Fusion and State Equation of Simple Liquids. I. Derivation of the Expressions for State Equation and Free Energy

By Kunihiko KIGOSHI

(Received June 22, 1950)

1. Introduction

The order-disorder theory of melting proposed by Lennard-Jones and Devonshire(1) promoted not only the theories of the fusion process but also the general theory of liquids based on the hole theory. From this stand point recently Toda(2) and Ono(3) clarified the critical phenomena. But in these theories the essential difficulty of the estimation of the intermolecular interaction energy is inevitable. A fair development of the theory by Kirkwood and Monroe(4) lighted a new way to the fusion process in which the liquid-solid transition was attributed to the vanishing of periodic distribution of molecules. Also in the case of Born's theory,(5) treating the fusion process as an abrupt change of rigidity, the change of a special character of solid and liquid phases was used for the base of fusion theories.

I will present the statistical theory of liquid to treat melting as a phase equilibrium of solid and liquid states and to find the fusion parameters in terms of intermolecular forces. For an estimation of the molecular interaction energies in liquid states an earlier theory of Lennard-Jones and Devonshire(6) gave a reasonable approximation using the spherical cells around each molecule, but the results obtained did not agree so well with experiments. The source of the disagreements may be considered that the number of the nearest neighbor molecules Z was taken as 12 in each molecule and the formation of cells around the molecules restricts the molecular motion too firm in the expanded state. Therefore the free volume calculated by this method is not satisfactory but when we use the number Z as a parameter it may give a good approximation near the melting point.

In the liquid state the distances between the nearest neighbors are nearly equal to the equilibrium distance detween two molecules. Different characters of the intermolecular potential for various substances would give a big influence to the physical properties of the liquids. The use of the inversepower potential might not be satisfactory to express the details of the potential functions, but for simplicity we use the following Lennard-Jones type intermolecular potential,

$$\mathcal{E}(r) = \mathcal{E}_0\left[\frac{6}{n-6}\left(\frac{r_0}{r}\right)^n - \frac{n}{n-6}\left(\frac{r_0}{r}\right)^6\right]. \quad (1)$$

The numerical calculation for the state equation is performed in the case of $n = 12$. As to the fusion process it is possible to discuss what influences will be given on the calculated melting temperature by the variation of the intermolecular potential.

2. Assumptions Regarding the Molecular Arrangements in the Liquids

In the solid state the molecular arrangement is determined by its lattice constants. In the liquid state we can know only about the radial distribution function around one molecule by X-ray experiments. We cannot expect the difinite solid like molecular arrangement around each molecule in the liquid, but it may be considered as a little displaced from the regular arrangement. We may consider the nearest neighbors around one molecule as in the case of solids, however the number of the nearest neighbors may differ in each molecule. Among N molecules $NP(Z)$ molecules have Z nearest neighbors and we assume that the number of the nearest neighbors around one molecule is independent of the arrangements of the molecules farther than the nearest neighbors. We can obtain only one function $P(Z)$ for any given molecular arrangement, although there exists a definite number of possible molecular arrangements which give a same function $P(Z)$. Since the density fluctuations in a dense system are small, the actual molecular arrangements may be derived by a small displacement of each

---

(1) J. E. Lennard-Jones, and A. F. Devonshire, *Proc. Roy. Soc.* A, **169**, 317 (1939); **170**, 464 (1939).

(2) M. Toda, *BUSSEIRON KENKYU* (in Japanese), No. 10, 1 (1948).

(3) S. Ono, *Memoirs of the Faculty of Engineering, Kyushu Univ.*, **10**, 195 (1947); S. Ono, and T. Sato, *J. Phys. Soc. Japan.*, **4**, 103 (1949).

(4) J. G. Kirkwood, E. Monroe, *J. Chem. Phys.*, **9**, 514 (1941).

(5) M. Born, *J. Chem. Phys.*, **7**, 519 (1939).

(6) J. E. Lennard-Jones, and A. F. Devonshire, *Proc. Roy, Soc.* A, **163**, 53 (1937); **165**, 1 (1938).

molecule situated on simple lattice points. When we neglect the differences of molecular arrangements caused by thermal motion of each molecule, we may suppose that almost all of the molecular arrangements are expressed by the assignments of the number Z to these simple lattice points. If we assume the unique determination of the arrangement by an assignment of Z on the N lattice points, we get the number of different molecular arrangements for a given distribution function $P(Z)$ as follows,

$$N\,!\,/\Pi_Z(NP(Z)!)\,, \tag{2}$$

which is a number of possible ways of arranging the different values of Z on the localized N points.

When we consider the molecular arrangement neglecting the thermal motion, in the solid state distances between the two nearest neighbors take a definite value r but in the liquid state the molecular arrangement determined by the function $P(Z)$ makes it impossible to take the same definite value for these distances. The distribution of the value r depends on the function $P(Z)$ in a complicated manner, but near the melting point owing to the small variation of $P(Z)$ we may neglect it. Near the critical point the result of numerical calculation shows the smallness of the effects of this distribution on the physical property. Therefore the dependence of $P(Z)$ on the distribution of r may be neglected without a great error and the next simple function for an expression of this distribution is adopted.

$$\left.\begin{aligned} f(R^*) &= \frac{3}{4}R^{-1}\delta^{-3}(\delta^2-(1-R^*/R)^2), \\ R^* &= r/r_0, \qquad R=[R^*]_{AV}, \end{aligned}\right\} \tag{3}$$

where $f(R^*)\,\mathrm{d}R^*$ gives the probability of finding R^* between R^* and $R^*+\mathrm{d}R^*$, and R^* is limited in the range of $R(1-\delta)\leq R^*\leq R(1+\delta)$. The average of R^* in this domain is R and the expression (3) takes a maximum in the case when $R^*=R$.

Eisenstein and Ginglich(7) have shown the radial distribution of the nearest neighbors of liquid argon by the measurements of the X-ray scattering. In order to correspond only formally the expression (3) to the radial distribution thus obtained, we make δ equal to about $1/5$. To compare the experimental results with our expression of the radial distribution we have to consider that the actual radial distribution of the nearest neighbors is obtained by the superposition of thermal motion on the function $f(R^*)$. According to Lindemann(8) the thermal motion of a molecule in a solid may be considered as a vibration with the amplitude of about $r/10$ at the melting point. In the liquid state this amplitude will become more or less larger. The estimation of this value near the melting point using the Lennard-Jones' cage model shows that the amplitude is smaller than $r/5$. Therefore the agreement between the experimental results of Eisenstein and Ginglich and the radial distribution expected by the superposition of this sort of thermal motion on Eq. (3) may be attained by assuming $\delta=0.10\sim0.15$. This result with respect to the order of magnitude of δ will be confirmed in Part II relating the discussions on the melting points.

3. The Partition Function of Liquid

The method of construction of partition function adopted here is based on the molecular arrangement as mentioned in the preceding section. It may be said that the most probable molecular distribution given by a function $P(Z)$ has a predominant contribution to the partition function. Therefore we may take the partition function for an assembly of the molecular arrangements determined by this function $P(Z)$. We shall use the approximation that the partition function of a whole assembly can be expressed as a product of the partition function of each molecule having Z nearest neighbors and the number of possible molecular arrangements given by expression (2). The thermal motion of each molecule is considered in a cell with the potential field of its immediate neighbors. We then adopt the following form for the partition function of the liquid state:

$$\begin{aligned}\Omega &= (2\pi mkT/h^2)^{3N/2}\frac{N\,!}{\Pi_Z(NP(Z)!)} \\ &\quad\times[\Pi_Z v_f(Z)^{NP(Z)}]\exp{(-U/kT)}J(T)^N, \end{aligned} \tag{4}$$

where $(2\pi mkT/h^2)^{3/2}v_f(Z)J(T)$ is a partition function of a molecule in a cell which consists of Z nearest neighbors situated uniformly on the spherical shell with radius Rr_0. $J(T)$ denotes the partition function for all the internal degrees of freedom and U is a total potential energy of N molecules when each molecule is at the center of its cell. When we neglect the small variation of R^* from the mean value R, free volume v_f may be written as following as has been obtained by Lennard-Jones and Devonshire.(6)

---

(7) A. Eisenstein and N. S. Gingrich, *Phys. Rev.*, **58**, 307(1940).

(8) F. A. Lindemann, *Physik. Zeit.* **11**, 609(1910).

$$\left.\begin{aligned} v_f(Z) &= 2\pi(r_0R)^3\int y^{1/2} \\ &\quad\times\exp(-\zeta R^{-12}l(y)+2\zeta R^{-6}m(y))\mathrm{d}y, \\ l(y) &= (1+12y-25.2y^2 \\ &\quad+12y^3+y^4)(1-y)^{-10}-1, \\ m(y) &= (1+y)(1-y)^{-4}-1, \end{aligned}\right\} \quad (5)$$

where the energy of interaction between a pair of molecules is assumed as follows,

$$\mathcal{E}(r) = \mathcal{E}_0(R^{-12}-2R^{-6}).$$

The results of numerical integration of the above expression for various combinations of different values of Z and R agrees with the following expression.

$$v_f = 2\pi(r_0R)^3\exp\{l_0+l_1R^{-6}MZ\zeta \\ +\ln[1+\exp(\beta_0+\beta_1R^{-6}+\beta Z\zeta)]\}, \quad (6)$$

where

$$\left.\begin{aligned} M &= (h_2R^{-12}+h_1R^{-6}+h_0)^{1/2} \\ &\quad+m_1R^{-6}+m_0, \quad \zeta=\mathcal{E}_0/kT, \\ l_0 &= -2.417, & m_0 &= -0.03868, \\ \beta_0 &= -0.6908, & \beta &= -0.2947, \\ l_1 &= -5.225, & m_1 &= -0.1851, \\ \beta_1 &= 2.993, & h_0 &= 0.02138, \\ h_1 &= -0.06566, & h_2 &= 0.07635. \end{aligned}\right\} \quad (6')$$

The differences between two expressions (5) and (6) are smaller than 2% within the range of $12 \geq Z \geq 4$ and $1.0 \geq R^{-6} \geq 0.1$. Even for the more general molecular interaction given by expression (1), v_f may be also expressed well by (5) using different numerical coefficients.

An exact evaluation of the term U is very difficult, but we can estimate it under the assumption of the solid like molecular arrangements in the liquid state. We denote by $\psi(Z)$ the potential energy of one molecule in the ideal arrangement of molecules with the same number of Z nearest neighbors and with the same distance r_0R between the two nearest neighbors. If we neglect the distribution of R^*, U may be written for the given function $P(Z)$ as following,

$$\sum_Z \frac{N}{2}\psi(Z, R)P(Z), \quad (7)$$

where

$$\psi(Z, R) = \frac{\mathcal{E}_0}{n-6}(6\varphi_rR^{-n}-n\varphi_aR^{-6}), \quad (7')$$

φ_r and φ_a are the functions of Z and they may be approximately obtained by considering the ideal crystal lattices *i.e.* in the cases of $Z=12$, 8, 6 and 4, or may be obtained also from the Bernal's calculations(9) on the values of Z and R for the molecules farther than the nearest neighbors. In the case of $n=12$, the rough approximation for φ_a and φ_r may be given by

$$\varphi_a = Z, \qquad \varphi_r = Z+2. \quad (7'')$$

The approximation of these linear expressions becomes bad at the small value of Z. Fortunately the terms with small values of Z give only small effects on free energy and the state equation of liquid state, and we can use expression (7″) for numerical calculations in Part II. The consideration on the distribution of R^* given by expression (3) may be introduced by a simple integral as follows, and we can obtain the approximate formula,

$$\begin{aligned} U &= \sum_Z P(Z)\frac{N}{2}\int_{R(1-\delta)}^{R(1+\delta)}f(R^*)\psi(Z, R^*)\mathrm{d}R^* \\ &= \sum_Z P(Z)\frac{N}{2}(\psi(Z, R)+(R^2\delta^2/10) \\ &\quad\times\mathrm{d}^2\psi/\mathrm{d}R^2+0(\delta^4)). \end{aligned} \quad (8)$$

This method of approach to the actual distribution of molecules includes the effects of the molecular distributions farther than the nearest neighbors. Therefore in equation (8) we have taken into considerations on the second and the third ······ nearest neighbors which have respectively the mean distances from the center R_1r_0 and R_2r_0 ······. And they have the radial distributions expressed by Eq. (3) with the alterations of R to R_1 and R_2 ······.

4. Free Energy and State Equation

When we substitute Eq. (8) in Eq. (4) and neglecting the last small term of the order δ^4, we obtain by usual process the free energy

$$\begin{aligned} F/N &= -kT\ln\Omega/N = -kT\frac{3}{2} \\ &\quad\times\ln[(2\pi mkT)/h^2]-kT\ln J \\ &\quad+kT\sum_Z[(\mathcal{E}_0/2kT)\Psi(Z, R) \\ &\quad-\ln v_f+\ln P(Z)]P(Z), \end{aligned} \quad (9)$$

$$\begin{aligned} \text{where } \Psi(Z, R) &= \psi(Z, R)/\mathcal{E}_0 \\ &\quad+(R^2\delta^2/10\mathcal{E}_0)\mathrm{d}^2\psi/\mathrm{d}R^2 \\ &= \frac{1}{n-6}[6\varphi_r(1+\delta^2n(n+1)/10)R^{-n} \\ &\quad-n\varphi_a(1+4.2\delta^2)R^{-6}]. \end{aligned} \quad (9')$$

---

(9) J. D. Bernal, *Trans. Faraday Soc.*, **32**, 27 (1936).

To obtain the pressure from this free energy, we have to know the volume as a function of R and $P(Z)$. Although the dependence of R on volume is easily supposed as proportional to $(r_0R)^3$ but that of $P(Z)$ is more complicated. A simplified treatment about the face centered cubic lattice with holes derives the dependence of $P(Z)$ as follows. Suppose a molecule and a hole occupy the same volume v_u in liquid and their positions in space form a slightly deformed face centered cubic lattice. Then a molecule with Z nearest neighbors should have 12-Z holes around it. When summing up holes around each molecule we count the same hole Z_h times, where Z_h is a mean number of molecules around a hole. Thus the total number of hores N_h is

$$\begin{aligned} N_h &= (12\,N - \sum_Z ZNP(Z))/Z_h \\ &= N(12 - [Z]_{AV})/Z_h\,. \end{aligned}$$

Therefore in the case of $N_h \ll N$

$$\begin{aligned} Nv = V &= (N + N_h)v_u \\ &= 12v_uN/[Z]_{AV} = g(r_0R)^3N/[Z]_{AV}. \quad (10) \end{aligned}$$

In this equation we put Z_h as equal to $[Z]_{AV}$. The constants g is determined as $g = 8.49$ using the special case of the face centered lattice, but this value will increase more or less at the expanded state in virtue of the nature of this approximation.

The distribution function $P(Z)$ is determined by the condition that Ω becomes maximum, *i.e.* by the equation $\delta F = 0$ with the variation of $P(Z)$ keeping T, P and V constant. From this condition we get

$$\begin{aligned} 0 = \delta F = \sum_Z \delta P(Z)&[\ln P(Z) \\ &+ (\varepsilon_0/2kT)\Psi - \ln v_f] \\ &+ \sum_Z P(Z)\left[(\varepsilon_0/kT)\frac{\partial\Psi}{\partial R} - \frac{\partial \ln v_f}{\partial R}\right]\delta R, \end{aligned} \tag{11}$$

where δR is a variation resulted from $\delta P(Z)$ and it is obtained by Eq. (10) taking the variation at constant volume, *i.e.*

$$\delta R = (v/3r_0^3R^2g)\sum_Z Z\delta P(Z). \tag{12}$$

Lagrange's method of elimination applied to Eqs. (11), (12) and $\sum_Z \delta P(Z) = 0$ results

$$\begin{aligned} \lambda = \ln P(Z) &+ \varepsilon_0\Psi/2kT - \ln v_f \\ &+ (Zv/3r_0^3R^2g)\sum_Z\left[(\varepsilon_0/2kT)\frac{\partial\Psi}{\partial R}\right. \\ &\left. - \frac{\partial \ln v_f}{\partial R}\right]P(Z), \end{aligned} \tag{13}$$

where λ is a constant. By the differentiation of free energy with respect to volume we can obtain the state equation

$$\begin{aligned} -P/kT = \sum_Z&\left[\frac{\partial P(Z)}{\partial v}(\ln P(Z) + \Psi\,\varepsilon_0/2kT\right. \\ &\left. - \ln v_f)\right] + \sum_Z P(Z)\frac{\partial R}{\partial v}\left[(\varepsilon_0/2kT)\frac{\partial\Psi}{\partial R}\right. \\ &\left. - \frac{\partial \ln v_f}{\partial R}\right]. \end{aligned} \tag{14}$$

The differentiation of Eq. (10) with respect to volume leads the term $\partial R/\partial v$ in the above expression

$$\frac{\partial R}{\partial v} = (v/3r_0^3R^2g)\sum_Z Z\frac{\partial F(Z)}{\partial v} + R/3v. \tag{15}$$

Using Eqs. (13) and (15) we can rewrite Eq. (14) in the form,

$$\begin{aligned} -P/kT &= (R/3v)\sum_Z P(Z) \\ &\times\left[(\varepsilon_0/2kT)\frac{\partial\Psi}{\partial R} - \frac{\partial \ln v_f}{\partial R}\right]. \end{aligned} \tag{16}$$

From Eqs. (13) and (16) we can obtain the explicit expression for $P(Z)$ as follows,

$$P(Z) = A\exp\left(\ln v_f - \frac{\zeta}{2}\Psi + ZR^{-3}\xi\zeta\right), \tag{17}$$

where

$$\xi = Pv^2/r_0^3g\varepsilon_0\,.$$

The normalization condition, $\sum_Z P(Z) = 1$ defines the constant A and we obtain

$$A^{-1} = \sum_Z \exp\left(\ln v_f - \frac{\zeta}{2}\Psi + \xi\zeta ZR^{-3}\right). \tag{18}$$

Using the Eqs. (18) and (17) we can rewrite Eq. (9)

$$\begin{aligned} F/N = -kT[&\ln[(2\pi mkT)^{3/2}/h] \\ &+ \ln J - \ln A - [Z]_{AV}R^{-3}\xi\zeta]. \end{aligned} \tag{19}$$

When we assume the molecular interation of the expression (1) with $n = 12$, we can use v_f given by Eq. (6). The function Ψ becomes

$$\begin{aligned} \Psi(Z,\,R) &= Z(1 + 15.6\delta^2)R^{-12} \\ &- (2Z + 4)(1 + 4.2\delta^2)R^{-6}, \end{aligned} \tag{20}$$

using the expressions (7′) and (7″). Substitutions of Eqs. (20), (5) and (17) into Eq. (16) yield the state equation in terms of ξ, ζ and R.

$$\zeta = \frac{1 - 2l_1R^{-6} - 2\beta_1R^{-6}Y/(Y+X\exp(-\alpha))}{2([Z]_{AV}+2)(1+4.2\delta^2)R^{-6} - 2[Z]_{AV}(1+15{\cdot}6\delta^2)R^{-12} - (R/3)(\mathrm{d}M/\mathrm{d}R)[Z]_{AV} + R^{-3}[Z]_{AV}\xi}, \tag{21}$$

where

$$\left.\begin{aligned}
[Z]_{AV} &= \frac{[X_Z + Y_Z\exp(-\alpha)]}{[X + Y\exp(-\alpha)]},\\
X &= \sum_Z \exp(\rho Z\zeta),\\
Y &= \sum_Z \exp((\rho+\beta)Z\zeta),\\
X_Z &= \sum_Z Z\exp(\rho Z\zeta),\\
Y_Z &= \sum_Z Z\exp((\rho+\beta)Z\zeta),\\
\rho &= (1+4.2\delta^2)R^{-6}\\
&\quad -\frac{1}{2}(1+15.6\delta^2)R^{-12}\\
&\quad +\xi R^{-3} + M,
\end{aligned}\right\} \tag{22}$$

$$\alpha = \beta_0 + \beta_1R^{-6}.$$

The summations in above expressions are extended to the probable integral values of Z.

Numerical calculations of state equation (21) and comparison with experimental values about critical data are given in Part II.

Geochemical Laboratory, Meteorological
Research Institute, Tokyo, Japan