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A New Theory of Melting at High Pressures

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As an improvement of the significant structure theory, a new partition function of monatomic liquid was derived:

$$Z_l(T, V_l) = \left\{\prod_{i=1}^{3N_v}\left[2\sinh\left(\frac{h\nu_i}{2kT}\right)\right]^{-1}\right\}\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{eV_f}{N_t}\right\}^{N_t}\exp\left\{-\frac{\Phi_l(V_l)}{kT}\right\}$$

where $3N_v$ and $3N_t$, ($N_v+N_t=N$; Avogadro number), are the numbers of freedom in vibrational and translational motions, respectively, ν_i the i-th normal vibration in the vibrational motion, m the mass of molecule, V_f the free volume of liquid, and $\Phi_l(V_l)$ the configurational potential energy of liquid. Melting of argon at high pressures is successfully interpreted by means of the partition function.

Theoretical interpretations of melting in terms of the partition function have been made by a number of investigators.[1-3] Of the theories suggested, few can give a satisfactory quantitative description of melting. This is connected partly with the confused state of theory of melting and partly with the inadequacy and/or the mathematical difficulty of various proposed partition functions of liquid. A satisfactory interpretation of melting seems to be achieved by the finding of a good partition function for liquid.

Though the significant structure theory of liquid developed by Eyring and his co-workers[4] yields good numerical agreement with experiment for a number of the thermodynamic properties of many types of liquids, Tuerpe and Keeler[5] have shown that it does not give a satisfactory description of melting phenomenon at high pressures. The theory, however, suggests two important facts: (1) the liquid consists of both vibrational and translational degrees of freedom, and (2) the partition function of liquid must be analogous to that of solid near the melting point and to that of gas toward the gas region.

Bearing these concepts in mind it seems worthwhile to investigate the possibility of deriving the partition function of liquid which is applicable to the melting process at high pressures. The purposes of this study are to present a new partition function of liquid differing somewhat from Eyring's one,[4] and to apply it to the melting phenomenon, in particular the melting of argon at high pressures.

Theoretical

Adopting the concept of the significant structure theory[4] that both vibrational and translational degrees of freedom coexist in the liquid state, let us assume that the number of atoms in the vibrational motion is N_v and that the number in the translational motion is N_t ($=N-N_v$, N: Avogadro number). Accordingly the numbers of freedom $3N_v$ and $3N_t$ are distributed between the two motions in the liquid. The significant structure theory also considers that movable holes of moclecular size produced by volume increase accompanying fusion and thermal expansion confer the translational degrees of freedom on some fractions of molecules of the liquid.

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[1] J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.* (London), **169**, 317 (1937); **170**, 464 (1939).

[2] John. G. Kirkwood and Elizabeth Monroe, *J. Chem. Phys.*, **9**, 514 (1941).

[3] G. A. Mansoori and F. B. Canfield, *ibid.*, **51**, 4958, 4967 (1969).

[4] H. Eyring, T. Ree, and N. Hirai, *Proc. Nat. Acan. Sci. U. S.*, **44**, 683 (1958), E. J. Fuller, T. Ree, and H. Eyring, *ibid.*, **45**, 1594 (1959), H. Eyring and T. Ree, *ibid.*, **47**, 526 (1961), H. Eyring and Mu Shik Jhon, "Significant Liquid Structure", John Wiley, New York, (1969), and references contained therein.

[5] D. R. Tuerpe and R. N. Keeler, *J. Chem. Phys.*, **47**, 4283 (1967).

If we assume that a hole in liquid moves about as freely as does a molecule in vapor, it is to be expected that a molecule in the translational motion can share the whole excess volume of the liquid. In other words, the molecules in the translational motion are statistically indistinguishable. Consider a molecule in the translational motion in the liquid. It may move randomly from one position into a neighboring hole by producing a hole behind and may be oscillatory there, but another molecule begins to make translational motion by jumping into the hole. So, as a whole, it may be visualized that a hole in the liquid moves freely from one position to another similar to a gas molecule in vapor. This view has been proposed and supported by many theoretical approaches and experimental evidences,[4,6–8] though not without a few objections.[9]

The energy level in the vibrational motion is given by

$$\varepsilon_i = h\nu_i\left(n_i+\frac{1}{2}\right) \tag{1}$$

where ν_i is the normal vibration of the i-th freedom in the vibrational motion, n_i the quantum number specifying vibrational state. The kinetic energy of the particle in the translational motion is

$$\frac{1}{2m}p_j^2 = \frac{1}{2m}(p_{xj}^2+p_{yj}^2+p_{zj}^2) \tag{2}$$

where p_{xj}, p_{yj}, and p_{zj} are, respectively, the x-, y-, and z-components of momentum p_j, and m the mass of molecule. Thus the energy state of the liquid is designated by the quantum numbers n_i $(i=1, 2, \cdots 3N_v)$ of normal vibration, momenta p_j $(j=1, 2, \cdots N_t)$ of atoms in the translational motion and the configurational potential energy arising from intermolecular forces $\Phi_l(V_l)$. Hence the total internal energy of the system is represented as follows.

$$E_l(V_l, n_i, p_j) = \Phi_l(V_l) + \sum_{i=1}^{3N_v}\left(n_i+\frac{1}{2}\right)h\nu_i + \sum_{j=1}^{N_t}\frac{p_j^2}{2m}. \tag{3}$$

Since the sum of states for one particle in the translational motion is given by

$$z_j = \iiint_{-\infty}^{+\infty}\iiint_{\text{volume}} \exp\left(-\frac{p_j^2}{2mkT}\right)\frac{1}{h^3}\mathrm{d}p_{xj}\mathrm{d}p_{yj}\mathrm{d}p_{zj}\mathrm{d}x\mathrm{d}y\mathrm{d}z \tag{4}$$

and the sum of states for the i-th vibrational motion is

$$z_i = \sum_{n_i=0}^{\infty}\exp\left\{-\frac{\left(n_i+\frac{1}{2}\right)h\nu_i}{kT}\right\} = \left\{2\sinh\left(\frac{h\nu_i}{2kT}\right)\right\}^{-1}, \tag{5}$$

the partition function for the liquid composed of N monatomic molecules is

$$\begin{aligned} Z_l(T, V_l) &= \sum_{\text{states}}\exp\left\{-\frac{E_l(V_l, n_i, p_j)}{kT}\right\} \\ &= \left\{\prod_{i=1}^{3N_v} z_i\right\}\frac{1}{N_t!}\left(\prod_{j=1}^{N_t} z_j\right)\exp\left\{-\frac{\Phi_l(V_l)}{kT}\right\} \\ &= \left\{\prod_{i=1}^{3N_v}\left[2\sinh\left(\frac{h\nu_i}{2kT}\right)\right]^{-1}\right\} \\ &\quad\times\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{eV_f}{N_t}\right\}^{N_t}\exp\left\{-\frac{\Phi_l(V_l)}{kT}\right\}, \end{aligned} \tag{6}$$

where V_f is the free volume of the liquid.[10] In this calculation it was assumed that each degree of freedom is separable. We also used Stirling's approximation $N_t!=(N_t/e)^{N_t}$ for the factorial $N_t!$ in the denominator of the partition function which arises from the indistinguishability of the particles in the translational motion. The condition for the validity of Eq. (6) is the separability of the internal energy into kinetic (vibrational and translational) and potential parts.

The Helmholtz free energy of the liquid becomes

$$\begin{aligned} F_l(T, V_l) &= -kT\log Z_l(T, V_l) \\ &= \Phi_l(V_l) + kT\sum_{i=1}^{3N_v}\log\left\{2\sinh\left(\frac{h\nu_i}{2kT}\right)\right\} \\ &\quad -N_t kT\log\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{eV_f}{N_t}\right\} \end{aligned} \tag{7}$$

There are two efficient approximation methods for the vibrational term in Eq. (7); Debye's approximation[11] and Einstein's.[12] According to the former, the number of modes of vibration in the frequency range from ν to $\nu+\mathrm{d}\nu$ is given by

$$g(\nu) = \frac{9N_v}{\nu_m^3}\nu^2$$

where ν_m is the highest allowed frequency of the vibration of the system. Applying this approximation to the vibrational term in Eq. (7), we get

$$\begin{aligned} F_l(T, V_l) &= \Phi_l(V_l) \\ &\quad + 9kN_vT(T/\theta_l)^3\int_0^{\theta_l/T}x^2\log\left\{2\sinh\left(\frac{x}{2}\right)\right\}\mathrm{d}x \\ &\quad - N_tkT\log\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{eV_f}{N_t}\right\} \end{aligned} \tag{8}$$

where $\theta_l(=h\nu_m/k)$ is the characteristic temperature of liquid. It is expected that θ_l is more strongly temperature dependent than that of solid.

Equation (8) has the same asymptotic behaviour as Eyring's equation:[4] When N_t approaches zero, Eq. (8) gives the Helmholtz free energy of a solid, and when N_v goes to zero, we have the Helmholtz free energy of a real gas.

In principle we can now derive all the thermodynamic properties of liquid from the usual thermodynamic equations, but in order to make further progress it is necessary to know the exact values of N_t (or N_v), θ_l, $\Phi_l(V_l)$, and V_f or their exact forms as functions of T and V_l.

According to the significant structure theory,[4] N_t, N_v, and V_f are represented by

$$N_t = N\left(\frac{V_l-V_s}{V_l}\right)$$

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6) L. Cailletet and E. Mathias, *C. R. Acad. Sci., Paris*, **102**, 1202 (1886); **104**, 1563 (1887).

7) H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

8) Dan McLachan, Jr., and Ernest G. Ehlers, *J. Geophys. Res.*, **76**, 2780 (1970).

9) J. H. Hildebrand and G. Archer, *Proc. Nat. Acad. Sci. U. S.*, **47**, 1881 (1961).

10) The term "free volume" is used in the free volume theory in a different meaning. In this theory, it is referred to as the sum volume of movable holes in the liquid.

11) P. Debye, *Ann. Physik.*, **39**, 789 (1912).

12) A. Einstein, *ibid.*, **22**, 180 (1970).

$$N_v = N\left(\frac{V_s}{V_l}\right) \tag{9}$$
$$V_f = V_l - V_s$$

where V_s and V_l are the volume of solid at melting point and the volume of liquid, respectively. These relations were derived on the assumption that in one mole of liquid there are $(V_l - V_s)/V_s$ moles of holes of molecular size and that the whole excess volume (the sum of the volumes of the movable holes) is communally utilized by the molecules in the translational motion. If we assume that a hole in the liquid completely surrounded by other molecules moves freely like a gas molecule in a vapor, the effective number of holes (the number of molecules in the translational motion) which behave like a gas molecule is obtained by multiplying the number of holes $N(V_l - V_s)/V_s$ by the probability of molecules occupying the positions around the hole V_s/V_l. The relation (9) are expected to be valid for the liquid forming closed packed crystal or nearly closed packed crystal and for the region not far from melting point. Adopting these relations to our formulation, we obtain the following expression for the Helmholtz free energy of liquid

$$\begin{aligned} F_l(T, V_l) &= \Phi_l(V_l) \\ &+ 9\boldsymbol{R}T(V_s/V_l)(T/\theta_l)^3\int_0^{\theta_l/T} x^2 \log\left\{2\sinh\left(\frac{x}{2}\right)\right\}\mathrm{d}x \\ &- \boldsymbol{R}T\left(\frac{V_l - V_s}{V_l}\right)\log\left\{\left(\frac{2\pi mkT}{\boldsymbol{h}^2}\right)^{3/2}\frac{eV_l}{\boldsymbol{N}}\right\} \end{aligned} \tag{10}$$

Now let us consider the melting process of monatomic molecule substances such as inert gas elements. From the thermodynamical point of view, fusion takes place when the Gibbs free energies of solid and of liquid intercept each other. This is expressed by the equation

$$F_s(T, V_s) + PV_s = F_l(T, V_l) + PV_l \tag{11}$$

where P is the pressure of the system.

In connection with the equation of liquid we formulated, we employ the partition function of Debye type for the solid phase. The Helmholtz free energy of the solid phase is thus given by

$$\begin{aligned} F_s(T, V_s) &= \Phi_s(V_s) \\ &+ 9\boldsymbol{R}T(T/\theta_D)^3\int_0^{\theta_D/T} x^2 \log\left\{2\sinh\left(\frac{x}{2}\right)\right\}\mathrm{d}x \end{aligned} \tag{12}$$

where $\Phi_s(V_s)$ is the configurational potential energy of solid, and θ_D the Debye characteristic temperature of the solid.

The theory of melting is required to be capable of evaluating the temperature of melting, the change of volume and the latent heat of melting from intermolecular potential. In this paper, however, the reverse method is employed to test the applicability of the present model since the adoption of the crude theories for evaluating the values of $\Phi_l(V_l)$ and θ_l may obscure the applicability of Eq. (10).

We choose the entropy change upon fusion and the volumes of solid and liquid at the triple point as adjustable parameters and adjust the characteristic temperature (θ_l) and the configurational potential energy of liquid $\Phi_l(V_l)$ to the condition of Eq. (11) at the triple point. Then with the aid of Eq. (11) we calculate the melting point, entropy change upon fusion, internal energies and entropies of both phases at the pressure P and compare them with experimental data.

From Eq. (10), we get

$$\begin{aligned} S_l(T, \theta_l) &= -\frac{\partial F_l(T, \theta_l)}{\partial T} \\ &= -9\boldsymbol{R}\left(\frac{V_s}{V_l}\right)\left(\frac{T}{\theta_l}\right)^3\int_0^{\theta_l/T} x^2 \log\left\{2\sinh\left(\frac{x}{2}\right)\right\}\mathrm{d}x \\ &+ 4.5\boldsymbol{R}\left(\frac{V_s}{V_l}\right)\left(\frac{T}{\theta_l}\right)^3\int_0^{\theta_l/T} x^3 \coth\left(\frac{x}{2}\right)\mathrm{d}x \\ &+ \boldsymbol{R}\left(\frac{V_l - V_s}{V_l}\right)\log\left\{\left(\frac{2\pi mkT}{\boldsymbol{h}^2}\right)^{3/2}\frac{eV_l}{\boldsymbol{N}}\right\} \\ &+ \frac{3}{2}\boldsymbol{R}\left(\frac{V_l - V_s}{V_l}\right) \end{aligned} \tag{13}$$

and for the solid we obtain

$$\begin{aligned} S_s(T, \theta_D) &= -9\boldsymbol{R}(T/\theta_D)^3\int_0^{\theta_D/T} x^2 \log\left\{2\sinh\left(\frac{x}{2}\right)\right\}\mathrm{d}x \\ &+ 4.5\boldsymbol{R}(T/\theta_D)^3\int_0^{\theta_D/T} x^3 \coth\left(\frac{x}{2}\right)\mathrm{d}x \end{aligned} \tag{14}$$

Accordingly, the entropy change on fusion (ΔS_m) is given by

$$\Delta S_m = S_l(T_m, \theta_l) - S_s(T_m, \theta_D) \tag{15}$$

With the aid of Eqs. (13), (14), and (15), and the observed values of V_s, V_l, and θ_D, we can determine the value of θ_l by fitting the calculated ΔS_m to experiment at the triple point. At the triple point of argon ($T_m = 83.81$ K), the observed values of V_s, V_l, and ΔS_m are 24.614,[13] 28.332 m*l*,[13] and 3.395 cal/mol K,[14] respectively. With the value of $\theta_D = 80$ K,[15] Eq. (15) gives the value θ_l of 54.8 K. Determination of $\Phi_l(V_l)$ at the triple point is a straightforward numerical problem: it is solved by utilizing the evaluated values of θ_l and $\Phi_s(V_s)$ and by satisfying Eq. (11). As the value of $\Phi_s(V_s)$ is -1955 cal/mol at the triple point,[16] the value of $\Phi_l(V_l)$ which is found to satisfy Eq. (11) is -1624 cal/mol. In this calculation we can neglect the terms PV_s and PV_l in Eq. (11) as they are small compared to $F_s(T, V_s)$ and $F_l(T, V_l)$ at ordinary pressures.

Next we proceed to consider the melting of argon at high pressures. We cannot now neglect the PV terms in Eq. (11), and several plausible approximations and estimations must be introduced to achieve numerical calculations. At high pressures the pressure effect on $\Phi_s(V_s)$, $\Phi_l(V_l)$, θ_D, and θ_l must be taken into account. For the configurational potential energy of the solid, we use the equation[16]

$$\Phi_s(V_s) = -\frac{z}{2}N\varepsilon\left\{2.4090\left(\frac{N\sigma^3}{V_s}\right)^2 - 1.0109\left(\frac{N\sigma^3}{V_s}\right)^4\right\} \tag{16}$$

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[13] K. Clusius and K. Weigand, *Z. Physik. Chem.*, **B46**, 1 (1940).

[14] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, *Proc. Phys. Soc.*, **78**, 1449 (1961).

[15] K. Clusius, *Z. Physik. Chem.*, **B31**, 459 (1936).

[16] R. H. Wentorf, R. J. Beuhler, J. O. Hirschfelder, and C. F. Curtiss, *J. Chem. Phys.*, **18**, 1484 (1950). The values $\varepsilon = 165 \times 10^{-16}$ ergs and $\sigma = 3.41 \times 10^{-8}$ cm obtained by E. Whalley and W. G. Schneider, *J. Chem. Phys.*, **23**, 1644 (1955) were used in numerical calculations.

where z is the number of nearest neighbor molecules, σ and ε are, respectively, the distance and energy characteristics of the system in the 6—12 Lennard-Jones potential, *i.e.*,

$$\phi(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \tag{17}$$

To obtain the value of $\Phi_l(V_l)$ at the pressure P, we introduce the approximation

$$\Phi_l(V_l) = \left(\frac{V_s}{V_l}\right)A\cdot\Phi_s(V_s) \tag{18}$$

where A is an adjustable parameter and determined to fit the data at the triple point. For the sake of simplicity A is taken to be independent of pressure, *i.e.*, constant. This approximation is based on the facts that the change of configurational potential energy on melting is mainly due to the decrease of the number of nearest neighbor molecules and that in the case of inert gas elements the contribution to the configurational potential energy from the non-nearest neighbor molecules is not so large. Combining the observed values of $\Phi_s(V_s) = -1955$ and $\Phi_l(V_l) = -1624$ cal/mol at the triple point, the value of A is found to be 0.9564.

The Grüneisen law[17] may be used to take account of the pressure effect on the characteristic temperature of both phases:

$$\gamma = -\frac{\partial \log\theta}{\partial \log V} \tag{19}$$

where γ is the Grüneisen parameter and θ the characteristic temperature of the system. If we assume that the Grüneisen parameter is constant, Eq. (19) may be integrated at once to yield

$$\begin{aligned} \gamma_s \log\left(\frac{V_s}{V_s^0}\right) &= \log\left(\frac{\theta_D^0}{\theta_D}\right) \\ \gamma_l \log\left(\frac{V_l}{V_l^0}\right) &= \log\left(\frac{\theta_l^0}{\theta_l}\right) \end{aligned} \tag{20}$$

where θ_D^0 and θ_l^0 are respectively the Debye temperature of solid and the characteristic temperature of liquid at a reference melting point. V_s^0 and V_l^0 are the corresponding volumes of solid and liquid, γ_s and γ_l are the Grüneisen parameters of solid and liquid, respectively. It seems clear that in the case of liquid phase the accuracy of Eq. (20) is not very high.

Although some of these approximations are not rigorous enough for accurate computations, it is expected that they are valid enough to show the main feature of melting phenomenon at high pressures. Once the values of $\Phi_s(V_s)$, $\Phi_l(V_l)$, θ_D, and θ_l are known as functions of volume of the system, we can evaluate the melting point, latent heat of fusion, internal energy of the system at the pressure P with the aid of Eq. (11) and the observed values of V_s and V_l at the melting point corresponding to P.

Calculations and Discussion

The results of calculations together with the experimental data[18] are shown in Table 1. The calculation procedure was follows. At first the values of $\Phi_s(V_s)$, $\Phi_l(V_l)$, θ_D, θ_l, N_l, and V_f were calculated by use of Eqs. (9), (16), (18), and (20), and the observed values of V_s and V_l at the melting point T_m of the pressure P.[18] We adopted the triple point of argon as a reference point. The value of γ_s and γ_l were assumed to be 2.21 and 2.10, respectively. Then substituting these values into Eq. (11), we found the melting temperature of the system at the pressure P, and using this calculated temperature the entropies and the internal energies of both phases were evaluated. Though the value of γ_s was taken from the data (the value of 80 K) summarized by Pollack,[19] the value of γ_l was chosen so as to fit the calculations to the experimental data. The internal energy was calculated by use of the well-known thermodynamic relation

TABLE 1. COMPARISON OF CALCULATED AND OBSERVED THERMODYNAMIC PROPERTIES OF ARGON AT MELTING TEMPERATURES

P	T_m		ΔS_m		$S_s(T_m)$		$S_l(T_m)$		$E_s(T_m)$		$E_l(T_m)$		θ_D	θ_l
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Calcd	
0.687	100	$103._2$	12.1	11.4_3	41.3	39.0_0	53.4	50.4_2	−5750	−5610	−4733	−4624	82.9_0	60.9_2
1.146	110	$114._2$	11.5	10.5_4	42.8	41.0_0	54.3	51.5_4	−5580	−5393	−4590	−4467	84.9_1	63.6_1
1.630	120	$124._8$	11.0	10.0_1	44.1	42.4_6	55.2	52.4_7	−5380	−5190	−4415	−4304	87.3_0	66.2_2
2.136	130	$134._9$	10.5	9.4_9	45.3	43.7_4	55.9	53.2_2	−5180	−4984	−4243	−4139	89.6_3	68.8_2
2.662	140	$144._6$	10.4	9.2_7	45.9	44.7_1	56.3	53.9_8	−5070	−4789	−4126	−3965	92.3_1	71.2_1
3.210	150	$154._2$	10.2	8.9_6	46.7	45.6_3	56.9	54.6_0	−4870	−4584	−3929	−3788	94.7_5	73.6_0
3.781	160	$163._5$	10.0	8.7_1	47.8	46.4_5	57.8	55.1_6	−4610	−4378	−3660	−3604	97.1_8	75.9_1
4.374	170	$172._8$	9.9	8.4_8	48.4	47.2_4	58.3	55.7_2	−4420	−4164	−3454	−3412	99.4_0	78.0_6
4.987	180	$182._0$	9.6	8.3_0	48.7	48.0_1	58.3	56.3_1	−4270	−3943	−3319	−3210	101.5_1	80.0_0
5.614	190	$190._8$	9.4	8.0_8	48.8	48.6_8	58.2	56.7_6	−4130	−3727	−3187	−3016	103.5_7	82.0_3
6.250	200	$199._5$	9.1	7.9_3	49.2	49.3_0	58.3	57.2_2	−3950	−3510	−3016	−2816	105.5_8	83.9_1

a) Pressure is in kilobars, temperature in degrees Kelvin. Energies are in joules per mole and entropies are in joules per mole K.

b) All observed T_m, ΔS_m, $S_s(T_m)$, $S_l(T_m)$, $E_s(T_m)$, $E_l(T_m)$ values were obtained from R. K. Crawford and W. B. Daniels, *J. Chem. Phys.*, **50**, 3171 (1969). The values of V_l and V_s used in the calculations were also obtained from the same reference.

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17) E. Grüneisen, "Handbuch der Physik," X, (1926), p. 1.

18) R. K. Crawford and W. B. Daniels, *J. Chem. Phys.*, **50**, 3171 (1969).

19) Gerald L. Pollack, *Rev. Mod. Phys.*, **36**, 748 (1964).

$$E(T) = -T^2\left\{\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right\} \tag{20}$$

Agreement between calculation and experiment[18] is excellent, but it is interesting to not that all the calculated ΔS_m, $S_l(T_m)$, $S_s(T_m)$, $E_l(T_m)$, and $E_s(T_m)$ values are systematically smaller in their absolute values than the corresponding observed values. This is considered to be in part due to the errors inherent in the various approximations introduced and to the neglect of anharmonic effect of vibrational motions in both solid and liquid. Bridgman[20] also reported the entropy change on fusion of argon at high pressures. The reported values of ΔS_m are 10.31, 8.64, 7.49, 6.64, 6.07, and 5.62 J/mol K at melting temperatures 106.3, 126.4, 144.9, 162.0, 178.0, and 193.1 K, respectively. They are all lower than the corresponding calculated values.

TABLE 2. VARIATION OF $\gamma_l(T_m)$, ΔS_m, $E_l(T_m)$, AND $S_l(T_m)$ WITH MELTING TEMPERATURE[a]

T_m (Obsd)	T_m (Calcd)	$\gamma_l(T_m)$[b]	ΔS_m	$E_l(T_m)$	$S_l(T_m)$
100	$100._1$	1.79	11.7_4	−4698	50.1_1
110	$110._0$	1.85	10.9_7	−4568	51.0_5
120	$120._0$	1.91	10.4_3	−4417	51.9_4
130	$130._1$	1.96	9.8_6	−4255	52.7_7
140	$140._3$	2.00	9.5_8	−4070	53.5_3
150	$149._8$	2.02	9.2_4	−3893	54.1_7
160	$160._2$	2.05	8.9_1	−3684	54.8_5
170	$169._6$	2.06	8.6_5	−3488	55.4_4
180	$180._2$	2.08	8.3_9	−3255	56.1_5
190	$189._8$	2.09	8.1_3	−3042	56.6_7
200	$199._5$	2.10	7.9_3	−2816	57.2_2

a) Temperature is in degrees Kelvin (K). Entropies are in joules per mole K (J/mol K) and energies in joules per mole (J/mol).

b) The value of γ_l was chosen so as to give the observed melting temperature at pressure P. The value of γ_s was assumed to be 2.21.

Dugdale and Frank[21] showed that in the case of solid helium the Debye temperature depends only on volume to a first approximation and that the Grüneisen law, *i.e.*, $\gamma_s = -\mathrm{d}\log\theta_D/\mathrm{d}\log V_s$, holds well along the melting curve up to high pressures. By fixing γ_s constant, *i.e.*, $\gamma_s = 2.21$, we can determine the value of γ_l which gives observed melting temperature at P. The variation of γ_l with the increase in pressure is shown in Table 2 along with the entropy change upon fusion, internal energy and entropy of liquid. The fact that γ_l approaches the value of γ_s with the increase in pressure expects that thermodynamic properties of liquid resemble more and more those of solid with the increase in pressure. Although the value of γ_s was fixed constant throughout the calculations, γ_s also varies with volume and temperature.

TABLE 3. SPECIFIC HEAT OF LIQUID INERT GAS ELEMENT AT MELTING POINT[a]

Element	Mp	θ_D	ΔH_m	θ_l (Calcd)	CV_l (T_m,θ_l) (Obsd)	CV_l (T_m,θ_l) (Calcd)
Ne	24.56	64	80.1	40.3	4.42[a]	4.92
Ar	83.81	80	284.5	54.8	5.50[b] 5.19[c]	5.46
Kr	115.78	63	392.0	44.0	5.38[d]	5.53
Xe	161.37	55	548.5	35.9	—	5.66

a) Melting temperature, θ_D and θ_l are in degrees Kelvin (K), ΔH_m (heat of fusion) is in calories per mole (cal/mol), $CV_l(T_m,\theta_l)$ is in calories per mole K (cal/mol K).

Sources of data: θ_D: K. Clusius, *Z. Phys. Chem.* (Leipzig), **B31**, 459 (1936). ΔH_m, V_s, and V_l: Gerald L. Pollack, *Rev. Mod. Phys.*, **36**, 748 (1964). $CV_l(T_m,\theta_l)$ observed; estimated from a) C. Gladun, *Cryogenics*, **6**, 27 (1966); b) A. Eucken and F. Hauk, *Z. Phys. Chem.*, **134**, 161 (1928); c) C. Gladun and F. Menzel, *Cryogenics*, **10**, 210 (1970); d) C. Gladun, *ibid.*, **11**, 205 (1971).

From Eq. (20), the specific heat of liquid at constant volume is obtained as

$$\begin{aligned} CV_l(T,\theta_l) &= \left\{\frac{\partial E_l(T,\theta_l)}{\partial T}\right\}_V \\ &= 9\boldsymbol{R}\left(\frac{V_s}{V}\right)\left(\frac{T}{\theta_l}\right)^3\int_0^{\theta_l/T}\frac{x^4e^x}{(e^x-1)^2}\mathrm{d}x \\ &\quad +\frac{3}{2}\boldsymbol{R}\left(\frac{V_l-V_s}{V_l}\right) \end{aligned} \tag{21}$$

With the aid of the computed θ_l value, we can evaluate $CV_l(T_m, \theta_l)$. Comparison of the calculated $CV_l(T_m, \theta_l)$ with experiment is given in Table 3 together with the data of other inert gas elements. Though the calculated $CV_l(T_m, \theta_l)$ value deviates systematically from experimental value for all inert gas elements, the agreement is fairly good. The fact that deviation between calculation and experiment becomes larger from krypton (xenon) to neon is attributable to the underestimation of the number of freedom in the translational motion. In other words, Eq. (9) gives a lower value than the actual one for the N_t value. The reason is as follows. From classical theory one would expect the V_s value at 0 K and zero pressure to be equal to $N\sigma^3$. For krypton and xenon this holds within experimental error and for argon this is nearly true, but for neon and helium the actual molar volumes are very much larger than those given by the formula $N\sigma^3$. Accordingly the validity of Eq. (9) is lost in the cases of neon and helium.

We used a most simple form for evaluating configurational potential energy of liquid, but it is to be pointed out that Eq. (18) does not give asymptotic consistency: it does not yield the potential of solid when V_l approaches V_s. However, the good agreement with experiment leads to the conclusion that the approximation is rather adequate for the evaluation of $\Phi_l(V_l)$. Obviously a detailed theoretical study for the accurate calculation of the configurational potential energy of liquid is required to complete the present theory. It seems very likely that development of the

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radial distribution function method[22,23] and/or the Monte Carlo method[24,25] will suffice the requirement in near future.

At the present time some ambiguities exist in the present theory, especially in the calculations of $\Phi_l(V_l)$, N_t (or N_v), V_f, θ_l, and γ_l. Neverthless there is little doubt that the partition function of liquid given here will work well for the liquid composed of monatomic molecules. A more detailed application of the partition function is clearly bounded up with a better understanding of the volume and temperature dependencies of $\Phi_l(V_l)$, N_l, V_f, θ_l, and γ_l.

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