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# On the Change of Electrical Conductivity of Metal on Melting

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A partition function of liquid recently proposed by the present author[1] has been applied to the change of the electrical conductivity of metal at melting point. The relation between $\sigma_s/\sigma_l$ and $\theta_D/\theta_l$ is more successfully interpreted by this partition function than that used by Mott.[2]

It was previously reported that a partition function proposed by the author was successfully applied to the melting of argon at high pressures.[1] The partition function of $N$ monatomic liquid is

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

where $N_t$ and $N_v$, $(N_t+N_v=N)$, are respectively the numbers of molecules in translational and vibrational motions, $\nu_i$ is the normal mode of the $i$-th vibrational motion, $m$ the mass of a molecule, $V_f$ the free volume of the liquid, and $\Phi_l(V_l)$ the configurational potential energy of the liquid.

It is worthwhile applying the partition function to other systems in order to examine its applicability and validity. The application to liquid metals is described in this paper with special emphasis on the characteristic temperature of liquid ($\theta_l$). Correlation between $\sigma_s/\sigma_l$ ($\sigma$: electrical conductivity of metal at melting point, and subscripts $s$ and $l$ denote respectively solid and liquid phases) and $\theta_D/\theta_l$ ($\theta_D$: Debye temperature of a solid metal) is interpreted more successfully by means of the partition function than that used by Mott.[2]

## Evaluation of Characteristic Temperature of Liquid

At present there is no well-defined theoretical model to evaluate the mean vibrational frequency of atoms in the vibrational motions in the liquid metal from their interatomic potentials. We adopt the same procedure as given previously[1] to evaluate the characteristic temperature of liquid at melting point.

The Helmholtz free energy of liquid metal is given, by

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

Applying the Debye approximation to the vibrational part in Eq. (2), and adopting the Eyring presentations[3] for $N_t$, $N_v$, and $V_f$, *viz*

$$\begin{aligned} N_v &= \frac{NV_s}{V_l} \\ N_t &= \frac{N(V_l-V_s)}{V_l} \\ V_f &= V_l - V_s \end{aligned} \quad (3)$$

where $V_s$ and $V_l$ are the volumes of solid at the melting point and of liquid, respectively, we obtain

$$\begin{aligned} F_l(T,V_l) &= \phi_l(V_l) \\ &\quad + 9RT\left(\frac{V_s}{V_l}\right)\left(\frac{T}{\theta_l}\right)^3\int_0^{\theta_l/T}x^2\log\left\{2\sinh\left(\frac{x}{2}\right)\right\}dx \\ &\quad - RT\left(\frac{V_l-V_s}{V_l}\right)\log\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{eV_l}{N}\right\}, \end{aligned} \quad (4)$$

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[1] H. Kanno, This Bulletin, **45**, 2687 (1972).

[2] N. F. Mott, *Proc. Roy. Soc. Ser., A*, **146**, 465 (1934).

[3] H. Eyring, T. Ree, and N. Hirai, *Proc. Nat. Acad. Sci. U. S.*, **44**, 683 (1958); H. Eyring and Mu Shik Jhon, "Significant Liquid Structure", John Wiley & Sons, New York (1969), and references contained therein.

where $\theta_l$ is the characteristic temperature of liquid (which corresponds to the Debye temperature of the solid). It should be pointed out that relations (3) are only approximate and are thought to be valid only for the low temperature region not far from melting point and for a close packed substance in its solid phase.

In correspondence to the partition function of liquid, we use the Debye equation for the solid phase

$$F_s(T, V_s) = \Phi_s(V_s) + 9RT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} x^2 \log\left\{2\sinh\left(\frac{x}{2}\right)\right\} dx \tag{5}$$

where $\Phi_s(V_s)$ is the configurational potential energy of solid metal and $\theta_D$ the Debye temperature.

The entropy change on melting $\Delta S_m$ is represented by

$$\Delta S_m = \frac{\Delta H_m}{T_m} = S_l(T_m, V_l) - S_s(T_m, V_s) = -\left\{\frac{\partial F_l(T, V_l)}{\partial T}\right\}_{T=T_m} + \left\{\frac{\partial F_s(T, V_s)}{\partial T}\right\}_{T=T_m} \tag{6}$$

where $\Delta H_m$ is the latent heat of fusion, $S_l(T_m, V_l)$ and $S_s(T_m, V_s)$ are the entropies of liquid and solid phases at melting point, respectively.

With the aid of the observed values of $\theta_D$, $V_l$, $V_s$, $\Delta S_m$, and Eq. (6), we can determine the characteristic temperature of liquid ($\theta_l$) at melting point by adjusting $\Delta S_m$ to give the experimental value.

## Calculations and Discussion

The data used for calculations are tabulated in Table 1. Though the values $T_m$, $V_l$, $V_s$, and $\Delta S_m$ are in fair agreement in literature, the $\theta_D$ values show some difference according to the method (elastic or thermal) and temperature range at which determination was carried out. We used the Debye temperature of about 298 K obtained from specific heat data.[4]

As regards the characteristic temperature of liquid metal, Mott[2] has made an interesting comparison. He showed that the ratio of electrical conductivity of liquid metal to that of solid metal (both measured at melting point) is well correlated to the ratio of the mean frequencies of thermal vibrations of atoms in solid and liquid phases.

The electrical conductivity of solid metal is expressed as[5]

$$\sigma_s = \text{const}\cdot\frac{e^2}{m^*}\left(\frac{\beta}{C_D}\right)^2 \frac{m\cdot\theta_D{}^2}{V_s T} \tag{7}$$

where $\beta/C_D$ and $m^*$ (effective mass of electron) represent the magnitude of the binding of the electron to the lattice, $e$ is the charge of electron.

When a metal melts, only a small percentage of volume increase is observed. Experimental evidences[6,7] show that structual configuration of liquid metal just above melting point retains most of the features of solid metal. Thus adopting Mott's hypothesis that electrical conductivity change at melting point is mainly due to the change of the electron scattering with phonon of high energy and utilizing the same formula as Eq. (7) for the electrical conductivity of liquid metal, we may easily derive the following formula

TABLE 1. DATA USED FOR THE CALCULATIONS

| Metal | Mp (K) | $V_s$ (m*l*) | $V_l$ (m*l*) | $\theta_D$ (K) | $\Delta S_m$ (cal/mol·K) |
|---|---|---|---|---|---|
| Li | 452 | 13.12[a] | 13.48 | 448 | $1.59_0$ |
| Na | 370.8 | 24.17[a] | 24.80 | 155 | $1.67_7$ |
| K | 336.6 | 46.43[a] | 47.74 | 100 | $1.65_1$ |
| Rb | 311.8 | $56.99_5$[a] | 58.42 | 59 | 1.80 |
| Cs | 301.8 | 69.98[a] | 71.80 | 43 | $1.67_7$ |
| Cu | 1356 | 7.610[b] | 7.951 | 310 | $2.30_0$ |
| Ag | 1234 | 11.16[c] | 11.54 | 221 | $2.25_3$ |
| Au | 1336.2 | 10.66[d] | 11.34 | 178 | 2.21 |
| Mg | 923 | 14.85[e] | 15.29 | 330 | 2.32 |
| Zn | 692.7 | 9.55[a] | 9.94 | 237 | $2.54_8$ |
| Cd | 594.2 | 13.48[a] | 14.02 | 221 | 2.49 |
| Hg | 234.28 | 14.132[f] | $14.64_9$ | 92 | $2.34_1$ |
| Al | 933.2 | 10.71[a] | 11.39 | 390 | 2.74 |
| In | 429.76 | 15.99[g] | 16.28 | 129 | 1.81 |
| Tl | 576.7 | 17.72[g] | 18.10 | 96 | 1.77 |
| Pb | 600.58 | 18.70[h] | 19.41 | 87 | 1.90 |

Sources of data: Melting point, Debye temp., and entropy of fusion—Ref. 4; volume of liquid at mp—Handbook of Chemistry and Physics, 50th ed., The Chemical Rubber Co. Pub., (1969) B255—259; volume of solid at mp—a) recalculated from the data tabulated in L. D. Lucas, *Mem. Sci. Rev. Met.*, **61**, 1 (1964), b) E. Widawaki and F. Sauerwald, *Z. Anorg. Allg. Chem.*, **192**, 145 (1930), c) F. Sauerwald, *Z. Metalk.*, **14**, 457 (1922), d) E. Gebhard and S. Dorner, *ibid.*, **42**, 353 (1951), e) P. J. McGonigal, A. D. Kirshenbaum, and A. V. Grosse, *J. Phys. Chem.*, **66**, 737 (1962), f) Ref. 12, see also Ref. a, g) A. Schneider and G. Heymer, *Z. Anorg. Allg. Chem.*, **286**, 118 (1956), h) cited in A. D. Kirshenbaum, J. A. Cahill, and A. V. Grosse, *J. Inorg. Nucl. Chem.*, **22**, 33 (1961).

$$\frac{\sigma_s}{\sigma_l} = \left(\frac{\theta_D}{\theta_l}\right)^2 \cdot \frac{V_l}{V_s} \tag{8}$$

In Mott's theory a liquid metal is assumed to consist only of vibrational freedom. He derived the following formula giving the relation between $\sigma_s/\sigma_l$ and $\theta_E/\theta$ by applying the harmonic oscillator model of liquid to the liquid metal at the melting point:

$$\frac{\Delta H_m}{T_m} = 3R\log\left(\frac{\theta_E}{\theta}\right)[+R]^{8)} \tag{9}$$

where $\theta_E$ is the Einstein temperature and $\theta$ is a characteristic temperature of liquid state which corresponds

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[4] K. A. Gschneider, Jr., in "Solid State Physics," Vol. **16**, F. Seitz and D. Turnbull Eds., Academic, New York, (1964), pp. 275—426.

[5] H. Jones, in "Handbuch der Physik," Bd **XIX**, edited by S. Flügge, Springer-Verlag, (1956), pp. 227—315.

[6] N. S. Gingrich, *Rev. Mod. Phys.*, **15**, 90 (1943).

[7] "The Properties of Liquid Metals", edited by P. D. Adams, H. A. Davies, and G. Epstein, Taylor and Francis, London, (1967), and *Advan. Phys.*, **16**, (1967), pp. 147—307.

[8] In Mott's original paper,[2] the term **R** was omitted. As first suggested by O. K. Rice, *J. Chem. Phys.*, **6**, 476 (1938) and shown by the significant structure theory[3] and the present theory, the communal entropy introduced on melting, which is the cause for the term **R** in Eq. (9), is in fact much smaller in most actual cases than **R**.

TABLE 2. COMPARISON OF CALCULATED $\sigma_s/\sigma_l$ VALUES WITH OBSERVED CONDUCTIVITY CHANGES

| Metal | $\sigma_s/\sigma_l$ Observed | $\sigma_s/\sigma_l$ Calcd by Mott$^{a)}$ | $\sigma_s/\sigma_l$ Calcd by this theory |
|---|---|---|---|
| Li | 1.59 | 1.75$^{a)}$ | 1.65 |
| Na | 1.45 | 1.80 | 1.69 |
| K | 1.58 | 1.79 | 1.66 |
| Rb | 1.60 | 1.87 | 1.75 |
| Cs | 1.67 | 1.80 | 1.68 |
| Cu | 2.1 | 2.26 | 2.01 |
| Ag | 2.1 | 2.20 | 2.00 |
| Au | 2.3 | 2.23 | 1.85 |
| Mg | 1.8 | 2.24 | 2.08 |
| Zn | 2.2 | 2.44 | 2.18 |
| Cd | 2.0 | 2.40 | 2.07 |
| Hg | 3.7—4.9 | 2.27 | 2.00 |
| Tl | 2.1 | 1.85 | 1.73 |
| Al | 2.2 | 2.67 | 2.26 |
| Pb | 1.9 | 1.96 | 1.76 |
| In | 2.2 | 1.87 | 1.76 |

Source of data: Observed values are taken from the tabulated data in Ref. 9.

a) Calculated with Eqs. (8) and (9) using tabulated data in Table 1. In this calculation the term $\boldsymbol{R}$ in Eq. (9) was omitted after Mott.

to the Einstein temperature.

The values of $\sigma_s/\sigma_l$ computed from Eqs. (6) and (8) compared with the values obtained by Mott's theory are given in Table 2. We see that the values $\sigma_s/\sigma_l$ calculated by Eq. (6) give better agreement to experiment than those deduced from Eq. (9). This might be due to the fact that in Mott's theory all $\Delta S_m$ are ascribed to the change of vibrational frequency, neglecting the communal entropy. Actually a part of $\Delta S_m$ is caused by the introduction of the partial indistinguishability of the particles upon melting. It should be pointed out that as Eyring's relations for $N_l$ and $V_f$, *i.e.*, Eq. (3), are not applicable to the open structure metals such as Bi, Sb, and Ga, it is impossible to evaluate the characteristic temperatures of these liquid metals by Eq. (6). The volume of the open structure metal contracts on melting and the $\sigma_s/\sigma_l$ values also show anomalous changes.[9)]

The general agreement of the calculated $\sigma_s/\sigma_l$ values with the observed ones indicates that the translational motions of metal atoms in liquid phase and the holes introduced make a negligible contribution to the change of electrical conductivity because of their small fractions in the $3N$ degrees of freedom in the liquid metal just above melting point.

Carlson, Eyring, and Ree[10)] applied the significant structure theory to liquid metals such as Na and Hg to interpret the thermodynamic properties of these metals, including viscosity and self-diffusion. The theory, however, assumes that the mean frequency of thermal vibrations of atoms in liquid phase is the same as that of solid phase. Thus it can not applied to the present problem.

In recent years a new approach has been made for describing the electrical conductivity of liquid metal in terms of the pseudopotential approximation.[11,12)] Although the agreement between theory and experiment is encouraging, quantitative comparison is still premature.

## Conclusion

Despite exceptions such as Hg, Ga, Sb, and Bi (some of them are semiconductors in the solid phase but ordinary metals when liquid), it is concluded in conjunction with Mott that most part of the change of electrical conductivity of metal on melting is ascribed to the change of the frequency of thermal vibrations in $3N$ degrees of freedom. The weakness of the liquid model used by Mott (communal entropy problem) was removed in the present model and a better agreement between theory and experiment was obtained.

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[9)] T. E. Faber, in "The Physics of Metals, I Electrons", edited by J. M. Ziman, Cambridge University Press, (1969), pp. 282—316.

[10)] C. M. Carlson, H. Eyring, and T. Ree, *Proc. Nat. Acad. Sci. U. S.*, **46**, 649 (1960).

[11)] J. M. Ziman, *Phil. Mag.*, **6**, 1013 (1961), *Advan. Phys.*, **13**, 89 (1964).

[12)] N. W. Ashcroft and J. Lekner, *Phys. Rev.*, **145**, 83 (1966).