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Vibrational Anharmonicity and Lattice Thermal Properties. II

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Following an earlier paper based on the Morse potential, the analysis of the thermal properties of a linear chain is now extended to cover an interatomic potential of arbitrary form. The Lennard-Jones potential is taken as an example and the results for the thermal expansion coefficient are compared with experimental data.

1. INTRODUCTION

In a previous paper[1] which we shall refer to as (I), an analysis was made of the statistical thermodynamics of a linear assembly of atoms interacting with nearest neighbors through a Morse potential. We now show that the analysis may be extended to cover an interatomic potential of arbitrary form, and apply the Lennard-Jones potential.

2. ANALYSIS

As in (I), we consider a linear chain of $N+1$ identical particles of mass m which at 0°K and under zero tension have a uniform separation A_0 (Fig. 1); let the potential energy between two particles, at arbitrary distance r, be $\Phi(r)$. We now assume that $\Phi(r)$ has the general form of Fig. 2 such that

$$\begin{aligned} &\text{(i)}\quad \Phi'(A_0)=0;\quad \Phi(A_0)=-D,\\ &\text{(ii)}\quad (a)\ \lim_{r\to\infty}\Phi(r)=0,\\ &\qquad\quad (b)\ \lim_{r\to\infty}\{r\Phi'(r)\}=0, \qquad\qquad (1)\\ &\qquad\qquad\quad \text{such that: } \int^{\infty} r\Phi'(r)dr \text{ exists}\\ &\text{(iii)}\quad \lim_{r\to-\infty}\{\Phi(r)/-r\}=\infty. \end{aligned}$$

The potential energy of the whole system with arbitrary displacements, y_n, is

$$V=\sum_{n=1}^{N}\Phi(A_0+y_n-y_{n-1})\equiv\sum_{n=1}^{N}\Phi(A_0+x_n),$$
$$=\sum_{n=1}^{N}D(\psi(ax_n)-1),$$

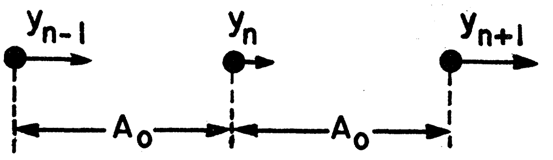

Fig. 1. Section of linear chain.

where

$$\psi(ax_n)=(ax_n)^2+\lambda_3(ax_n)^3+\cdots+\lambda_s(ax_n)^s+\cdots,[2]$$

so that

$$a=(\Phi''(A_0)/2D)^{\frac{1}{2}},\quad \lambda_s=\{2^{s/2}D^{(s-2)/2}\Phi^{(s)}(A_0)\}/s!(\Phi'')^{s/2},\tag{2}$$

and (writing $z=ax$)

$$\psi(z)=1\quad\text{for}\quad\begin{cases} z\longrightarrow\infty\\ z=-z_0\end{cases}\quad\text{(see Fig. 3).}$$

We now proceed essentially as in (I) to set up the partition function $Z_G(P,N,T)$, which may then be written

$$Z_G(P,N,T)=(2\pi mkT)^{N/2}\exp\left(-\frac{NPA_0-ND}{kT}\right)a^{-N}I^N,$$
$$\equiv KI^N;$$

where

$$I=\int_{-\infty}^{+\infty}\exp\left\{-\left(\frac{Pz}{akT}+\frac{D}{kT}\psi(z)\right)\right\}dz$$
$$=-\frac{akT}{P}\left[\exp\left\{-\left(\frac{Pz}{akT}+\frac{D}{kT}\psi(z)\right)\right\}\right]_{-\infty}^{\infty}$$
$$-\frac{aD}{P}\left\{\int_{-\infty}^{-z_0}+\int_{-z_0}^{\infty}\exp\left\{-\left(\frac{Pz}{akT}+\frac{D}{kT}\psi(z)\right)\right\}\times\psi'(z)dz\right\}.$$

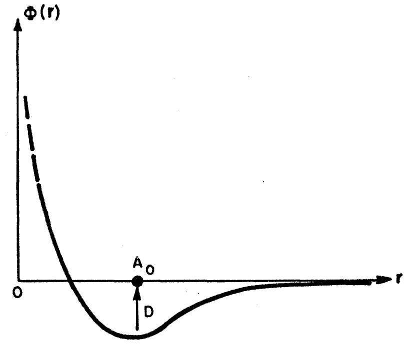

Fig. 2. General form of interatomic potential.

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[1] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **96**, 57 (1954).

[2] It follows readily that the one-dimensional Grüneisen parameter, $\gamma\equiv-d\log\nu/d\log L$ is given by $\gamma=-\frac{3}{2}\lambda_3 aA_0$ (ν: characteristic frequency; L: length of chain).

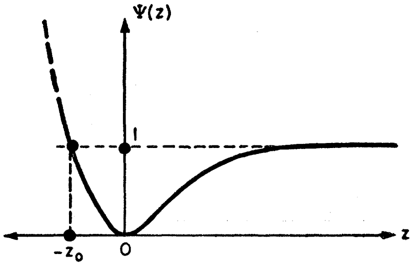

FIG. 3. General form of normalized interatomic potential.

The first term then vanishes identically for all $P>0$, using 1 (iii). In the curly brackets, the first term becomes significant as $P\rightarrow 0$, assuming the form $(akT/P)\times\exp(-D/kT)$, and corresponds exactly as in (I) to the gas-like state at sufficiently low "pressures." The remaining term, say J, which is dominant for all normal values of P, determines the properties of the condensed state and we shall now evaluate it.

3. CONDENSED STATE

Writing $\chi(z)=\psi(z)-z^2=\lambda_3 z^3+\lambda_4 z^4+\cdots$,

$$J=-\frac{aD}{P}\sum_{s=0}^{\infty}\left(-\frac{P}{akT}\right)^s\frac{1}{s!}\int_{-z_0}^{\infty}\exp\left\{-\frac{D}{kT}z^2\right\}z^s \times\exp\left\{-\frac{D}{kT}\chi(z)\right\}\psi'(z)dz.$$

Assuming $D/kT\gg 1$, we may now extend the lower limit of integration to $-\infty$, and evaluate the integrals by expansion of the *second* exponential factor.

Hence:

$$Z_G=K(\pi kT/D)^{N/2}\{1+A_1(kT/D)+A_2(kT/D)^2+\cdots +B_1(P/aD)+B_2(P/aD)(kT/D)+\cdots +C_1(P/aD)^2(kT/D)^{-1}+C_2(P/aD)^2+\cdots\},$$

where

$$A_1=\tfrac{3}{16}(5\lambda_3{}^2-4\lambda_4),$$

$$A_2=-(15/8)[\lambda_6-(7/4)\lambda_4{}^2+(7/2)\lambda_3\lambda_5+(63/8)\lambda_4\lambda_3{}^2-(231/64)\lambda_3{}^4],$$

$$B_1=\tfrac{3}{4}\lambda_3,\quad B_2=\tfrac{3}{8}[5\lambda_5-(35/2)\lambda_3\lambda_4+(105/8)\lambda_3{}^3],$$

$$C_1=\tfrac{1}{4},\quad C_2=\tfrac{1}{8}[-(15/2)\lambda_4+(105/8)\lambda_3{}^2].$$

TABLE I. Table of values of $(m+n+3)/mn$.

$n\diagdown m$	1	2	3	4
6	1.67	0.92	0.67	0.54
9	1.44	0.78	0.56	0.44
12	1.33	0.71	0.50	0.40

Thus,

$$G=-kT\ln Z_G =-NkT\ln(2\pi^2mk^2/a^2D)^{\frac{1}{2}}-NkT\ln T+PNA_0 -ND-ND\{A_1(kT/D)^2+D_2(kT/D)^3+\cdots +B_1(P/aD)(kT/D)+E_2(P/aD)(kT/D)^2+\cdots +C_1(P/aD)^2+\cdots\},\quad (3)$$

where

$$D_2=A_2-\tfrac{1}{2}A_1{}^2=(15/8)(-\lambda_6+\tfrac{3}{5}\lambda_4{}^2+(7/2)\lambda_3\lambda_5-(15/2)\lambda_3{}^2\lambda_4+(27/8)\lambda_3{}^4),$$

$$E_2=B_2-A_1B_1=(15/8)(\lambda_5-(16/5)\lambda_3\lambda_4+(9/4)\lambda_3{}^3),$$

$$F_2=C_2-\tfrac{1}{2}B_1{}^2-A_1C_1=\tfrac{3}{4}(-\lambda_4+\tfrac{3}{2}\lambda_3{}^2).$$

4. SPECIFIC INTERATOMIC POTENTIALS

If we now introduce the values of the λ's [Eq. (2)] to generate the Morse potential (i.e., $\lambda_3=-1$, $\lambda_4=7/12$, $\lambda_5=-1/4$, $\lambda_6=31/360$, etc.), we find complete agreement with the direct analysis given in (I). Let us consider also the well-known Lennard-Jones potential:

TABLE II. Alkali metals (Structure: b.c.c.).

Element	D(cal/mole)[a]	$\alpha_{\exp}$(deg^{-1})	αD
Li	36 000	5.6×10^{-5}	2.02
Na	26 200	7.2×10^{-5}	1.89
K	21 900	8.3×10^{-5}	1.82
Rb	20 600	9.0×10^{-5}	1.85
Cs	18 700	9.7×10^{-5}	1.81

[a] D is interpreted as the latent heat of vaporization at absolute zero.

$$\Phi(r)=\frac{A}{r^n}-\frac{B}{r^m}\quad(n>m>0),$$

which satisfies the conditions of (1) above. Then from (2):

$$\lambda_3=-(2/mn)^{\frac{1}{2}}(m+n+3)/3,$$
$$\lambda_4=(1/6nm)(n^2+nm+m^2+6n+6m+11),\qquad (4)$$
$$\lambda_s=\{(-)^s2^{s/2}/s!\}[(n+1)(n+2)\cdots(n+s-1)-(m+1)(m+2)\cdots(m+s-1)/(n-m)(nm)^{\frac{1}{2}s-1}].$$

Following (I) let us discuss two properties in particular, the thermal expansion and the specific heat.

Thermal Expansion

Using $L=(dG/dP)_T$ with Eq. (3), we obtain

$$\frac{1}{L_0}\left(\frac{dL}{dT}\right)_P=-\frac{k}{aA_0D}\{B_1+2E_2(kT/D)+\cdots +2F_2(P/aD)+\cdots\},$$

which, for $(kT/D)\ll 1$ and $(P/aD)\ll 1$ gives:

$$\frac{1}{L_0}\left(\frac{dL}{dT}\right)_{P\simeq 0}\equiv\alpha=\frac{3}{4}\frac{k\lambda_3}{aA_0D}=\frac{k}{2}\left(\frac{m+n+3}{mnD}\right).^{[3]} \qquad (5)$$

Noting also that now

$$\gamma=(m+n+3)/2,$$

we may write

$$\alpha=k\gamma/Dmn.$$

This may be compared with the relationship deduced by Grüneisen[4]:

$$\bar{\alpha}=C_v\bar{\gamma}/\Lambda_0\bar{m}\bar{n}.$$

$\bar{\alpha}$, $\bar{\gamma}$, $\bar{m}$, $\bar{n}$ are the appropriate analogs in three-dimensions, and Λ_0 is the sublimation energy at absolute zero. To compare with experiment, Grüneisen then evaluated approximately the factor $\bar{\gamma}/\bar{m}\bar{n}$; however, we can proceed more directly from Eq. (5). If then we risk a comparison with the experimental data on metals, one might expect that for a reasonable approximation to the physical potential m would lie between the extreme values 1 and 4 and n between 6 and 12. Table I then shows that the factor $(m+n+3)/mn$ lies between the extreme values 1.67 and 0.40. Taking therefore unity as a mean value for this factor, we find from Eq. (5) that $\alpha\approx 0.5k/D$, which we may compare with Grüneisen's result: $\bar{\alpha}\approx 0.6C_v/\Lambda_0$.

TABLE III. Noble metals (Structure: f.c.c.).

Element	D(cal/mole)[a]	$\alpha_{\exp}$(deg^{-1})[b]	αD
Cu	81.7×10^3	16.4×10^{-6}	1.34
Ag	69.4×10^3	19.0×10^{-6}	1.31
Au	90.7×10^3	14.4×10^{-6}	1.31

[a] Extracted from Landolt-Börnstein Tables.
[b] Extracted from *Smithell's Metals Reference Book* (Butterworth's Publications, London, 1949).

Using the data collected in (I) (Table II), we have the results of Table II, while in Table III similar calculations have been made for the noble metals (Cu, Ag, Au) (see also Grüneisen[5]).

The relative constancy of the last column in Tables II and III suggests that within the limits of the model the values of m and n may be considered as constant within each of these monovalent metal groups, i.e., that a law of corresponding states is valid within each group.

Turning to the Group II metals (Be, Mg; Ca, Sr, Ba; Zn, Cd, Hg) the experimental data conflict in a number of cases, but Table IV shows that, even in this very diverse group of metals, αD is still sufficiently constant to lead us to suggest that the as yet unknown expansion coefficient of Sr should be close to 23×10^{-6}, and that the uncertain value for Ba taken from Smithell's Handbook is possibly low.

TABLE IV. Group II metals.

Element	D(cal/mole)[a]	$\alpha_{\exp}$(deg^{-1})[b]	αD	Structure
Be	55×10^3	$18.7^{c}\times 10^{-6}$	1.03	hex.
Mg	36.6×10^3	26×10^{-6}	0.95	hex.
Ca	42.9×10^3	22×10^{-6}	0.94	f.c.c.
Zn	31.4×10^3	31.2×10^{-6}	0.98	hex.
Sr	40×10^3	...	...	f.c.c.
Cd	27.0×10^3	29×10^{-6}	0.79	hex.
Ba	40.9×10^3	$(18?)\times 10^{-6}$	0.74	b.c.c.
Hg	15.5×10^3	...	...	rhomb.

[a] Extracted from Landolt-Börnstein Tables.
[b] Extracted from *Smithell's Reference Book* (Butterworth's Publications, London, 1949).
[c] The value of α at room temperature is 12×10^{-6}/°C and this has been multiplied by the ratio $3R/C_v$ (θ for Be$\sim$1000 °K). All the other metals considered are essentially classical at room temperature.

Considering now solids such as the frozen inert gases where the binding forces are of the van der Waals' type, we should expect that here the requirements of central forces and nearest-neighbor interaction [implicit in the model—see (I)] would be best satisfied. Using data deduced from gas-kinetic studies, we may estimate values for the linear thermal expansion coefficient, α. In Table V data are collected for the heavier inert gases (Xe, Kr, A).

For these solids $m=6$ semitheoretically and, as is common, n is taken as 12. Thus

$$\alpha=21k/144D.$$

Although $\alpha_{\exp}$ for argon is only approximate, the agreement with theory is sufficiently good to suggest that the at present unknown values for Kr and Xe must be close to those predicted.

Since the Lennard-Jones and Morse potentials give results which appear physically quite reasonable, it might be thought that any hypothetical interatomic potential which satisfies the elementary requirements of a large repulsive energy for $r=0$, a finite value at $r=+\infty$ and a single intervening minimum would suffice. However, one may readily choose an artificial potential (e.g., see Fig. 4) which satisfies *these* require-

TABLE V. The heavier inert gases.

Element	D(cal/mole)	$\alpha_{\text{theor.}}$	$\alpha_{\exp}$
Xe	448[a]	6.5×10^{-4}	...
Kr	344[b]	8.4×10^{-4}	...
A	237[c]	1.21×10^{-3}	1×10^{-3} [d]

[a] Beattie, Barriault, and Brierley, J. Chem. Phys. **19**, 1223 (1951).
[b] Beattie, Brierley, and Barriault, J. Chem. Phys. **20**, 1613 (1952).
[c] R. L. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1949).
[d] F. E. Simon and F. Kippert, Z. physik. Chem. **135**, 113 (1928).

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[3] It then follows that the one-dimensional Grüneisen relationship $\gamma=\alpha L/\beta C_L$, where $\beta=(1/L)(dL/dP)_T$, holds true to the first approximation.

[4] E. Grüneisen, Ann. Physik. **39**, 289 (1912).

[5] E. Grüneisen, Verhandl. deut. physik. Ges. **10**, 322 (1912).

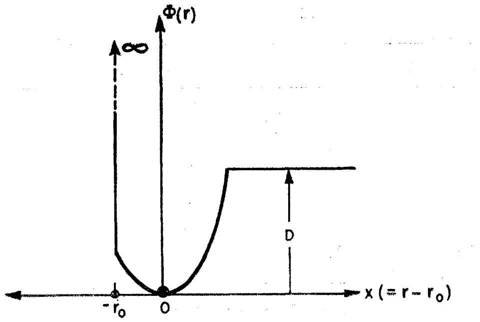

FIG. 4. Hypothetical form of interatomic potential.

ments but which predicts physically quite unrealistic behavior for the thermal expansion.

Specific Heat

Using $C_P = -T(\partial^2 G/\partial T^2)_P$ with Eq. (3), we find

$$C_P = Nk\{1+\tfrac{3}{8}(5\lambda_3{}^2-4\lambda_4)kT/D+\cdots\},$$

and thus, using $C_P - C_L = T(\partial L/\partial T)_P(\partial P/\partial T)_L$,

$$C_{L;P\simeq 0} = Nk\{1+\tfrac{3}{4}(\lambda_3{}^2-2\lambda_4)kT/D+\cdots\}.$$

Introducing now the Lennard-Jones potential [see Eq. (4)], we obtain

$$C_{P;P\simeq 0} = Nk\{1+(1/12mn)(2m^2+2n^2+7mn+12m+12n+27)kT/D+\cdots\},$$

$$C_{L;P\simeq 0} = Nk\{1-(1/12mn)[(n-m)^2+nm+6m+6n+15]kT/D-\cdots\}.$$

Thus, for *all* $m,n>0$, $C_{P;P\simeq 0}$ is predicted to increase with T, whereas $C_{L;P\simeq 0}$ is predicted to diminish with T as found also in (I) for the Morse potential.

The general condition that the term in C_L linear with temperature should be negative may be written (see also Damköhler[6])

$$[\Phi'''(A_0)]^2 > \tfrac{3}{2}\Phi''(A_0)\Phi^{\text{iv}}(A_0).$$

This inequality is satisfied by both the Morse and Lennard-Jones potentials (whatever the values of n and m). We may therefore conclude, as foreseen in (I), that it is extremely unlikely that any physically plausible potential would give rise to a C_L increasing with temperature, in agreement with Damköhler's conclusions.

We are most grateful to Dr. J. S. Dugdale for many helpful discussions in the preparation of this paper.

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[6] G. Damköhler, Ann. Physik. 24, 1 (1935).

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Physical Defects in Silver Halides[*]

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The concentrations of imperfections in silver halides grown from the melt were investigated by comparing the measured densities with the ideal densities computed from the lattice dimensions. The density defect of the most perfect specimen of silver bromide was $\Delta\rho/\rho = -0.8\times 10^{-4}$. The greatest amount of imperfection was $\Delta\rho/\rho = -18\times 10^{-4}$ in a specimen of silver bromide containing about 4 mole percent silver iodide. Considering the effects of various configurations of voids, it seems reasonable to attribute most of the density defect in the best crystals to immobile aggregates of vacancies and to dislocations associated with small-angle mosaic structure. The contributions of large-angle grain boundaries and Schottky defects are negligible.

INTRODUCTION

THE concentration of imperfections in a crystal is of importance in determining many of its properties. In the silver halides considered here, the number of imperfections is undoubtedly closely associated with photographic behavior and with such related properties as optical absorption and electron- and hole-trapping.[1]

A direct method of obtaining information on the soundness of a crystal is to compare the measured density with an ideal density computed from the weight and volume of material in the unit cell. Straumanis[2] has recently reconsidered this type of measurement, and has determined the best values of atomic constants to use in the computations, assuming calcite to be a perfectly sound crystal.

The present investigation is a study of the defects at room temperature in pure specimens, prepared from the melt, of silver bromide, silver chloride, and solid solutions of a few mole percent silver iodide in silver bromide. Measurements reported by Keith and Mitchell[3]

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[*] Communication No. 1690 from the Kodak Research Laboratories.

[1] F. Seitz, Revs. Modern Phys. 23, 328 (1951).

[2] M. E. Straumanis, Phys. Rev. 92, 1155 (1953).

[3] H. D. Keith and J. W. Mitchell, Phil. Mag. 7, 42, 1331 (1951).