

Bifurcation of Crystalline Solutions and Freezing

Takeshi YOSHIDA and Hiroaki KUDO

Department of Physics, Kyushu University, Fukuoka 812

(Received September 9, 1977)

The nonlinear integral equation for the singlet distribution function, deduced from the first equation of the BBGKY hierarchy on the assumption that the difference in short range correlation between fluid and crystalline solid may be ignored, is solved near the bifurcation point for a system of hard spheres. The bifurcation point is the point at which crystalline solutions branch off continuously from the fluid solution, and has been recently obtained by Raveché and Stuart. The branch of the solution with face-centered cubic symmetry is shown to grow in a direction of decreasing density near bifurcation. This is not surprising, because freezing is a first order phase transition. It is argued that the crystalline state for this solution is unstable and the bifurcation point does not represent the metastability limit of the crystalline phase. Cases in which the integral equation has different kernels are also discussed in relation to the fluid instability.

§ 1. Introduction

Since Kirkwood and Monroe's study,¹⁾ freezing transitions have often been discussed on the basis of the integro-differential equations for the molecular distribution functions.^{2)~10)} In such an approach to freezing, it is the principal problem how crystalline distributions arise and develop from a uniform and isotropic fluid state when the fluid is cooled or compressed. As is well known, however, the equations for the distribution functions form a hierarchy of coupled equations,¹¹⁾ and it is difficult to deduce a closed set of equations which includes essential features to freezing phenomena. There exists no satisfactory set of equations at present.

Much attention has been paid to the singlet distribution function which is constant in a fluid state but has a certain periodic property in a crystalline state. A natural first step from this point of view may be to ask whether it is possible to predict a crystalline singlet distribution from a knowledge of fluid-like pair distribution functions. We take this point of view in this paper.

To answer the above question, the pair distribution function has often been assumed to be written as

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)g(|\mathbf{r}_1 - \mathbf{r}_2|), \quad (1.1)$$

where $\rho(\mathbf{r})$ is the singlet distribution function and g is a fluid-like pair correlation function. This assumption means that the difference in short range correlation between fluid and crystalline solid may be neglected.

Besides (1.1), Kirkwood and Monroe¹⁾ made another assumption of ignoring

some effects of partial coupling and derived a nonlinear integral equation for $\rho(\mathbf{r})$ from the first equation of the Kirkwood coupling parameter hierarchy.¹⁰ Considering only the contribution from the nearest points in a reciprocal lattice, they solved this equation numerically and found periodic solutions characteristic of a crystalline state. Weeks, Rice and Kozak^{4),5)} studied the integral equation from an analytical viewpoint and discussed the relationship between the existence of multiple solutions and phase transitions. The relationship is, however, not simple, especially for first-order phase transitions such as freezing, and few explicit results have been obtained.

On the assumption (1.1), the first equation of the BBGKY hierarchy¹¹⁾ can also be transformed to an integral equation of the same form without any other approximations.²⁾ The only difference lies in the kernel. Raveché and Stuart^{7)~9)} have recently investigated bifurcation points of this equation for hard sphere systems. The bifurcation point is the point at which crystalline solutions branch off continuously from the fluid solution. They have shown that there exists the bifurcation point for the solution with face-centered cubic symmetry, and have given a physical interpretation to this point: The metastable extension of the stable solid branch meets the stable fluid branch at the bifurcation point and thus the bifurcation point represents the metastability limit of the crystalline phase.^{8),9)}

We have some doubt as to their interpretation. To make it clear, it is necessary to solve the nonlinear integral equation near bifurcation. In general, it is important for the study of freezing transitions to investigate the way in which crystalline solutions, including those for different kernels, bifurcate. In this paper we present crystalline solutions near bifurcation.

In § 2 we give the basic integral equation for $\rho(\mathbf{r})$ and its Fourier representation. A method of obtaining crystalline solutions near bifurcation is presented in § 3, which is applicable to nonlinear equations of the same form. It is shown that the branch of the solution with face-centered cubic symmetry grows in a direction of decreasing density near the bifurcation point. On the basis of this result, discussion about the relations of bifurcation points to freezing transitions is given in the last section.

§ 2. Basic equations

We consider the integral equation

$$\chi\rho(\mathbf{r}_1) = \rho \exp\left[-\beta \int_V d\mathbf{r}_2 \psi(r_{12})\rho(\mathbf{r}_2)\right] \quad (2.1)$$

for the singlet distribution function $\rho(\mathbf{r})$ in a system of spherical molecules having a number density ρ in a volume V , where $\beta = 1/k_B T$, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and the kernel ψ is a kind of effective potential which depends on T and ρ . Here χ is a quantity determined by the normalization condition

$$\frac{1}{V} \int_V \rho(\mathbf{r}) d\mathbf{r} = \rho \tag{2.2}$$

and thus χ is a functional of $\rho(\mathbf{r})$ for given T and ρ .

As stated in the Introduction, Eq. (2.1) is equivalent to the first equation of the BBGKY hierarchy if we assume (1.1) for the pair distribution function. In this case ψ is given by

$$\nabla\psi(r) = g(r)\nabla\phi(r) \quad \text{or} \quad \psi(r) = - \int_r^\infty g(r)\phi'(r) dr, \tag{2.3}$$

where $\phi(r)$ is the pair interaction potential in pairwise additive force models and the prime indicates the derivative.^{2),7)} Though other expressions are possible, we take this kernel in the present paper.

The constant density $\rho(\mathbf{r}) = \rho$ is always a solution of Eqs. (2.1) and (2.2), for which χ , denoted by χ_0 , is given by

$$\ln \chi_0 = -\beta\rho \int_V d\mathbf{r}_2 \psi(r_{12}) = -2\left(\frac{\beta P}{\rho} - 1\right). \tag{2.4}$$

This solution represents the uniform fluid (stable or metastable) in certain regions of the density-temperature plane, and P in (2.4) is the pressure of this fluid phase.

Let us define

$$s(\mathbf{r}) = [\rho(\mathbf{r}) - \rho] / \rho, \tag{2.5}$$

then Eq. (2.1) is written as

$$\chi_s [1 + s(\mathbf{r}_1)] = \exp \left[-\beta\rho \int_V d\mathbf{r}_2 \psi(r_{12}) s(\mathbf{r}_2) \right], \tag{2.6}$$

where $\chi_s = \chi/\chi_0$. Linearization of this equation with respect to $s(\mathbf{r})$ leads to

$$s(\mathbf{r}_1) = -\beta\rho \int_V d\mathbf{r}_2 \psi(r_{12}) s(\mathbf{r}_2). \tag{2.7}$$

If a new solution branches off continuously from the above-mentioned constant solution $s(\mathbf{r}) = 0$, its bifurcation point is determined by the linear eigenvalue problem (2.7). Raveché and Stuart^{8),9)} have studied bifurcation points of solutions with crystalline symmetry for hard sphere systems. They have used the results of computer simulations for (2.4).

The eigenfunctions of (2.7) are the plane waves since the kernel ψ depends only on the distance r_{12} between the two positions \mathbf{r}_1 and \mathbf{r}_2 . With a given crystal structure in mind, we seek solutions which have the symmetries of the lattice. Thus $s(\mathbf{r})$ may be expanded in the Fourier series:

$$s(\mathbf{r}) = \sum_{\mathbf{K}(\neq 0)} \sigma(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{2.8}$$

$$\sigma(\mathbf{K}) = \frac{1}{A} \int_A s(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r}, \tag{2.9}$$

where \mathbf{K} is a vector in the reciprocal lattice of the assumed structure. Integration in (2.9) is performed over the volume \mathcal{A} of the unit cell of the space lattice.

Inserting (2.8) into the right-hand side of (2.6), we have

$$\chi_s[1+s(\mathbf{r})] = \exp\left[\sum_{\mathbf{K}(\neq 0)} \alpha(\mathbf{K}) \sigma(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}}\right], \quad (2.10)$$

where

$$\alpha(\mathbf{K}) = \alpha(|\mathbf{K}|) = -\beta\rho \int d\mathbf{r} \phi(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}}. \quad (2.11)$$

For the kernel ϕ of a short range, the integration in (2.11) may be taken over infinite volume. The quantity χ_s can be determined by integrating (2.10) over \mathcal{A} :

$$\chi_s = \frac{1}{\mathcal{A}} \int_{\mathcal{A}} \exp\left[\sum_{\mathbf{K}(\neq 0)} \alpha(\mathbf{K}) \sigma(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}}\right] d\mathbf{r}. \quad (2.12)$$

It follows from (2.12), (2.10) and (2.9) that

$$\partial \ln \chi_s / \partial \sigma(-\mathbf{K}) = \alpha(\mathbf{K}) \sigma(\mathbf{K}). \quad (2.13)$$

Since χ_s in (2.12) is a known function of $\sigma(\mathbf{K})$ for given $\alpha(\mathbf{K})$, Eq. (2.13) is a set of simultaneous equations which suffice to determine $\sigma(\mathbf{K})$. Equations (2.12) and (2.13) were first derived by Kirkwood and Monroe.^{1),2)}

If the generating functional is defined by

$$f(\{\sigma(\mathbf{K})\}; \{\alpha(\mathbf{K})\}) \equiv -\ln \chi_s + \frac{1}{2} \sum_{\mathbf{K}(\neq 0)} \alpha(\mathbf{K}) \sigma(\mathbf{K}) \sigma(-\mathbf{K}), \quad (2.14)$$

Eq. (2.13) is equivalent to

$$\partial f / \partial \sigma(-\mathbf{K}) = 0. \quad (2.15)$$

The quantity $\ln \chi_s$ may also be written as

$$\ln \chi_s = \sum_{\mathbf{K}(\neq 0)} \alpha(\mathbf{K}) \sigma(\mathbf{K}) \sigma(-\mathbf{K}) - \frac{1}{\mathcal{A}} \int_{\mathcal{A}} [1+s(\mathbf{r})] \ln [1+s(\mathbf{r})] d\mathbf{r}, \quad (2.16)$$

where $s(\mathbf{r})$ is given in (2.8). This expression is obtained by integrating the products of the logarithms of both sides of (2.10) and $[1+s(\mathbf{r})]$ over the unit cell volume \mathcal{A} .

§ 3. Solution near the bifurcation point

We show here how the solution with face-centered cubic (fcc) symmetry to the nonlinear integral equation (2.6) branches off from $s(\mathbf{r})=0$.

The reciprocal lattice vectors are

$$\mathbf{K} = (2\pi/a) (n_1, n_2, n_3), \quad (3.1)$$

where a is the edge length of the unit cube and so $a^3 = \mathcal{A} = 4/\rho$, and n_1, n_2, n_3 are integers which are either all even or all odd. The origin to which $s(\mathbf{r})$ is referred

is arbitrary. We take one of the atomic positions of the fcc lattice as the origin and represent the position \mathbf{r} by the Cartesian components: $\mathbf{r}=a(x_1, x_2, x_3)$. This choice of coordinate system implies that we take out one solution from multiple solutions which are caused by the translational and rotational invariance of the kernel $\psi(r_{12})$. The translational symmetry of the fcc lattice means that $s(x_1+m_1/2, x_2+m_2/2, x_3+m_3/2)=s(x_1, x_2, x_3)$, where m_1, m_2, m_3 are integers such that $m_1+m_2+m_3=\text{even}$. The rotational symmetry of the cubic point group means that $s(x_1, x_2, x_3)$ is a symmetric and even function of x_1, x_2, x_3 . Thus $\sigma(\mathbf{K})\equiv\sigma(n_1, n_2, n_3)$ given in (2.9) is symmetric and even with respect to n_1, n_2, n_3 , and becomes real.

Let us use J to denote the set of the reciprocal lattice points at which $\sigma(\mathbf{K})$ has the same value owing to the above symmetry properties, then $\sigma(\mathbf{K})$ is specified by J and (2.8) can be written as

$$s(x_1, x_2, x_3) = \sum_J \sigma_J \zeta_J(x_1, x_2, x_3), \tag{3.2}$$

$$\zeta_J(x_1, x_2, x_3) = \sum_{(n_1, n_2, n_3) \in J} \exp[2\pi i(n_1x_1 + n_2x_2 + n_3x_3)]. \tag{3.3}$$

The set J itself can be specified by (n_1, n_2, n_3) such that $n_1 \geq n_2 \geq n_3 \geq 0$. Since \mathbf{K} which belongs to each J has the same value of $|\mathbf{K}|, \alpha(K)$ in (2.11) may be denoted by α_J . It should be noted, however, that two or more J have the same K for some of large K .

Equation (2.16) is

$$\ln \chi_s = \sum_J c_J \alpha_J \sigma_J^2 - \langle [1+s] \ln [1+s] \rangle, \tag{3.4}$$

where c_J is the number of \mathbf{K} which belongs to J , s is given in (3.2), and

$$\langle A \rangle = \int_0^1 dx_1 \int_0^1 dx_2 \int_0^1 dx_3 A(x_1, x_2, x_3). \tag{3.5}$$

Since $\langle s \rangle = 0$ and $\langle s^2 \rangle = \sum_J c_J \sigma_J^2$, we have

$$\langle [1+s] \ln [1+s] \rangle = \frac{1}{2} \sum_J c_J \sigma_J^2 + \sum_{l=3}^{\infty} \frac{(-1)^l}{l(l-1)} \langle s^l \rangle. \tag{3.6}$$

The generating functional (2.14) thus takes the form

$$f(\{\sigma_J\}; \{\alpha_J\}) = \frac{1}{2} \sum_J c_J (1-\alpha_J) \sigma_J^2 + \sum_{l=3}^{\infty} \frac{(-1)^l}{l(l-1)} \langle s^l \rangle, \tag{3.7}$$

and the equations to be solved for σ_J are

$$\frac{\partial f}{\partial \sigma_J} = c_J (1-\alpha_J) \sigma_J - \sum_{l=3}^{\infty} \frac{(-1)^l}{l} \langle \zeta_J s^l \rangle = 0. \tag{3.8}$$

The linear eigenvalue problem (2.7) is written as

$$(1-\alpha_J) \sigma_J = 0. \tag{3.9}$$

For a system of hard spheres in which $\phi(r) = \infty$ for $r < d$, and $\phi(r) = 0$ for $r > d$, we have from (2.3) and (2.11)

$$\alpha_J(\eta) = \lambda(\eta) [Kd \cos Kd - \sin Kd] / (Kd)^3, \tag{3.10}$$

where

$$\lambda(\eta) = 4\pi\rho d^3 g(d) = 6(\beta P/\rho - 1) \tag{3.11}$$

and

$$Kd = (12\pi^2\eta)^{1/3} (n_1^2 + n_2^2 + n_3^2)^{1/2}. \tag{3.12}$$

In these equations, η is the packing fraction defined by $\eta = (\pi/6)\rho d^3$. For the hard-sphere system, α_J is a function of the density only. The equation of state for the fluid phase is accurately approximated by the Carnahan-Starling equation¹²⁾

$$\beta P/\rho = (1 + \eta + \eta^2 - \eta^3) / (1 - \eta)^3 \tag{3.13}$$

and we can easily calculate $\alpha_J(\eta)$ as a function of η .

At low densities, $1 - \alpha_J$ is positive for all J , and $\sigma_J = 0$ for all J is the only solution of Eq. (3.8). When the density increases, $1 - \alpha_J$ for $J = (1, 1, 1)$, that is, for the nearest neighbor lattice points in the reciprocal lattice, is found to vanish at $\eta = \eta_c = 0.4228755\dots$, while the others remain positive. The five α_J for small K are shown in Fig. 1. For $J = (1, 1, 1)$ there is no degeneracy in the eigenvalue problem (3.9) and therefore $\eta = \eta_c$ is the bifurcation point for the solution with fcc symmetry. This point corresponds to that obtained by Raveché and Stuart.⁸⁾

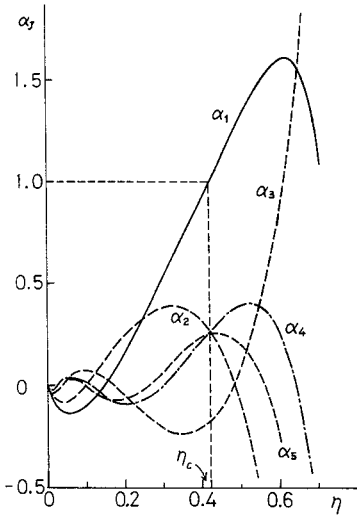


Fig. 1. The first five α_J as a function of η .

We now give the solution near the bifurcation point. Let us denote σ_J for $J = (1, 1, 1)$ by σ_1 and write s in (3.2) as $s = \sigma_1 \zeta_1 + \xi$. Then we have from (3.8)

$$\begin{aligned} c_J(1 - \alpha_J)\sigma_J = & (1/2)\sigma_1^2 \langle \zeta_1^2 \zeta_J \rangle + \sigma_1 \langle \zeta_1 \zeta_J \xi \rangle + (1/2)\langle \zeta_J \xi^2 \rangle \\ & - (1/3)\sigma_1^3 \langle \zeta_1^3 \zeta_J \rangle + \dots \end{aligned} \tag{3.14}$$

We put

$$\varepsilon = 1 - \alpha_1(\eta) = -\alpha_1'(\eta_c)(\eta - \eta_c) + \dots, \tag{3.15}$$

where the prime represents the derivative with respect to η and $\alpha_1'(\eta_c)$ is positive as known from Fig. 1. It can be assumed that the order of magnitude of σ_J other than σ_1 is smaller than σ_1 , because $1 - \alpha_J(\eta_c)$ is positive and not small

except (3.15). As is easily calculated, $\langle \zeta_1^2 \zeta_J \rangle = 24, 24$ and 8 for $J = (2, 0, 0), (2, 2, 0)$ and $(2, 2, 2)$ respectively, and $\langle \zeta_1^2 \zeta_J \rangle = 0$ otherwise. Thus, denoting σ_J for these J by $\sigma_2, \sigma_3, \sigma_5$ respectively, we have from (3.14)

$$\sigma_2 = \frac{2}{1-\alpha_2} \sigma_1^2, \quad \sigma_3 = \frac{1}{1-\alpha_3} \sigma_1^2, \quad \sigma_5 = \frac{1}{2(1-\alpha_5)} \sigma_1^2, \quad (3.16)$$

if we take only the leading terms into account, where the values $c_2=6, c_3=12$ and $c_5=8$ have been used.

Next we denote σ_J for $J = (3, 1, 1), (3, 3, 1)$ and $(3, 3, 3)$ by σ_4, σ_7 and σ_{10} respectively. Then we have $\langle \zeta_1^4 \rangle = 216, \langle \zeta_1^3 \zeta_4 \rangle = 216, \langle \zeta_1^3 \zeta_7 \rangle = 72, \langle \zeta_1^3 \zeta_{10} \rangle = 8$ and $\langle \zeta_1^3 \zeta_J \rangle = 0$ otherwise. Also $\langle \zeta_1 \zeta_2 \zeta_4 \rangle = (1/2) \langle \zeta_1 \zeta_3 \zeta_4 \rangle = \langle \zeta_1 \zeta_3 \zeta_7 \rangle = \langle \zeta_1 \zeta_5 \zeta_4 \rangle = \langle \zeta_1 \zeta_5 \zeta_7 \rangle = 24, \langle \zeta_1 \zeta_5 \zeta_{10} \rangle = 8$ and $\langle \zeta_1 \zeta_2 \zeta_7 \rangle = \langle \zeta_1 \zeta_2 \zeta_{10} \rangle = \langle \zeta_1 \zeta_3 \zeta_{10} \rangle = 0$. It thus follows from (3.14) and (3.16) that

$$\begin{aligned} (1-\alpha_4)\sigma_4 &= \sigma_1(\sigma_2 + 2\sigma_3 + \sigma_5 - 3\sigma_1^2) = \left[\frac{2}{1-\alpha_2} + \frac{2}{1-\alpha_3} + \frac{1}{2(1-\alpha_5)} - 3 \right] \sigma_1^3, \\ (1-\alpha_7)\sigma_7 &= \sigma_1(\sigma_3 + \sigma_5 - \sigma_1^2) = \left[\frac{1}{1-\alpha_3} + \frac{1}{2(1-\alpha_5)} - 1 \right] \sigma_1^3, \\ (1-\alpha_{10})\sigma_{10} &= \sigma_1\sigma_5 - \frac{1}{3}\sigma_1^3 = \left[\frac{1}{2(1-\alpha_5)} - \frac{1}{3} \right] \sigma_1^3, \end{aligned} \quad (3.17)$$

up to the leading terms, where the values $c_4=24, c_7=24$ and $c_{10}=8$ have been used. In this way we generally have

$$\sigma_J = O(\sigma_1^n), \quad (3.18)$$

where $n = \max\{|n_1|, |n_2|, |n_3|\}$.

In the lowest order of ε we thus have from (3.14) for $J = (1, 1, 1)$

$$c_1 \varepsilon \sigma_1 = [\langle \zeta_1^2 \zeta_2 \rangle \sigma_2 + \langle \zeta_1^2 \zeta_3 \rangle \sigma_3 + \langle \zeta_1^2 \zeta_5 \rangle \sigma_5] \sigma_1 - (1/3) \langle \zeta_1^4 \rangle \sigma_1^3,$$

namely, with the use of (3.16) and $c_1=8,$

$$[2\varepsilon - B(\eta_c) \sigma_1^2] \sigma_1 = 0, \quad (3.19)$$

where

$$B(\eta_c) = \frac{12}{1-\alpha_2(\eta_c)} + \frac{6}{1-\alpha_3(\eta_c)} + \frac{1}{1-\alpha_5(\eta_c)} - 18. \quad (3.20)$$

We have $\alpha_2(\eta_c) = 0.2629, \alpha_3(\eta_c) = -0.1757, \alpha_5(\eta_c) = 0.2461$ from (3.10), (3.11), (3.12) and (3.13), hence $B(\eta_c) = 4.710$. For $\varepsilon < 0$ ($\eta > \eta_c$), $\sigma_1 = 0$ is the only solution of (3.19). For $\varepsilon > 0$ ($\eta < \eta_c$) we have another solution

$$\sigma_1^2 = [2\alpha_1'(\eta_c) / B(\eta_c)] (\eta_c - \eta) = 1.717 (\eta_c - \eta), \quad (3.21)$$

where $\alpha_1'(\eta_c) = 4.044$ has been used. By (3.16) we have $\sigma_2 = \sigma_3 = \sigma_5 = 0$ for $\eta > \eta_c$, and

$$\sigma_2 = 4.658 (\eta_c - \eta), \quad \sigma_3 = 1.460 (\eta_c - \eta), \quad \sigma_5 = 1.139 (\eta_c - \eta) \quad (3.22)$$

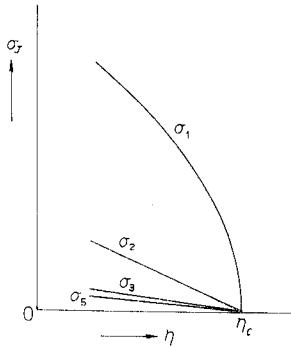


Fig. 2. Schematic representation of branching near the bifurcation point η_c .

for $\eta < \eta_c$. Figure 2 shows the way in which this crystalline solution branches off from the bifurcation point. Since the negative solution $\sigma_1 = -[2\alpha_1'(\eta_c)/B(\eta_c)]^{1/2}(\eta_c - \eta)^{1/2}$ merely implies a change in origin from the point $(0, 0, 0)$ to the point $(1/2, 1/2, 1/2)$, we may only consider the positive solution.

In this connection it may be stated that the generating functional f is invariant under the transformation $\sigma_J \rightarrow \theta\sigma_J$, where θ is -1 for J with odd n_i , called an odd J , and $+1$ for J with even n_i , called an even J . This follows immediately from $\zeta_J(x_1 - 1/2, x_2 - 1/2, x_3 - 1/2) = \theta\zeta_J(x_1, x_2, x_3)$. In the expansion as in (3.7) we may use the fact that $\langle H\zeta_J \rangle = \langle H\theta\zeta_J \rangle$. Therefore, corresponding to one solution $\{\sigma_J\}$ of Eq.

(3.8), there exists another solution $\{\theta\sigma_J\}$, both being physically equivalent.

If we solve Eq. (3.8) with respect to σ_J other than σ_1 for a fixed σ_1 , σ_J for even J becomes an even function of σ_1 , while σ_J for odd J becomes an odd function, because $J = (1, 1, 1)$ is in itself odd. When we insert these σ_J into f , f becomes an even function of σ_1 . Near η_c we have

$$f = 4\epsilon\sigma_1^2 - B(\eta_c)\sigma_1^4 + \dots \tag{3.23}$$

Since $B(\eta_c) > 0$, the solution obtained above gives a maximum of f :

$$f = 4\epsilon^2/B(\eta_c) = 4[\{\alpha_1'(\eta_c)\}^2/B(\eta_c)](\eta_c - \eta)^2. \tag{3.24}$$

§ 4. Discussion

We have shown that the branch of the solution with fcc symmetry grows in a direction of decreasing η near the bifurcation point η_c . This is not surprising, but merely signifies that η_c is not a point of second-order phase transition. It may also be inferred from this that there exist at least two finite solutions to the nonlinear equation (3.8) for the density region $\eta_{lb} < \eta < \eta_c$, the two solutions being congruent with each other at the lower bound η_{lb} .

Kirkwood and Monroe¹⁾ made the assumption that every α_J vanishes except α_1 and then found that for $\alpha_1 < 0.973$ the only solution is $\sigma_1 = 0$, while for $\alpha_1 > 0.973$ there were, in addition, two positive solutions. As they did, it is convenient to use the expression (2.12) for χ_s on this assumption. Thus we have

$$\chi_s = \langle \exp(\alpha_1\sigma_1\zeta_1) \rangle = \sum_{l=0}^{\infty} \frac{[(2l)!]^2}{(l!)^6} (\alpha_1\sigma_1)^{2l}, \tag{4.1}$$

and σ_1 is determined by

$$\partial \ln \chi_s / \partial \sigma_1 - 8\alpha_1\sigma_1 = 0. \tag{4.2}$$

The bifurcation point of (4.2) is determined by $\alpha_1=1$, as is also the case in (3.8). The solution σ_1 as a function of α_1 is shown in Fig. 3. For the hard sphere system, $\alpha_1=0.9730$ corresponds to $\eta=0.4162$. Hence we have $\eta_{lb}=0.4162$ in this approximation.

It should be noted that the above assumption does not imply that all σ_J other than σ_1 vanish. Indeed, we have from (2.10) $\chi_s(1+s) = \exp(\alpha_1\sigma_1\zeta_1)$, and therefore from (2.9)

$$c_J\sigma_J = \chi_s^{-1} \langle \zeta_J \exp(\alpha_1\sigma_1\zeta_1) \rangle. \quad (4.3)$$

Near the bifurcation point we may use the expansion $\ln \chi_s = 4(\alpha_1\sigma_1)^2 + (\alpha_1\sigma_1)^4 + \dots$, and have from (4.2) $\sigma_1^2 = 2\varepsilon$, which agrees with the solution obtained from (3.19) if we put $\alpha_2 = \alpha_3 = \alpha_5 = 0$. Using this σ_1 , we have from (4.3) $\sigma_2 = 2\sigma_1^2$, $\sigma_3 = \sigma_1^2$, $\sigma_5 = (1/2)\sigma_1^2$, $\sigma_4 = (3/2)\sigma_1^3$, $\sigma_7 = (1/2)\sigma_1^3$ and $\sigma_{10} = (1/6)\sigma_1^3$, which correspond to (3.16) and (3.17) with $\alpha_2 = \alpha_3 = \alpha_5 = \alpha_4 = \alpha_7 = \alpha_{10} = 0$. The leading power of σ_1 in σ_J is given by the least n such that $\langle \zeta_J \zeta_1^n \rangle \neq 0$, which is nothing but n given in (3.18). A more detailed study including the finite solutions distant from the bifurcation point will be reported in a succeeding paper.

The generating functional f defined by (2.14) is a free energy-like functional of $s(\mathbf{r})$ for given ρ and T . If we suppose that f is an excess Helmholtz free energy owing to a nonvanishing ordered structure [$\sigma(\mathbf{K}) \neq 0$], the ordered state corresponding to the solution near η_c obtained in § 3 will be unstable, because as shown in (3.23) f is maximum with respect to σ_1 . It is therefore impossible that the system takes this state without any external constraints. By the use of f given in (3.24), which is supposed here to be the excess free energy per particle multiplied by β , the excess pressure of this unstable ordered state is given by

$$\beta P_e / \rho = \eta \partial f / \partial \eta = -8\eta_c [\{ \alpha_1'(\eta_c) \}^2 / B(\eta_c)] (\eta_c - \eta) + \dots \quad (4.4)$$

Figure 4 shows schematically the manner in which the pressure of this state branches off from the pressure of fluid state.

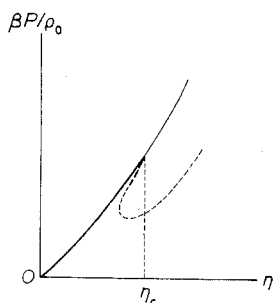


Fig. 4. One of the possible manners of branching in the pressure-density isotherm (schematic). $\beta P / \rho_0$ is the reduced pressure, $\rho_0 = \sqrt{2}/d^3$ being the closest packing density. The broken line represents the pressure given by (4.4) and the dotted line shows a continuous extension to the stable solid.

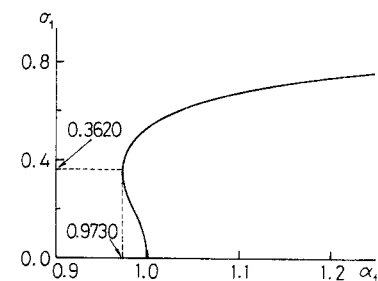


Fig. 3. Solution σ_1 as a function of α_1 on the assumption that $\alpha_J=0$ for all J except $J=(1,1,1)$.

It should be pointed out, however, that on this supposition for f , η_c becomes the limit of metastability of the fluid phase. Therefore η_c must be larger than the freezing density η_f . Computer experiments, however, indicate that $\eta_f=0.494$,¹⁸⁾ larger than the present η_c . This unfitness may be ascribed to the above supposition for f . Unfortunately, we are presently not aware of the expression for the free energy in terms of $s(\mathbf{r})$ suitable to the initial assumption (1.1). We should also remember that the basic equation in § 2 itself is an approximation for crystalline states.

As found in an Ising model or some others, the so-called molecular field approximation predicts a phase transition temperature which is too high. Since the ordered state in the present case appears at high densities, a too low freezing density corresponds to a too high phase transition temperature. In this sense the treatment mentioned just above is similar to the molecular field approximation, though a force field is absent originally in the hard sphere system.*³⁾ For a one-dimensional hard rod system, the basic equation in § 2 also has a bifurcation point for a crystalline solution.⁹⁾ Therefore, the supposition that f is the free energy on the assumption (1.1) leads incorrectly to a phase transition in this one-dimensional system. This is also an erroneous aspect similar to the molecular field approximation.

Another way²⁾ of calculating thermodynamic properties is to use the pressure equation

$$\beta P/\rho = 1 - (\beta/6\rho V) \int \int_V r_{12} \phi'(r_{12}) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (4.5)$$

On the assumption (1.1) we have from (4.5)

$$\beta P_e/\rho = (1/6) \sum_J c_J \beta_J \sigma_J^2 \quad (4.6)$$

for the excess pressure due to non-vanishing σ_J , where

$$\beta_J = \beta(|\mathbf{K}|) = -\beta\rho \int d\mathbf{r} r \phi'(r) g(r) e^{-i\mathbf{K}\cdot\mathbf{r}} \quad (4.7)$$

and for the hard sphere system

$$\beta_J(\eta) = \lambda(\eta) \sin(Kd)/Kd. \quad (4.8)$$

We have $\beta_1(\eta_c) = 0.6594$, and for the solution (3.21),

$$\beta P_e/\rho = [8\beta_1(\eta_c) \alpha_1'(\eta_c)/3B(\eta_c)] (\eta_c - \eta) + \dots, \quad (4.9)$$

which is positive for $\eta < \eta_c$ and is different from (4.4). This may be considered

*³⁾ Brout¹⁴⁾ obtained an integral equation of the same form as (2.1) from the point of view of molecular field theory. The kernel in his equation is given by $\phi(r) = \phi(r)g(r)$ or in a somewhat devised version $\psi(r) = \phi_1(r)g_h(r)$ instead of (2.3), where $g_h(r)$ is the hard-sphere correlation function and $\phi_1(r)$ is the perturbation potential added to an assumed hard-sphere potential. Therefore, his theory does not apply to the pure hard sphere system as it stands.

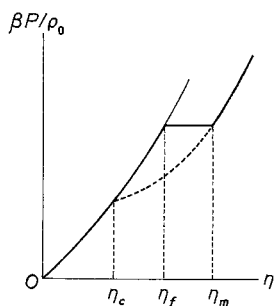


Fig. 5. Metastable extension of the stable solid proposed by Raveché and Stuart^{8),9)} is shown by the dotted line. The bold line represents the stable fluid and solid, η_f and η_m being the freezing and melting densities, respectively. The computer experiment indicates that $\eta_f=0.494$ and $\eta_m=0.545$.¹³⁾

to indicate an inconsistency in the approximations.

In any case, however, the pressure corresponding to the solution with fcc symmetry branches off from η_c in a direction of decreasing η near η_c . Therefore, if we draw a curve representing a continuous extension from η_c to the stable solid, there exists necessarily a portion of negative compressibility on the curve. This contradicts Raveché and Stuart's interpretation^{8),9)} that the bifurcation point η_c represents the limit of metastability of the crystalline phase. The present study asserts that the limit of metastability of the crystalline phase may be the point at which the compressibility becomes negative. They have considered that the metastable extension of the stable solid may be represented by the dotted curve depicted in Fig. 5. For such an isotherm, however, we can show that the Helmholtz free energy of the solid branch f_s is less than that of the fluid branch f_f :

$$f_s(v) - f_f(v) = \int_v^{v_c} (P_s - P_f) dv < 0 \quad \text{for } v < v_c, \quad (4.10)$$

where P_s is the pressure of the solid branch, P_f is that of the fluid branch, $v=1/\rho$, and v_c is the volume at η_c . The point η_c therefore becomes a point of second-order phase transition.

Finally, we should note that the relation between $\rho(\mathbf{r})$ and the direct correlation function $C(\mathbf{r}_1, \mathbf{r}_2)$ derived by Lovett, Mou and Buff¹⁵⁾ can also be cast into the form of Eq. (2.1) if we assume that $C(\mathbf{r}_1, \mathbf{r}_2) = C(r_{12})$. In this case the kernel ψ is given by

$$-\beta\psi(r) = C(r) \quad (4.11)$$

and the bifurcation point, if it exists, is a metastability limit of the fluid phase in the sense that at this point the liquid structure factor becomes infinite for a certain value of wave vectors. Lovett¹⁰⁾ has shown that the hard sphere fluid does not become unstable at any density when the solution of the Percus-Yevick integral equation is used for $C(r)$. This does not necessarily mean that no instability will be found for the hard sphere fluid, because the Percus-Yevick equation is itself an approximation. Since the metastability limit of the fluid phase is not a point of second order phase transition, if the bifurcation point of the solution with

fcc symmetry exists for the kernel (4.11), the new solution to the nonlinear integral equation will also grow in a direction of decreasing density near the bifurcation point. The crystalline state for this solution will probably be unstable. However, the question of whether such an instability can actually occur in a fluid is left open at present.

In order to develop a molecular theory of freezing satisfactorily, further studies will be required which include the pursuit of the finite solutions with crystalline symmetry and the density change on freezing in addition to the stability analysis of the single phase.

References

- 1) J. G. Kirkwood and E. Monroe, *J. Chem. Phys.* **9** (1941), 514.
- 2) H. S. Green, *The Molecular Theory of Fluids* (North-Holland, Amsterdam, 1952), p. 108.
- 3) B. Jancovici, *Physica* **31** (1965), 1017; **32** (1966), 1663.
- 4) J. D. Weeks, S. A. Rice and J. J. Kozak, *J. Chem. Phys.* **52** (1970), 2416.
- 5) J. J. Kozak, S. A. Rice and J. D. Weeks, *Physica* **54** (1971), 573.
- 6) I. S. Cheng and J. J. Kozak, *J. Math. Phys.* **14** (1973), 632.
- 7) H. J. Raveché and C. A. Stuart, *J. Chem. Phys.* **63** (1975), 1099.
- 8) H. J. Raveché and C. A. Stuart, *J. Chem. Phys.* **65** (1976), 2305.
- 9) H. J. Raveché and C. A. Stuart, *J. Math. Phys.* **17** (1976), 1949.
- 10) R. Lovett, *J. Chem. Phys.* **66** (1977), 1225.
- 11) T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), Chap. 6.
- 12) N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51** (1969), 635.
- 13) W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **49** (1968), 3609.
- 14) R. Brout, *Physica* **29** (1963), 1041; **30** (1964), 459. See also, R. Brout, *Phase Transitions* (Benjamin, New York, 1965).
- 15) R. Lovett, C. Y. Mou and F. P. Buff, *J. Chem. Phys.* **65** (1976), 570.