Theory of Anharmonic Lattice Vibration in Metallic Fine Particles. I

Takeo MATSUBARA, Yūjirō IWASE* and Akitaka MOMOKITA*

Department of Physics, Kyoto University, Kyoto 606
and
**Department of Material Physics, Faculty of Engineering Science
Osaka University, Toyonaka 560*

We apply the self-consistent Einstein model to the theory of anharmonic lattice vibration in metallic fine particles, and discuss the size dependence of the melting and superconducting transition temperatures in the connection to the softening of the surface lattice vibrations. Assuming a simple interatomic potential and certain distribution of the particle size, we express both transition temperatures as functions of the average radius of fine particles and show that the numerical results calculated from the theoretical expressions are in fairly good accord with the experiments.

§ 1. Introduction

In a previous paper, one of the present authors has discussed, on the basis of a self-consistent Einstein model, that the atoms on the surface of metal crystal perform oscillations with much larger amplitudes compared with the interior atoms.[1] The large surface lattice vibration is related to the softening of the frequencies of the surface atoms and also closely related to the so-called surface relaxation of the lattice constant. Since the surface to volume ratio of metallic fine particles is increased with decreasing size, the surface softening should give appreciable effects in the various thermal properties of metallic fine particles with sufficiently small radii. Up to the present time, there are many accumulated experimental facts to show that this is indeed the case. It has long been known for instance that the metallic fine particles have melting points much lower than those of the corresponding bulk metals. The first observation of this depression of the melting point was made by Takagi[2] on Pb, Sn and Bi thin films by the use of the electron diffraction method. Since then similar observations have been reported, for example, on Sn by Wronski,[3] on Pb and In by Coombes,[4] on Au by Buffat and Borel[5] and so on. This phenomena are undoubtedly due to the surface effects, and phenomenological theories based on the thermodynamic arguments have been presented.[6] A simple microscopic theory was first proposed by one of the present authors[7] with a pretty success in explaining the main experimental facts. This paper contains a sophistication of the previous theory.

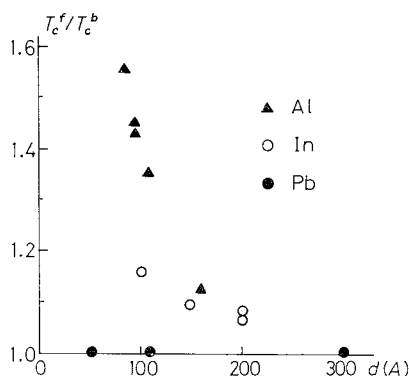Another example of the phenomena which seem to be related with the surface

Fig. 1. Size dependence of the superconducting transition temperature of metallic fine particles. T_c^f is the transition temperature of fine particle, T_c^b of bulk metal and d average diameter.

softening is the remarkable increase in the superconducting transition temperature of metallic fine particles. Matsuo et al. have measured the superconducting transition temperature T_c of Al, In and Pb fine particles as functions of the average radii. Their result is reproduced in Fig. 1.[8] Several different interpretation of this size dependence of T_c are suggested, but the most promising one which is capable of explaining the experiments seems to be that the origin is attributed to the softening of the lattice vibrations. We discuss this problem in this paper as an application of our theory.

Most direct observation on the softening of the lattice vibration will be provided by the X-ray, electron and neutron scattering experiments. From the observed Debye-Waller factor, for instance, the value of the mean square displacement $\langle u^2 \rangle$ of atoms in metallic fine particles can be deduced. Such experiments of the X-ray scattering from metallic fine particles have been done by Kashiwase et al. for Ag[9] and by Harada et al. for Au,[10] and it is found that the $\langle u^2 \rangle$ values derived from their experiments are very large, indicating the presence of the softening of the surface lattice vibrations.

In this paper we present a simple theory of anharmonic lattice vibration in metallic fine particles which enables us to interpret all the phenomena mentioned above in rather simple and straightforward way. In contrast to the conventional theory of lattice dynamics in the harmonic approximation, we consider an assembly of independently oscillating atoms, each of which has each own frequency determined self-consistently from the knowledge of interatomic potential and the averaged motions of all atoms. Although each atom is assumed to perform harmonic oscillation, the self-consistent equations to determine the frequencies are highly non-linear and give rise to a complicated coupling among the softening of frequencies, increase of amplitude and weakening of the effective potential. Thus the size effect of the frequency as well as the cooperative softening mechanism are built in the self-consistent equations. With increasing temperature the softening mechanism works with an enhanced rate and at last the system attains instability which may be somehow related to the melting phenomena. A merit of the present theory is that the local frequencies are directly treated so that the change in the frequencies due to the presence of the surface can be easily evaluated, enabling us to discuss the phenomena related with the surface softening.

The organization of this paper is as follows: In §2 a full account of the model is given and general formulation is presented. In §3 the general theory

is simplified by taking a special Gaussian potential and the basic equations are reformulated. The parameters included in the potential are properly chosen for typical 16 cubic metals with BCC or FCC structure. In § 4 the theory is applied to the melting of metallic fine particles and compare the results of the theoretical calculation with the experiments. In § 5 an application of the theory to the size dependence of the superconducting transition temperature of metallic fine particles is presented. The last section is devoted to a brief summary and discussion.

§ 2. General formulation

Self-consistent Einstein model is a simplified version of the more general self-consistent phonon theory which is founded on the basis of the variation principle at finite temperature.[1] A full derivation of the self-consistent Einstein model from the variation principle has been already given in the previous paper[1] for the case of the one-dimensional finite lattice. Since a generalization to the three-dimensional case is quite straightforward, we omit it here and present a formulation of the model in a rather intuitive manner.

Let us consider a fine particle composed of atoms forming a Bravais lattice $\{R_n\}$ in a spherical region with a radius R. Let $v(r-r')$ be the interatomic potential between two atoms at r and r'. For the sake of simplicity we assume that each atom performs independent isotropic oscillation and denote the frequency of an atom oscillating around R_n by $\omega(R_n)$, the atomic mass by M and the displacement vector by $u(n)$. Then $\phi(R_n) = M\omega(R_n)^2$ is given by the average curvature of the potential acting at R_n as

$$M\omega(R_n)^2 = \phi(R_n) = \sum_{n'}\sum_{x}\langle v_{xx}(R_n + u(n) - R_{n'} - u(n'))\rangle/3 . \tag{1}$$

The average in the right-hand side of (1) should be taken over a canonical ensemble of the Einstein oscillators with the frequencies $\{\omega(R_n)\}$. In the high temperature approximation, it holds that

$$\langle \exp[i(q\cdot u(n))]\rangle = \exp[-\langle(q\cdot u(n))^2\rangle/2]$$
$$= \exp[-q^2 k_B T/2\phi(R_n)] . \tag{2}$$

Therefore if the potential $v(r)$ is decomposed into Fourier component

$$v(r) = \int dq\, V(q)\exp(iq\cdot r), \tag{3}$$

Eq. (1) can be written, upon using (2) and (3), as

$$\phi(R_n) = -\int dq\,(q^2/3)\,V(q)\sum_{n'}\exp[iq(R_n - R_{n'})]$$
$$\times \exp[-(q^2 k_B T/2)(\phi(R_n)^{-1} + \phi(R_{n'})^{-1})] . \tag{4}$$

We first simplify the problem by assuming that ϕ is independent of the atomic position. This assumption is not of course justified, but we expect it is to be

a reasonable first approximation because the variation of $\phi(\boldsymbol{R})$ is restricted only near the surface. We shall come back again in later section to the question of the $\boldsymbol{r}$-dependence of $\phi(\boldsymbol{r})$. Now taking $\phi(\boldsymbol{R})=\phi$ and $\boldsymbol{R}_n=0$, we write Eq. (4) as

$$\phi = - \int d\boldsymbol{q}\,(q^2/3)\,V(\boldsymbol{q})\exp[-(q^2 k_B T/\phi)]\sum_{n'}\exp(-\boldsymbol{q}\cdot\boldsymbol{R}_{n'}).\tag{5}$$

The size effect comes from the last factor on the right-hand side of (5). If we define the following functions:

$$Z(\boldsymbol{r}) = (\sum_n \delta(\boldsymbol{r}-\boldsymbol{R}_n))\theta(R-|\boldsymbol{r}|)\tag{6}$$

$$\theta(x) = \begin{cases} 1 & \text{for } x \geq 0, \\ 0 & \text{for } x < 0, \end{cases}$$

then it is obvious that

$$\sum_n \exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_n) = \int d\boldsymbol{r}\,Z(\boldsymbol{r})\exp(-i\boldsymbol{q}\cdot\boldsymbol{r}).\tag{7}$$

Since $Z(\boldsymbol{r})$ is a product of two functions of $\boldsymbol{r}$, (7) is expressed as a convolution of two functions of $\boldsymbol{q}$ corresponding to their Fourier transforms. Thus we have

$$\sum_n \exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_n) = V_c^{-1}\sum_h f(\boldsymbol{q}-\boldsymbol{B}_h),\tag{8}$$

where the $\{\boldsymbol{B}_h\}$'s are the lattice vectors reciprocal to $\{\boldsymbol{R}_n\}$, V_c the volume of a unit cell, and $f(\boldsymbol{q})$ the Fourier transform of $\theta(R-|\boldsymbol{r}|)$ defined by

$$\begin{aligned} f(\boldsymbol{q}) &= \int_{|\boldsymbol{r}|<R} \exp(-i\boldsymbol{q}\cdot\boldsymbol{r})\,d\boldsymbol{r} \\ &= (4\pi R^3)(qR)^{-3}(\sin qR - qR\cos qR).\end{aligned}\tag{9}$$

The summation $\sum_h$ is taken over all the reciprocal lattice vectors. Substituting (8) and (9) into (5) and performing the integration with respect to q yield an equation to determine ϕ.

$$\phi = -\sum_h \int d\boldsymbol{q}\,(q^2/3V_c)\,V(\boldsymbol{q})\exp[-(q^2 k_B T/\phi)]f(\boldsymbol{q}-\boldsymbol{B}_h).\tag{10}$$

It turns out that this equation ceases to have solution above a certain temperature T_m. To see this, put

$$W = k_B T/\phi.\tag{11}$$

Then the right-hand side of (10) is a function of W and R, and hence Eq. (10) takes the form

$$\phi = F(W, R) \quad \text{or} \quad k_B T = WF(W, R).\tag{12}$$

The function $F(W, R)$, the sum of the integrals on the right-hand side of Eq. (10), is obviously a decreasing function of W, and $WF(W, R)$ should be bounded

above.   Therefore we can find a point

$$k_B T_m = [WF(W, R)]_{max} \tag{13}$$

above which there exists no solution for $W(T)$.   Going back to the original variation formulation, we find that this corresponds to the disappearance of a local minimum of the free energy, indicating an instability of the crystal lattice.   Although T_m is not equal to (actually much larger than) the melting temperature, we may regard T_m as a proportional measure of the melting temperature of fine particles.   For $T < T_m$, there are two solutions of Eq. (12) for W, smaller one of which is the desired solution corresponding to the minimum free energy.   Once the solution W is determined as a function of T and R, various quantities of physical interest can be immediately evaluated.   For instance, W itself is nothing but the mean square displacement

$$W = k_B T / \phi = \langle u^2 \rangle \tag{14}$$

and is proportional to the Debye-Waller factor.   By the definition, the frequency of the oscillator is given by

$$M \omega^2 = \phi = k_B T / W . \tag{15}$$

§ 3.   Simplification for Gaussian potential

In order to avoid the computational difficulty, we simplify the calculation in two ways.   First we choose as the interatomic potential a simple form of Gaussian type

$$v(\boldsymbol{r}) = A \exp(-ar^2) - B \exp(-br^2) \tag{16}$$

and the four parameters A, B, a and b are fixed by the following procedure: Many years ago Girifalco and Weizer[12] proposed a simple Morse type function

$$v_M(r) = D[\exp\{-2\alpha(r - r_0)\} - 2 \exp\{-\alpha(r - r_0)\}] \tag{17}$$

as the interatomic potential of cubic metals and they determined the values of the potential parameters D, α and r_0 so that the lattice constant, the compressibility and the sublimation energy calculated from the potential for 16 cubic metals fit the corresponding experimental data.   Instead of following a similar method, however, we try to make $v(r)$ fit to the Morse potential $v_M(r)$ in the important parts.   Namely we require the following four conditions:

$$v_M(r_0) = -D = v(r_0),$$
$$v_M'(r_0) = 0 = v'(r_0),$$
$$v_M''(r_0) = 2\alpha^2 D = v''(r_0),$$
$$v_M(r_c) = 0 = v(r_c). \tag{18}$$

In Table I the potential parameters thus determined are listed up for 16 cubic

Table I. Gauss potential constants for the pairwise atomic interaction in cubic metals.

Metal	A(eV)	B(eV)	a(Å^{-2})	b(Å^{-2})	d_{cal}	d_{exp}
Pb	59.16	1.224	0.4934	0.1019	3.49	3.49
Ag	69.27	1.612	0.6922	0.1395	2.88	2.88
Ni	59.07	1.759	0.8269	0.1578	2.50	2.49
Cu	45.06	1.400	0.7713	0.1457	2.56	2.55
Al	31.066	1.050	0.5884	0.1089	2.86	2.86
Ca	16.24	0.5996	0.2930	0.05305	3.94	3.93
Sr	15.14	0.5590	0.2458	0.0445	4.31	4.30
Mo	220.2	4.324	0.7844	0.1637	2.69	2.72
W	210.6	4.839	0.7324	0.1480	2.73	2.73
Cr	99.73	2.207	0.8944	0.1821	2.49	2.49
Fe	58.86	1.748	0.7897	0.1508	2.49	2.48
Ba	11.68	0.4883	0.2064	0.03618	4.41	4.34
K	2.788	0.1586	0.1379	0.02214	4.74	4.62
Na	3.162	0.1834	0.1957	0.03124	3.94	3.71
Cs	2.219	0.1295	0.09745	0.01553	5.57	5.24
Rb	2.167	0.1314	0.1063	0.01673	5.22	4.87

metals. Of course the theoretical lattice constants calculated using the potential (16) with the condition (18) are different from the experimental lattice constants, to which Girifalco and Weizer have referred for determining the potential parameters. Fortunately the differences between the calculated nearest neighbour distance d_{cal} and the experimental one d_{exp} are fairly small as seen in Table I. We need later the Fourier transform of $v(r)$ which is given by

$$V(\boldsymbol{q}) = \Gamma \exp(-\xi q^2) - \Lambda \exp(-\eta q^2) \qquad (19)$$

with

$$\Gamma = A(4\pi a)^{-3/2}, \quad \Lambda = B(4\pi b)^{-3/2},$$

$$\xi = 1/4a, \quad \eta = 1/4b. \qquad (20)$$

The second simplification is to replace the function

$$f(q) = (4\pi R^3)(qR)^{-3}(\sin qR - qR \cos qR)$$

in Eqs. (8), (9) and (10) by a simple Gaussian

$$f(q) = 8\pi^{3/2} \bar{R}^3 \exp(-\bar{R}^2 q^2). \qquad (21)$$

This form for $f(q)$ is in fact quite a good approximation, because in reality the radii of fine particles are distributed around some average value. Although $\bar{R}$ may be thought of as an effective radius to be determined, we leave it as an adjustable parameter in the present theory. Putting (19) and (21) into (10), and performing the integration with respect to q, we arrive at the final result which can be summarized as

$$k_B T/G^3 = zF(z, \rho)$$

$$= (\pi^{3/2}/2)z[\Gamma(x+z)^{-5/2} - \Lambda(y+z)^{-5/2}]$$

$$- \sum_h (4/9\sqrt{3})z\left[\Gamma \frac{\rho^{5/2}}{x+z+\rho} \cdot \exp\left(-\frac{(x+z)n_h^2\rho}{x+z+\rho}\right)\left(\frac{3}{2} + \frac{n_h^2\rho}{x+z+\rho}\right)\right.$$

$$\left. - \Lambda \frac{\rho^{5/2}}{y+z+\rho} \cdot \exp\left(-\frac{(y+z)n_h^2\rho}{y+z+\rho}\right)\left(\frac{3}{2} + \frac{n_h^2\rho}{y+z+\rho}\right)\right]. \quad (22)$$

Here G is the magnitude of the smallest reciprocal lattice vector

$$G = \begin{cases} (2\pi/d)\sqrt{3} & \text{for FCC}, \\ (2\pi/d)\sqrt{2} & \text{for BCC}. \end{cases} \quad (23)$$

d the lattice constant, and $G_h = n_h G$. Other symbols are defined as

$$x = \xi G^2, \quad y = \eta G^2, \quad \rho = \bar{R}^2 G^2,$$

$$z = k_B T G^2/\phi. \quad (24)$$

An equation for the bulk state is derived from (22) by taking the limit $\rho \to \infty$:

$$k_B T/G^3 = zF(z, \infty)$$

$$= (\pi^{3/2}/2)z[\Gamma(x+z)^{-5/2}$$

$$- \Lambda(y+z)^{-5/2}]$$

$$- \sum_h (4/9\sqrt{3})zn_h^2$$

$$\times [\Gamma \exp\{-(x+z)n_h^2\}$$

$$- \Lambda \exp\{-(y+z)n_h^2\}]. \quad (25)$$

As an example, the right-hand side of Eqs. (22) and (25) for the case of Ag is plotted as functions of z for several values of ρ or $\bar{R}$ in Fig. 2.
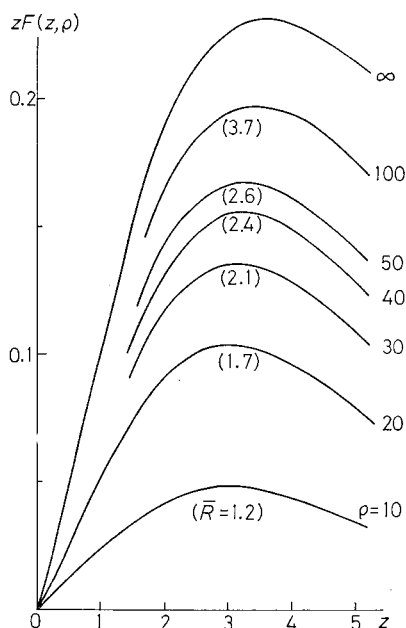

Fig. 2. $zF(z, \rho)$ vs z curves for various ρ values. The used parameters correspond to Ag metal.

§ 4.   Application to melting of fine particles

As discussed in § 2, there is a critical temperature above which the self-consistent equation has no solution. This temperature can be readily determined by looking for the maximum of the right-hand side of Eq. (22) or (25). Thus we have

$$T_m{}^f/T_m{}^b = \frac{[zF(z, \rho)]_{\max}}{[zF(z, \infty)]_{\max}} \quad (26)$$

as a function of ρ. Let us assume that $T_m{}^f/T_m{}^b$ is a proportional measure of the melting temperature of metallic fine particles relative to that of the bulk material. In Fig. 3 $T_m{}^f/T_m{}^b$ is plotted as functions of $\bar{R}$ for several metals and a comparison between the theory and experiment is made for a particular case of Pb in Fig. 4. If we use a scale such that

$$\bar{R} \cong R/10, \tag{27}$$

the agreement between the theoretical curve and experimental data becomes excellent. The change of the scale required in (27) may be somewhat large, but not so unreasonable from the following reason. We have so far neglected the posi-
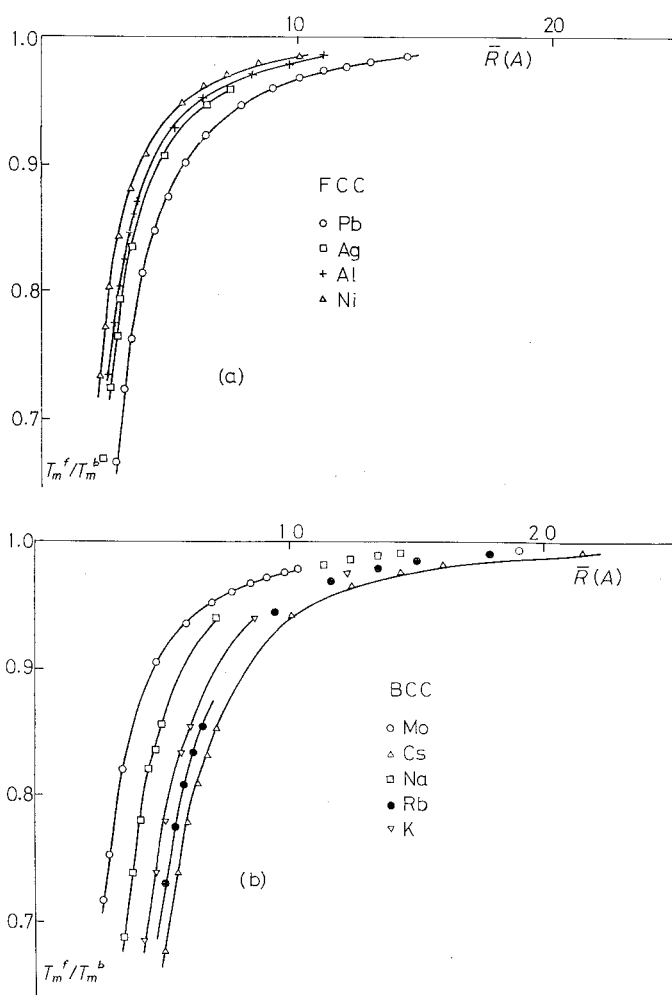

Fig. 3. $T_m{}^f/T_m{}^b$ as functions of the effective average radius $\bar{R}$ for (a) FCC metals and (b) BCC metals.

tional dependence of $\phi(\boldsymbol{R})$ and replace $\phi(\boldsymbol{R})$ by $\phi(0)$, the value at the center of fine particle. This apparently results in an overestimation of ϕ, because $\phi(\boldsymbol{R})$ is expected to diminish rapidly near the surface. Inspecting the curves in Fig. 2, we observe that in order to have smaller ϕ or larger z for given temperature, a smaller value of $\bar{R}$ should be chosen. Therefore good agreement between the theory and the experiment will be attained when $\bar{R}$ is set to a value smaller than the real average radius R as suggested in (27). We need however more discussion to justify the scaling given in Eq. (27) and we shall come back again to this point in the last section.
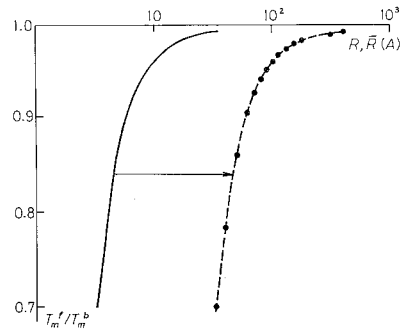

Fig. 4. Comparison of $T_m{}^f/T_m{}^b$ between the calculated curve (solid line) and the experimental data (black points) for Pb. By a suitable change of the scale, it is possible to make the theoretical curve coincide with the experimental curve (dotted line).

§ 5. Size dependence of superconducting transition temperature

As mentioned in the Introduction, the superconducting transition temperature T_c of metallic fine particle is generally increased with decreasing size of particle (see Fig. 1). It is believed that this increment of T_c is mainly due to the surface softening. Then it would be very interesting to see how the present theory can be applied to this phenomena.

We begin with the well-known expression for T_c due to McMillan:[13]

$$T_c = \frac{\Theta}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right]. \tag{28}$$

In this formula, Θ is the Debye temperature, μ^* a parameter related to the screened Coulomb repulsion between electrons, λ the electron-phonon coupling constant. It is known that μ^* is nearly constant (≈ 0.1) for most polyvalent metals, while λ is expressed as

$$\lambda = N(0)\langle J^2 \rangle / M \langle \omega^2 \rangle, \tag{29}$$

where $N(0)\langle J^2 \rangle$ turns out empirically to be almost constant for all material. As example we list in Table II the bulk values of λ, $N(0)\langle J^2 \rangle$ and T_c for three

Table II.

		Pb	In	Al
λ		1.12	0.71	0.38
$N(0)\langle J^2 \rangle$	(eV. A^{-2})	2.34	1.76	2.0
T_c	(K)	7.19	3.40	1.16

metals Pb, In and Al. We have a similar formula for T_c of metallic fine particle, but with different parameters modified through the change in the phonon spectrum: Θ and λ are to be different for the bulk state and fine particle. Taking the ratio of the two expressions for T_c yields

$$T_{cf}/T_{cb} = \frac{\Theta_f}{\Theta_b} \exp\left[-\frac{1.04(1+\lambda_b)}{\lambda_b - \mu^*(1+0.62\lambda_b)} - \frac{1.04(1+\lambda_f)}{\lambda_f - \mu^*(1+0.62\lambda_f)} \right], \quad (30)$$

where the suffices f and b refer to fine particle and bulk respectively. In our self-consistent Einstein model it holds that

$$3\hbar^2 T/Mk_B\Theta^2 = \langle u^2 \rangle = k_B T/\phi = k_B T/M\omega^2 \quad (31)$$

and hence we may put

$$\Theta_f/\Theta_b = \omega_f/\omega_b. \quad (32)$$

On the other hand, assuming $N(0)\langle J^2 \rangle$ a constant, we can approximate

$$\lambda_f/\lambda_b = \langle \omega_b^2 \rangle / \langle \omega_f^2 \rangle \cong \omega_b^2/\omega_f^2. \quad (33)$$
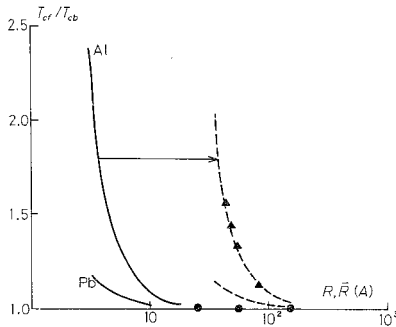

Fig. 5. Theoretical curves of superconducting transition temperature as functions of effective average radius $\bar{R}$ for Al and Pb. By a change of the scale, the theoretical curve for Al coincides with the experimental curve.

Since the ratio $(\omega_f/\omega_b)^2$ is easily obtained from the slopes of the $k_B T/G^3$ vs z curves such as Fig. 2, upon substituting (32) and (33) into (30), T_{cf}/T_{cb} is determined as a function of $\bar{R}$. The numerical results calculated in this manner for Al and Pb are shown in Fig. 5 together with the experimental data. Here again the same scaling as Eq. (27) gives rise to an excellent agreement between the theory and the experiment for Al in spite of the crude approximation which cannot be applied at low temperatures. The agreement for the case of Pb is poor, but this will be probably due to the fact that Pb is the well-known strong coupling superconductor for which a simple theory does not work.

§ 6. Summary and discussion

In the previous sections, we have developed a theory of anharmonic lattice vibration in metallic fine particles on the basis of the self-consistent Einstein model, and applied it to the discussion on the size dependence of the melting and super-conducting transition temperatures of fine particles. To facilitate practical application of the theory to the fine particles of real cubic metals, a Gaussian potential for pair-wise atomic interaction is proposed and the potential constants are deter-

mined in such ways that the calculated lattice constant, compressibility and sublimation energy for 16 cubic metals agree with the corresponding experimental data. Then, by assuming certain distribution of particle size, an effective average radius $\bar{R}$ is introduced and the ratios of the melting and superconducting transition temperatures of fine particles to bulk metal are derived as functions of $\bar{R}$. Surprisingly good agreement between the theory and experiments is obtained when $\bar{R}$ is chosen as about tenth of the average radius R. Thus except for the ambiguity in choosing the scale for the effective average radius, the present theory seems very successful in accounting main phenomena which are related with the surface softening of metallic fine particles. We are therefore in a position to examine more carefully the meaning of $\bar{R}$.

By definition $f(\boldsymbol{q})$ is the Fourier transform of the step function $\theta(R-|\boldsymbol{r}|)$ (see Eqs. (6) and (9)). The replacement of $f(\boldsymbol{q})$ with the Gaussian form Eq. (21) means, therefore, to take a Gaussian distribution function instead of $\theta(R-|\boldsymbol{r}|)$:

$$g(r) = \exp(-r^2/4\bar{R}^2). \tag{34}$$

This replacement certainly reflects some distribution of the particle size R, but if the scaling relation $\bar{R}=R/10$ is put into (34), we find

$$g(r) = \exp[-(5r/R)^2]$$

which gives rise to an extremely small probability for $g(R)$. In another word, with the present approximation, quantitative agreement between the theory and experiments is attained only by assuming an effective radius much smaller than the given R, admitting significant reduction of the contribution from the surface parts. This result is of course caused by that we neglect the positional dependence of $\phi(\boldsymbol{r})$ and the cooperative interaction between the surface and interior atoms is not enough taken into consideration. As proved in the previous paper,[1] the effect of the non-linear cooperative coupling between the surface softening and weakening of the effective interaction potential should be very important when the surface to volume ratio becomes large as in the metallic fine particles. However we will not enter this point any further, leaving it as a future problem.

References

1) T. Matsubara and K. Kamiya, Prog. Theor. Phys. **58** (1977), 767.
2) M. Takagi, J. Phys. Soc. Japan **9** (1954), 359.
3) C. R. M. Wronski, Brit. J. Appl. Phys. **18** (1967), 1731.
4) C. J. Coombes, J. Phys. **2** (1972), 441.
5) P. Buffat and J. P. Borel, Phys. Rev. **A13** (1976), 2287.
6) M. Blackman and A. E. Curzon, *Structure and Properties of Thin Films* (John Willey, New York, 1959), p. 217.
7) A. Nakanishi and T. Matsubara, J. Phys. Soc. Japan **39** (1975), 1415.
8) S. Matsuo, H. Sugiura and S. Noguchi, J. Low Temp. Phys. **15** (1974), 481.
   S. Matsuo, H. Miyata and S. Noguchi, Japan. J. Appl. Phys. **13** (1974), 351.
9) Y. Kashiwase, I. Nishida, Y. Kainuma and K. Kimoto, J. Phys. Soc. Japan **38** (1975), 899.

10) J. Harada, S. Yao and A. Ichimiya, Acta Cryst. **A31** S3 (1975), 204.
11) See for instance, *Dynamical Properties of Solids*, edited by G. W. Horton and A. M. Maradudin (North-Holland, American Elsevier, Amsterdam, 1974), Chap. 9.
12) L. A. Girifalco and V. G. Weizer, Phys. Rev. **114** (1959), 687.
13) W. L. McMillan, Phys. Rev. **167** (1968), 331.