansion (3.19), and the zero-temperature limit of the reduced moment μ_{2l}.] The cancellation seems almost complete in the sixth-moment approximation with a nearly horizontal slope in the melting curve, while for each phase the cancellation in the free energy occurs better in the fourth-moment result.