On a Hard-Sphere Crystal

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On the basis of the effective potential method, the single-particle distribution-function in the three-dimensional hard-sphere crystal is investigated. The effective potential in a unit cell which is determined self-consistently depends not only on the displacement of a particle from the lattice point but also on the configuration of its neighboring lattice points. The effective potential is expanded in terms of the above displacement up to the quadratic terms including a linear term and its coefficients are determined by the use of the self-consistent equations. The well-localized distribution of particles around their own lattice sites is obtained below a threshold specific volume and the hard-sphere crystal cannot exist stably above that volume.

The correlations between displacements of a pair of particles in the directions parallel and perpendicular to the line connecting the nearest-neighboring sites are discussed. The pressure and the isothermal compressibility as a function of volume are also studied. The effective two-body interaction potential is introduced in an intuitive way. By the use of it, the dispersion relations of the lattice vibration are investigated.

§ 1. Introduction

The hard-core part of interaction potential between particles plays an essential role for the appearance of crystalline phase. By computer simulations and experiments of monodisperse latex, it has been found that the periodic lattice structure appears even in the case of repulsive-particle systems. Many theoretical attempts for these systems have been made in order to understand the physical mechanism of melting phenomena.

As the hard-core potential is limited in a very short range, it is required to take into consideration the details of the relative motion of a pair of particles at a small separation. Short-range and long-range correlations are both important and must be treated with a great care in the investigation of the repulsive-particle crystal, particularly in the case of the hard-sphere system.

The hard-sphere system can be regarded as a reference system in discussing the liquid-solid transition. In the study of simple liquid, some authors regarded the system with a hard-sphere potential as a reference system. Recently, Yoshiida gave a freezing criterion, from the point of view that the structure factors of the liquid argon and of the simple liquid metal near the freezing point should have a form similar to the one of the hard-sphere fluid. Even in a 'natural'
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On a hard-sphere crystal, the influence of the hard-core part of the interaction potential tends to be much important in a sufficient vicinity of the melting point, due to the large thermal fluctuation of atom. Thus we can consider the 'natural' crystal to have similar properties to the hard-sphere crystal in the vicinity of this point.

In a previous paper (referred to as I), we introduced the effective potential on a particle acting from one of the nearest-neighboring particles. This is determined self-consistently on the basis of the cluster variation method in the second order approximation. The single-particle distribution-function in a certain cell can be expressed in terms of this effective potential. In the case of crystalline phase, the single-particle distribution-function possesses a maximum just at a lattice point. The liquid phase, on the other hand, is characterized by a uniform distribution in the cell. Our general formulation developed in I is reviewed in §2.

We took in I a further approximation for the effective potential to investigate the premelting phenomena. It was represented in the same form as in the isotropic harmonic oscillator. Owing to this oversimplified treatment, however, we failed to obtain any finite solutions both for liquid and solid phases in the case of repulsive potential. Hence in the succeeding note (referred to as II), applying our theory to the hard-disc system, we solved the self-consistent equations by means of the numerical method and the solid-liquid transition is successfully discussed. We emphasized there the importance of the anisotropy of the effective potential due to the short-range correlations of the distribution of particles. The effective potential depends not only on the displacement of a particle from the lattice point but also on the lattice structure (i.e., the lattice constant as well as lattice type). Though our theory is essentially based upon ‘one-body’ approximation, we can take account of the effect of ‘two-body’ correlation due to the steep repulsive-potential.

The purpose of this paper is to apply the present theory to the three-dimensional hard-sphere system and to investigate the stability of its crystalline phase. In §3 the effective potential is expanded in linear as well as quadratic terms of the displacement from the lattice point. On account of the short-range correlation, these terms are divided into two parts: one represents the long-range order and the other the short-range order of distributions of particles in the crystal. The contributions of the latter part vanishes when all the effective potentials due to the particles surrounding one lattice site are summed up. Without this part, however, we cannot discuss the crystalline phase in the system of repulsive potential.

The well-localized distribution around each lattice point is obtained as a function of the specific volume below a threshold value of this volume. Above the threshold, the solutions of the self-consistent equations cannot be obtained, and the stable crystalline phase can no longer exist. The effective potential in the crystal

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* In this paper, we call the crystal in which the cohesion is due to the attractive part of interaction potential and lattice structure appears as its result even without the application of external pressure the ‘natural’ crystal.
structure has a singular character in the system of the hard-sphere crystal; that
is, any pair of particles repel each other. It is considered that each particle tends
to be settled down at its own equilibrium point in consequence of shoving and
pushing one another in the limited space. It seems that this is characteristic not
only of the hard-sphere system but also more generally of the repulsive-particle
system.

By the use of the solutions of the above-mentioned self-consistent equations
we investigate the thermodynamic properties and obtain pressure, isothermal com­
pressibility and displacement-displacement correlations of the hard-sphere crystal
in § 4. The correlation functions peculiar to the repulsive-force is obtained. At
the end of § 4, we investigate the lattice vibration in the hard-sphere crystal. In
order to introduce the collective aspect, we define the effective two-body inter­
action potential in an intuitive way. By its use, the dispersion relation of the
lattice vibration and the sound velocities are discussed. Brief discussion is given in
the last section.

§ 2. General formulation

In this section, the general formulation developed in I is reviewed briefly.

Let us divide the volume $V$ of the system into $N$ Wigner-Seitz cells the
centers of which compose a face-centered cubic lattice. Our
attention is focused
on the single occupancy version of the cell model.

By means of the cluster variation method in the second order approximation,7
we derive the self-consistent equations determining the effective potential. The
Helmholtz free energy $F$ (the contribution from kinetic energy excepted here and
hereafter) can be calculated on the basis of the variational principle:

$$F = \min \mathcal{F},$$

$$\mathcal{F} = \sum_j \int d\mathbf{u}_j \int d\mathbf{u}_k \varphi(\mathbf{u}_j - \mathbf{u}_k + \mathbf{R}_j - \mathbf{R}_k) \rho_z(\mathbf{u}_j, \mathbf{u}_k)$$

$$+ \beta^{-1} \sum_j \int d\mathbf{u}_j \rho_1(\mathbf{u}_j) \ln \rho_1(\mathbf{u}_j)$$

$$+ \beta^{-1} \sum_{j<k} \left\{ \int d\mathbf{u}_j \int d\mathbf{u}_k \rho_2(\mathbf{u}_j, \mathbf{u}_k) \ln \rho_2(\mathbf{u}_j, \mathbf{u}_k) 
- \int d\mathbf{u}_j \rho_1(\mathbf{u}_j) \ln \rho_1(\mathbf{u}_j) 
- \int d\mathbf{u}_k \rho_1(\mathbf{u}_k) \ln \rho_1(\mathbf{u}_k) \right\}, \quad (2.1)$$

where $\beta^{-1} = k_B T$. The minimum should be obtained with respect to the single­
particle distribution-function $\rho_1(\mathbf{u}_j)$ and to the two-particle one $\rho_2(\mathbf{u}_j, \mathbf{u}_k)$. They
should satisfy the normalization condition

$$\int d\mathbf{u}_j \rho_1(\mathbf{u}_j) = 1 \quad (2.2a)$$
and the recurrence relation

$$\int d\mathbf{u}_k \rho_2 (\mathbf{u}_j, \mathbf{u}_k) = \rho_1 (\mathbf{u}_j). \quad (2.2b)$$

The function $\varphi(\left| \mathbf{u}_j - \mathbf{u}_k + \mathbf{R}_j - \mathbf{R}_k \right|)$ is the interaction potential between the $j$-th and $k$-th particles which are situated at the displacements $\mathbf{u}_j$ and $\mathbf{u}_k$ from the lattice points $\mathbf{R}_j$ and $\mathbf{R}_k$, respectively. In the present paper, $\varphi(\left| \mathbf{u} \right|)$ is a hard-sphere potential with a diameter $\sigma$. The integration $\int d\mathbf{u}_j$ with respect to the $j$-th particle is taken over the volume $v = V/N$ within the $j$-th cell.

We obtain, after performing the variation, for the distribution functions

$$\rho_1 (\mathbf{u}_j) = \exp [\beta \{ f_j - W_j (\mathbf{u}_j) \}], \quad (2.3a)$$

$$\rho_2 (\mathbf{u}_j, \mathbf{u}_k) = \rho_1 (\mathbf{u}_j) \rho_1 (\mathbf{u}_k) \exp \left[ -\beta \{ \varphi(\left| \mathbf{u}_j - \mathbf{u}_k + \mathbf{R}_j - \mathbf{R}_k \right|) - U_{jk} (\mathbf{u}_k) - U_{kj} (\mathbf{u}_j) \} \right], \quad (2.3b)$$

and for the free energy

$$F = \sum_j f_j, \quad (2.3c)$$

where we have the relation

$$W_j (\mathbf{u}_j) = \sum_{k \neq j} U_{kj} (\mathbf{u}_j) \quad (2.3d)$$

and $\beta^{-1} = \beta^{-1} N + f_j$ and $\beta^{-1} \ln \rho_1 (\mathbf{u}_j) - U_{kj} (\mathbf{u}_j)$ have been introduced as the Lagrange multipliers for the respective subsidiary conditions $(2.2)$. From $(2.3)$, we can see the physical meanings of $f_j (= f)$ and $U_{kj} (\mathbf{u}_j)$; the former represents the free energy per particle and the latter the effective potential acting on the $j$-th particle through the interaction with the $k$-th particle. $W_j (\mathbf{u}_j)$ is the total effective potential for the $j$-th particle due to its surrounding particles.

The free energy $f$ and the effective potential $U_{kj} (\mathbf{u}_j)$ can be determined so that $(2.3)$ satisfy the subsidiary conditions $(2.2)$. Expressions $(2.2)$ and $(2.3)$ constitute a set of self-consistent equations for $f$ and $U_{kj} (\mathbf{u}_j)$. Since the self-consistent equations are nonlinear, it is very difficult to obtain the analytical solutions. We introduce a further approximation in $\S$ 3. If the $k$-th and $j$-th cells are distant from each other enough $\varphi(\left| \mathbf{u}_j - \mathbf{u}_k + \mathbf{R}_j - \mathbf{R}_k \right|)$ to be negligible, $U_{kj} (\mathbf{u}_j)$ can be neglected, as shown in the Appendix.

It can be seen from $(2.2b)$, $(2.3a)$ and $(2.3b)$ that $U_{kj} (\mathbf{u}_j)$ has a uniaxial symmetry about the axis $\mathbf{R}_{kj} = \mathbf{R}_k - \mathbf{R}_j$ and a reflection symmetry: $U_{kj} (\mathbf{u}_j) = U_{kj} (-\mathbf{u}_j)$, where $\mathbf{R}_{kj} = -\mathbf{R}_{jk}$. On the other hand, $W_j (\mathbf{u}_j)$ possesses a symmetry characteristic of the lattice structure.

We emphasise here that the strong anisotropy of $U_{kj} (\mathbf{u}_j)$ is due to the short-range correlation of the distribution of particles. The effective potential $U_{kj} (\mathbf{u}_j)$ is a function only of a single variable $\mathbf{u}_j$. However, the effect of the ‘two-body’ correlation can be taken into account through this effective potential.
$W_j(u_j)$ is considered to represent the long-range order of crystalline phase. If $W_j(u_j)$ is found to have a deep minimum at $u_j=0$, the well-localized distribution of particles is expected to appear at the lattice points. In the liquid phase, we obtain the solution of $W_j(u_j)$ which is constant throughout the cell and the uniform distribution of particle in each cell occurs. We note here that $U_{kj}(u_j)$ cannot be constant even in the liquid phase. This circumstance has already been shown in the case of the hard-disc system in II.

§ 3. Effective potential for the hard-sphere crystal

In this section, the effective potential $U_{kj}(u_j)$ will be determined as a solution of self-consistent equations by means of the moment method, in order to investigate the three-dimensional hard-sphere crystal.

We first expand $U_{kj}(u_j)$ in a power series of $u_j$ and retain up to the quadratic terms. Owing to the well-localized nature of particles at their lattice sites, this is regarded as a reasonable approximation for the crystalline phase. In view of the uniaxial and reflection symmetries, we assume

$$U_{kj}(u_j) = \begin{cases} U_0 + au_j \cdot e_{kj} + b (3(u_j \cdot e_{kj})^2 - u_j^2) + \omega^2 u_j^2, & (j, k: \text{nearest neighbor}), \\ 0, & \text{(otherwise)}, \end{cases} \quad (3.1)$$

where $e_{kj}$ is a unit vector parallel to $R_{kj}$. Here we have neglected the contribution from the particle in the $k$-th cell unless this is the nearest neighboring to the $j$-th one (see the Appendix). If the crystal under consideration has a cubic symmetry, the total effective potential $W_j(u_j)$ can be expressed as

$$W_j(u_j) = zU_0 + z\omega^2 u_j^2, \quad (3.2)$$

where $z$ is the coordination number. The effective spring constant $z\omega^2$ of the Einstein-type oscillators is regarded as the long-range order-parameter for the crystalline phase. The other parameters $a$ and $b$ are necessary to take account of the strong anisotropy of $U_{kj}(u_j)$ and represent the effect of the short-range correlation of particles at a small separation.

The effective potential for the nearest-neighboring pair can be rewritten in the form for an anisotropic harmonic oscillator including a linear term as

$$U_{kj}(u_j) = U_0 + au_j \cdot e_{kj} + 3\omega^2 (u_j \cdot e_{kj})^2 + 3\omega^2 (u_j \times e_{kj})^2, \quad (3.3)$$

where $\omega^2 = (\omega^2 + 2b)/3$ and $\omega^2 = (\omega^2 - b)/3$.

The parameters $f$, $U_0$, $a$, $\omega^2$ and $\omega^2$ are determined, so as to satisfy the self-consistent equations, by means of the moment method. Thus we obtain

$$\int d\mathbf{u} \rho_j(u) = 1, \quad (3.4a)$$
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\[\int_0^\varrho \int_0^\varrho \rho_2(u, u') = 1, \quad (3.4b)\]
\[\int_0^\varrho \int_0^\varrho \rho_2(u, u') = \int_0^\varrho (u \cdot e) \rho_1(u) = 0, \quad (3.4c)\]
\[\int_0^\varrho \int_0^\varrho \rho_2(u, u') = \int_0^\varrho (u \cdot e) \rho_1(u) \quad (3.4d)\]

and
\[\int_0^\varrho \int_0^\varrho (u \times e) \rho_2(u, u') = \int_0^\varrho (u \times e) \rho_1(u), \quad (3.4e)\]

where \(u\) and \(u'\) are the respective displacements from a pair of lattice points which are nearest-neighboring to each other and are distant by \(R_e\).

From (3.4a,b), the free energy \(\beta f\) per particle as a function of \(\beta a\), \(\beta b\) and \(\beta \omega^2\) can be derived as
\[\beta f = \beta f_1 + (z/2) (\beta f_2 - 2\beta f_1), \quad (3.5)\]

where
\[\exp(-\beta f_1) = \int_0^\varrho \exp\{-\beta z \omega^2 u^2\}, \quad (3.5a)\]
\[\exp(-\beta f_2) = \int_0^\varrho \int_0^\varrho \exp\{-\beta V(u, u')\} \quad (3.5b)\]

and
\[V(u, u') = \varphi(|u - u' + R|) + (z - 1) \omega^2(u^2 + u'^2) - (u - u') \cdot e \]
\[- b \{3(u \cdot e)^2 - u^2 + 3(u' \cdot e)^2 - u'^2\}. \quad (3.5c)\]

Now we can easily show that \(\beta f\) is a concave function of \(\beta a\) and \(\beta b\). It follows from the fact that
\[\partial^2 (\beta f) / \partial (\beta a)^2 = (z/2) \partial^2 (\beta f_1) / \partial (\beta a)^2 \]
\[= -z/2 \langle\langle(u - u') \cdot e\rangle\rangle - \langle\langle(u - u') \cdot e\rangle\rangle \leq 0 \quad (3.6a)\]

and
\[\partial^2 (\beta f) / \partial (\beta b)^2 = (z/2) \partial^2 (\beta f_2) / \partial (\beta b)^2 \]
\[= -z/2 \langle\langle 3(u \cdot e)^2 - u^2 + 3(u' \cdot e)^2 - u'^2\rangle\rangle \]
\[- \langle\langle 3(u \cdot e)^2 - u^2 + 3(u' \cdot e)^2 - u'^2\rangle\rangle \leq 0. \quad (3.6b)\]

Here we have used such a notation as
\[\langle A \rangle = \int_0^\varrho \int_0^\varrho A(u, u') \exp\{-\beta V(u, u')\} / \exp(-\beta f_2). \quad (3.7)\]

On account of the localization of particles in the crystal at their own lattice sites, we can neglect the contribution from the boundaries of the cells and extend
the integration of \((3·5a,b)\) over the whole space. Then the free energy takes the form

\[
\beta f(\beta a, \beta b, \beta \omega^3) = \text{constant} + z \ln \beta \lambda + (z/4) \ln \beta \nu \\
- (3/2) (z-1) \ln \beta \omega^3 + (z/4) \beta \nu \bar{R}^2 - (z/2) \beta a \bar{R} \\
- (z/2) \ln \int_0^\infty ds \mathcal{J}(s), \quad (3·8)
\]

where \(\beta \lambda = \{(z-1)\beta \omega^3 + \beta b\} \sigma^2\), \(\beta \nu = \{(z-1)\beta \omega^3 - 2\beta b\} \sigma^2\), \(\beta a = \beta a \sigma\), \(\beta \omega^3 = \omega \sigma^2\) and \(\bar{R} = R/\sigma\). The integrand \(\mathcal{J}(s)\) is given by

\[
\mathcal{J}(s) = \begin{cases} 
\exp \left( -\beta \lambda /2 \right) \exp \left[ \beta (\lambda - \bar{v}) s^2 /2 + (\beta \nu \bar{R} - \beta a) s \right], & 0 \leq s \leq 1, \\
\exp \left[ -\beta \nu s^2 /2 + (\beta \nu \bar{R} - \beta a) s \right], & 1 \leq s.
\end{cases} \quad (3·8a)
\]

The singularity of the hard-sphere potential leads to the discontinuity of the differential of \(\mathcal{J}(s)\) at \(s=1\). The other parameters \(\beta a, \beta b\) and \(\beta \omega^3\) should be given either from the consistency conditions \((3·4c~e)\) with \((3·5)\sim(3·5c)\) and

\[
\beta U_0 = (1/2) (\beta f_1 - 2\beta f), \quad (3·5d)
\]

or from the stationary condition for \(\beta f\) that

\[
\partial (\beta f) / \partial (\beta a) = \partial (\beta f) / \partial (\beta b) = \partial (\beta f) / \partial (\beta \omega^3) = 0 . \quad (3·9a)
\]

These conditions \((3·9a)\) can also be rewritten as

\[
\partial (\beta f) / \partial (\beta a) = \partial (\beta f) / \partial (\beta \omega^3) = 0 \quad (3·9b)
\]

or

\[
\partial (\beta f) / \partial (\beta \omega^3) = 0 . \quad (3·9c)
\]

Since \(\beta f\) is the concave function of \(\beta a\) and \(\beta b\), as seen from \((3·6)\), it has only one stationary point as a function of \(\beta a\) and \(\beta b\) with \(\beta \omega^3\) fixed. Such values of \(\beta a\) and \(\beta b\) that make \(\beta f\) stationary vary monotonically with \(\beta \omega^3\). Substitution of such \(\beta a\) and \(\beta b\) into \((3·8)\) yields \(\beta f\) which is a function of \(\beta \omega^3\) for a given volume \(\bar{v} = v/v_c\) \((v_c = \sigma^3)\). \(\beta f(\beta \omega^3)\) have two stationary points as a function of \(\beta \omega^3\) below the threshold value \(\bar{v}^* = 1.293\), which is given as \(\bar{v}^* = 1.19\) by the computer experiment. These correspond to the minimum and the maximum values of \(\beta f\), respectively. Both stationary points coincide with each other at \(\bar{v} = \bar{v}^*\) and there is no solution of \((3·9a)\) for \(\bar{v} > \bar{v}^*\). Then it can be concluded that the crystalline phase appear for \(\bar{v} < \bar{v}^*\) and becomes unstable at \(\bar{v} = \bar{v}^*\).

The various parameters are plotted in Fig. 1 as functions of \(\bar{v}\). The long-range order-parameter \(\beta \omega^3\) decreases with the increase of \(\bar{v}\), and falls down very sharply in the vicinity of \(\bar{v}^*\), where it is proportional to \((\bar{v}^* - \bar{v})^{1/2}\). It can be said that the hard-sphere crystal tends to be soft steeply as the volume approaches the threshold value. The root-mean square displacement is estimated as \(0.078 \bar{R}\).
at the threshold, $\bar{v} = \bar{v}^*$. As $\beta a$ and $\beta b$ depend on $\bar{v}^3$ linearly in the vicinity of $\bar{v} = \bar{v}^*$, they also vary as $(\bar{v}^* - \bar{v})^{1/2}$.

The signs of $\beta a$ and $\beta \bar{w}_i$ should be noted. We can see from the repulsive-force between particles that $\beta a$ is positive and $\beta \bar{w}_i$ is negative. A pair of particles in the hard-sphere crystal escape from each other. As a consequence of shoving and pushing one another in a cramped space, they becomes settled down at their own equilibrium points.

Fig. 1. The dependence of the various parameters on the specific volume $\bar{v}$.

§ 4. Thermodynamic properties and lattice vibration

By the use of the results obtained in the previous section, let us investigate the thermodynamic properties of the hard-sphere crystal. The Helmholtz free energy $\beta f$ multiplied with the inverse temperature for the hard-sphere system (excepted for the kinetic energy) is independent of the temperature (see the Appendix). Then we study here the pressure $P$, the isothermal compressibility $\kappa_T$ and the displacement-displacement correlations. The lattice vibration in the hard-sphere crystal is also investigated in an intuitive way.

1) Pressure and isothermal compressibility

The dimensionless pressure $\tilde{P}(=\beta \bar{P} \bar{v}_c)$ can be derived from a thermodynamic relation

$$\tilde{P} = - (\partial \beta f / \partial \bar{v})_g . \tag{4·1}$$

By using the stationary condition (3·9a), it leads to

$$\tilde{P} = - (\partial \beta f / \partial \bar{v})_g,_{\beta a, \beta b, \beta a, \beta b} = (\bar{R}/6 \bar{v}) \{ \beta a - \beta \bar{w}(\bar{R} - \bar{s}) \}, \tag{4·1a}$$

where

$$\bar{s} = \int_0^s ds^2 s J(s) / \int_0^\infty ds J(s). \tag{4·2}$$

Since the term $\bar{R} - \bar{s}$ in (4·1a) vanishes due to the stationary condition for $\beta f$ with respect to $\beta a$, the final expression for the pressure is obtained as
\[ \bar{P} = \frac{(z \bar{R}/6\bar{\sigma})}{\beta \bar{a}}. \quad (4 \cdot 1b) \]

We note here that the \( \beta \bar{a} \) is proportional to the pressure. It shows that the linear term of \( U_{ij}(u_j) \) comes from the application of an external pressure.

The isothermal compressibility \( \kappa_T \) can be straightforwardly obtained as

\[ \beta \kappa_T^{-1} \bar{v} = -\bar{v} (\beta \bar{P}/\partial \bar{v})_\beta = (2/3) \bar{P} \{ 1 - (3/2) (\partial \ln \beta \bar{a}/\partial \ln \bar{v}) \}. \quad (4 \cdot 3) \]

The pressure and isothermal compressibility are plotted in Fig. 2 as a function of \( \bar{v} \). As mentioned in § 3, \( \beta \bar{a} \) varies as \( (\bar{v}^* - \bar{v})^{1/2} \) near the threshold. The second term in the curly-bracket of \( (4 \cdot 3) \) increases with \( \bar{v} \) and as its result the inverse of the isothermal compressibility decreases to cross the coordinate at a certain point \( \bar{v}/\bar{v}_c (=1.291) \) which is nearly equal to \( \bar{v}^* \). Above \( \bar{v}/\bar{v}_c \), the system becomes thermodynamically unstable, as seen from the negative compressibility. This shows that our theory is not effective in the vicinity of the threshold \( \bar{v}^* \).

![Fig. 2. The pressure and isothermal compressibility vs volume. The scale of the left (right) side associates with the one of the pressure (the compressibility).](image)

![Fig. 3. Components of the displacement-displacement correlations in the parallel and perpendicular directions to \( R \) as a function of \( \bar{v} \).](image)

2) \textit{Displacement-displacement correlations}

On the basis of the present theory, the dyadic of the displacement-displacement correlation can be calculated with the use of the two-particle distribution-function \( \rho_t(u_j, u_s) \), by
where \( u_j \) and \( u_k \) are the respective displacement from the lattice points which are distant by \( R_{jk} \). Unless the \( j \)-th and \( k \)-th cells are nearest-neighboring to each other, the two-particle distribution function \( \rho_t(u_j, u_k) \) can be written as the product of single-particle ones (see the Appendix). Since \( \rho_t(u_j) \) has a cubic symmetry, the correlation function vanishes. On account of the uniaxial symmetry of \( \rho_t(u_j, u_k) \) about \( R_{jk} \), only the diagonal components of the correlation are finite. They are expressed, in the units of \( \sigma \), as

\[
\langle u_j u_k \rangle = \int_0^1 du_j \int_0^1 du_k \rho_t(u_j, u_k),
\]

where \( u_j \) and \( u_k \) are the respective displacement from the lattice points which are distant by \( R_{jk} \). Unless the \( j \)-th and \( k \)-th cells are nearest-neighboring to each other, the two-particle distribution function \( \rho_t(u_j, u_k) \) can be written as the product of single-particle ones (see the Appendix). Since \( \rho_t(u_j) \) has a cubic symmetry, the correlation function vanishes. On account of the uniaxial symmetry of \( \rho_t(u_j, u_k) \) about \( R_{jk} \), only the diagonal components of the correlation are finite. They are expressed, in the units of \( \sigma \), as

\[
(1/4) \left( (1/\beta) - \bar{s}^2 + \bar{s}^3 \right)
\]

and

\[
-(1/8) (1 - \bar{s}^2)
\]

for the cases of the components parallel and perpendicular to \( R_{jk} \), respectively, where

\[
\bar{s}^{\alpha} = \int_0^1 ds s^\alpha J(s) / \int_0^\infty ds J(s).
\]

These are shown in Fig. 3. The sign of these quantities are due to the effect of the repulsive potential. The magnitudes of these continue to increase as the volume approaches the threshold value, although they do not diverge.

3) Lattice vibration

The present theory is based on the single-particle picture. In order to introduce the collective picture, we define the effective two-body interaction \( \phi_{kj}(|u_j - u_k + R_{jk}|) \) as

\[
U_{k,j}(u_j) = \int_0^1 du_k \phi_{k,j}(|u_j - u_k + R_{jk}|) \rho_t(u_k),
\]

which represents a sort of recurrence relation between two kinds of the effective potentials.

We expand \( \phi_{k,j} \) in terms of the relative displacement \( u_{jk} = u_j - u_k \) in such a way as

\[
\phi_{k,j}(|u_j - u_k + R_{jk}|) = \phi_{k,j}^{(0)} + u_{jk} \cdot \phi_{k,j}^{(1)} + (1/2) u_{jk} \cdot \phi_{k,j}^{(2)} \cdot u_{jk} + \cdots.
\]

In order to investigate the lattice vibration in the harmonic approximation, it is sufficient to take the first three terms in (4.8). Substituting (4.8) into the righthand side of (4.7), we obtain

\[
\phi_{k,j}^{(0)} + \phi_{k,j}^{(1)} \cdot u_j + \frac{1}{2} u_{jk} \cdot \phi_{k,j}^{(2)} \cdot u_j + \frac{1}{2} \int_0^1 du_k u_k \cdot \phi_{k,j}^{(2)} \cdot u_k \rho_t(u_k) + \cdots
\]

with the use of the normalization condition (3.4a) and cubic symmetry (3.4c) of \( \rho_t(u) \). These coefficients are equated term by term with the coefficients of \( U_{k,j}(u_j) \).
Thus we have
\[ \psi_{k,j}^{(0)} = U_0 - \frac{1}{2} \int_0^\infty d\omega \omega \Phi_{k,j} \cdot u_k \Phi_{k,j} \cdot u_k \psi_{k,j}^{(0)}(u_k), \] (4.9a)
\[ \psi_{k,j}^{(1)} = a \omega \Phi_{k,j}, \] (4.9b)
\[ \psi_{k,j}^{(2)} = \Phi_{k,j}, \] (4.9c)
where \( \Phi_{k,j} \) is a \( 3 \times 3 \) matrix of which \( \gamma \delta, \delta = x, y, z \) elements is given by
\[ \Phi_{k,j}^{ij} = 6\omega_i \delta_{ij} + 6(\omega_i^2 - \omega_j^2) e^i_{k,j} e_j^{k,j}. \] (4.10)

Unless the \( k,j \) pair is the nearest-neighbor one, all the coefficients should be taken to be zero.

The linear term of \( \psi_{k,j} \) which is proportional to \( P \Phi_{k,j} \) represents the energy due to the external pressure. However, this term does not matter to the behavior of the lattice vibration. Then we can obtain the effective Hamiltonian for the lattice vibration such as
\[ H_{\text{eff}} = \sum J \left( \frac{p_j^2}{2m} + \frac{1}{4} \sum_{j,k} \Phi_{k,j} \cdot u_k \cdot \Phi_{k,j} \cdot u_j \right). \] (4.11)

The normal modes of the lattice vibration are determined from the secular equation
\[ \Phi_q^{\infty} \epsilon_q^{\infty} = m^{-1} \sum_{k,j} \Phi_{k,j}^{ij} \epsilon_q^{ij}, \] (4.12)
where \( \Phi_q^{\infty} \) is the Fourier component of the effective spring constant \( \Phi_{k,j}^{\infty} \), given by
\[ \Phi_q^{\infty} = \sum_{k,j} [1 - \exp(-i \mathbf{q} \cdot \mathbf{R}_{k,j})] \Phi_{k,j}^{\infty}. \] (4.12a)

Various results that are immediately obtained from (4.12) are presented in Figs. 4 and 5. In Fig. 4, we have plotted the dispersion curves as functions of \( \mathbf{q} \) (\( d = \sqrt{2} \mathbf{R}_1 \); lattice constant in the units of \( \sigma \)) along the [100], [110], and [111] directions.
[110] and [111] directions for \( \tilde{\nu} = 1.200 \) and \( \tilde{\nu} = \tilde{\nu}^* \). Note that these dispersion curves have the familiar shape that is characteristic of f.c.c lattices except for \( T_2 \) branch in the direction of [110] at \( \tilde{\nu} = \tilde{\nu}^* \). In Fig. 5 we present the longitudinal and transverse sound velocities \( \sqrt{m \beta} c \) in the various symmetry directions as functions of \( \tilde{\nu} \). All \( (\partial c/\partial \tilde{\nu})^{-1} \) tend to vanish at the threshold, in place of \( c_{T_2} \) which should vanish in the usual Born\(^9\) theory.

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Fig. 5. Sound velocities in symmetry directions as a function of \( \tilde{\nu} \). The symbols L and T refer to longitudinal and transverse branches, respectively.

§ 5. Discussion

We have succeeded in the description of the hard-sphere crystal by means of the effective potential \( U_{kj}(u_j) \), which depends not only on the displacement \( u_j \) of the \( j \)-th particle from \( R_j \) but also on the lattice distance \( R_{kj} \). Since we abandon the investigation of the liquid phase, the volumes \( v_p, v_m \) at the freezing and melting points cannot be determined in the present paper. On account of the insufficiency mentioned above, only the crystalline phase of hard-sphere system is investigated below the threshold volume at which the crystal structure becomes unstable. However, in principle, the liquid phase can be discussed, if we carry out the tedious numerical integrations of (3·5b) within the region of the \( j \)-th and \( k \)-th cells as done in II. If the free energies of both liquid and crystalline phases of hard-sphere system are calculated by means of the present method, the transition pressure \( P_t \) can be determined by the condition that the chemical potential of both phases should be equal at \( P_t \). If \( v_m \) obtained in this way is smaller than \( \tilde{\nu} \), the failure mentioned in § 4·1 can be removed. We shall here emphasise the following fact: In the liquid state, \( W_j(u_j) \) is constant everywhere in the cell, whereas the coefficients \( a \) and \( b \) of \( U_{kj}(u_j) \) in (3·1) have non-zero values so as \( U_{kj}(u_j) \) to depend on \( u_j \). The long-range and short-range order parameters may depend on \( P \) with certain discontinuities at \( P_t \).

In preparing this paper, we have found recent work by Barker,\(^{10}\) who has developed the formulation identical with ours in order to investigate the hard-
sphere solid and its transition to the liquid phase. He has solved analytically the self-consistant equations similar to (2·2) and (2·3) in the two limiting cases. The first case corresponds to the hard-sphere solid at high densities near the close-packed state. Neglecting the part \((3·8a)\) in \(J(s)\), we can obtain his result, in which \(\beta\sigma^2\) vanishes. As seen from Fig. 1, however, the magnitude of \(\beta\sigma^2\) increases with the increase of the density and, as a result, it does not approach zero at the close-packed state. We note that the repulsion due to the effect of its nearest-neighboring particle becomes strong, as the system becomes dense. Then we can say that the neglect mentioned above brings about a failure even in the vicinity of the close-packed state. He has considered the second solution, in which the root-mean-square displacement from the lattice site is proportional to \((\bar{R} - 1)^{1/2}\), to correspond to the fluid phase. His interpretation is very doubtful, however, because that the single-particle distribution-function in this case has also a maximum at the lattice site as in the case of the first solution. As seen in II for the case of the hard-disc system, the fluid state should be described by the uniform distribution, even on the single occupancy version of the cell model.

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**Appendix**

Let us show here that \(U_{kj}(u_j)\) vanishes if the \(k\)-th and \(j\)-th cells are so distant that \(\varphi(u_j - u_k + R_{jk})\) can be regared as zero. Equations (2·2) and (2·3) for \(\beta f\) and \(\beta U_{ij}(u_j)\) can be rewritten as

\[
\exp(-\beta f) = \int_0^\infty du_j \exp[-\beta W_j(u_j)] \tag{A·1}
\]

and

\[
\exp(-\beta U_{ij}(u_j)) = e^{\beta} \int_0^\infty du_k \exp[-\beta \{\varphi(u_j - u_k + R_{jk})
+ W_k(u_k) - U_{jk}(u_k)\}] \tag{A·2}
\]

If \(\varphi(u_j - u_k + R_{jk})\) vanishes everywhere in the \(k\)-th cell, it is obvious from (A·2) that \(\exp(-\beta U_{ij}(u_j))\) becomes constant. We shall denote it as \(K\). In view of the symmetry, we see that

\[
\exp(-\beta U_{jk}(u_k)) = K. \tag{A·3}
\]
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Substituting \((A\cdot 3)\) into \((A\cdot 2)\) and using the relation \((A\cdot 1)\), we can express the right-hand side of \((A\cdot 2)\) as \(K^{-1}\). Since \(K^2 = 1\) and \(K\) is positive, \(K\) is the unity. Thus we have

\[ \beta U_{ij}(u_j) = \beta U_{jk}(u_k) = 0. \] \hspace{1cm} (A\cdot 4)

Substitution of \((A\cdot 4)\) into \((2\cdot 3b)\) shows immediately that

\[ \rho_s(u_j, u_k) = \rho_i(u_j) \rho_i(u_k). \] \hspace{1cm} (A\cdot 5)

From \((A\cdot 1)\) and \((A\cdot 2)\), moreover, it is seen that \(\beta f\) and \(\beta U_{ij}(u_j)\) are independent of the temperature in the case of hard-sphere system.

References