

Vibrational Anharmonicity and Lattice Thermal Properties

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It has been believed for some time that anharmonicity of lattice vibrations is responsible for the continued rise of the specific heats of certain solids in the classical temperature region. A general analysis is here carried out of the linear chain model interacting through a Morse potential. All the major thermal properties, such as specific heats, thermal expansion, and compressibility are derived, and a tentative comparison is made with observed properties of the alkali metals.

It is found that the linear chain then exists in two widely different states with properties characteristic of condensed and gas-like phases; these two states are separated by a relatively narrow transition region in temperature where the specific heat passes through a rather sharp maximum (except at high pressures when the maximum ultimately disappears).

1. INTRODUCTION

THE atomic heats of the alkali metals Li, Na, K, and Rb all show anomalous behavior at temperatures greater than their characteristic temperatures. Apart from the sharp increase in specific heats as the melting temperature is approached (this and the corresponding behavior of the electrical resistance are attributed to the formation of defects in the lattice),^{1,2} there is also a steady rise in atomic heat at constant volume above the value $3R$ which is the classical limit if only harmonic vibrations of the lattice are considered. Furthermore, this excess atomic heat is too large to be accounted for on the basis of a free electron contribution. It was suggested by Lindemann³ that such anomalous behavior might be due to the anharmonicity of the lattice vibrations and this explanation has generally been regarded as probably correct. Born and Brody, Born,⁴ Waller,⁵ and Damköhler⁶ have all made estimates of the influence of anharmonicity on the specific heat of a lattice.

Anharmonicity is an important feature of the behavior of lattices for other reasons. There are many significant properties of a lattice such as thermal expansion, the change of specific heat with pressure, etc., which are zero if a purely harmonic potential is assumed. Finally the anharmonicity of lattice vibrations is responsible for the establishment of thermal equilibrium among the modes of vibration of the lattice and for the existence of a finite thermal conductivity.^{7,8} For these reasons further study of the influence of anharmonicity was considered desirable.

In the treatment of anharmonicity given by Born and Brody (Waller's conclusions are essentially the same) the precise model is not defined well enough to enable

the conclusions to be clearly interpreted and in addition there are problems of convergence which were not considered (see also reference 5). Damköhler, on the other hand, considered a precise model (a linear chain) with specified boundary conditions, and because this makes the problem directly tractable a linear chain model is considered in this paper. The treatment here is, we believe, considerably simpler and more direct than that of Damköhler; we evaluate the Gibbs free energy analytically instead of by numerical approximation, and consequently our results can be carried to any desired degree of precision. The analysis is also readily extended to include next-nearest neighbor interaction in good approximation. Moreover, the procedure adopted here reveals certain other properties of the model which are of interest in their own right. It is found that at low pressures there exists a relatively narrow temperature region in which the specific heat at constant pressure passes through a sharp maximum (at higher pressures the maximum ultimately disappears), above which the equation of state of the chain approximates to that of a perfect linear "gas", while below this "transition" the chain has the properties of a condensed state.

2. GENERAL ANALYSIS

The linear chain model has been considered in a large number of papers.⁹⁻¹¹ In the treatment given here, a single physically realistic interatomic potential (the Morse potential) is employed and all the important thermodynamic properties of such a chain are derived for temperatures high enough that classical statistics are applicable. Although the application to three dimensions of results derived on a one-dimensional model is necessarily very tentative, we have, in order to keep in touch with physical reality, interpreted some of the quantities appearing in the analysis in terms of the physical properties of sodium, since we are particularly interested in the alkali metals.

¹ L. G. Carpenter, *J. Chem. Phys.* **21**, 2244 (1953).

² D. K. C. MacDonald, *J. Chem. Phys.* **21**, 177 (1953).

³ F. A. Lindemann, *Phil. Mag.* **45**, 1119 (1923).

⁴ M. Born and E. Brody, *Z. Physik* **6**, 132 (1921); M. Born, *Handbuch der Physik* (Springer Publishing Company, Inc., Berlin, 1933), Vol. 24, Part 2, p. 675.

⁵ I. Waller, *Ann. Physik* **83**, 153 (1927).

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

⁷ R. Peierls, *Ann. Physik* **3**, 1055 (1929).

⁸ R. Peierls, *Ann. inst. Henri Poincaré* **5**, 177 (1935).

⁹ T. Nagamiya, *Proc. Phys.-Math. Soc. Japan* **22**, 705, 1034 (1940).

¹⁰ H. Takahasi, *Proc. Phys.-Math. Soc. Japan* **24**, 63 (1942).

¹¹ F. Gürsey, *Proc. Cambridge Phil. Soc.* **46**, 182 (1950).

We consider then a system of $(N+1)$ identical particles of mass m equally separated (at 0°K and under zero tension) by a distance A_0 (see Fig. 1). These initial

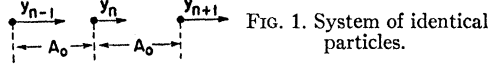


FIG. 1. System of identical particles.

positions of the particles are then chosen as the origins of measurement for the displacements of the respective particles, and that of the n th particle from its origin is denoted by y_n . Without loss of generality, we may consider as fixed the zeroth particle so that y_0 is always zero. The interatomic potential of two particles separated by a distance r is $\Phi(r)$. Thus the energy of interaction between the n th and the $(n-1)$ th particle is $\Phi(A_0 + y_n - y_{n-1})$, and the potential energy of the whole system is

$$V = \sum_{n=1}^N D(e^{-a(y_n - y_{n-1})} - 1)^2, \quad (1)$$

where we use the Morse potential and initially restrict the analysis to nearest-neighbor interaction. Hence, if we write

$$x_n = y_n - y_{n-1},$$

then

$$V = \sum_{n=1}^N D(e^{-ax_n} - 1)^2. \quad (2)$$

We now set up what may be called the partition function at constant force, $Z_G(P, N, T)$, (see for example, Fowler and Guggenheim¹²) where P is the applied force, analogous to pressure in a three-dimensional problem. Then

$$Z_G(P, N, T) \equiv \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \times e^{[-H(y_1, \dots, y_N) + PL]/kT} dp_1 \cdots dq_N \cdots, \quad (3)$$

where $L = NA_0 + \sum_1^N x_n$. Takahasi¹⁰ and Gürsey¹¹ have also shown analytically that this form of partition function may be derived from the more usual form, Z_F , the partition function at constant length (volume). Thus

$$Z_G = m^N \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \exp\left\{-\left[\sum_n D(e^{-ax_n} - 1)^2 + P(NA_0 + \sum_n x_n) + m \sum_n \dot{y}_n^2/2\right]/kT\right\} dy_1 \cdots \times dy_n dy_1 \cdots dy_n; \quad (4)$$

that is,

$$Z_G = K \left[\int_{-\infty}^{+\infty} \exp\left(-\frac{Pz}{akT} + \frac{D}{kT}(e^{-z} - 1)^2\right) dz \right]^N, \quad (5)$$

where

$$K = (2\pi mkT)^{N/2} e^{-NPA_0/kT} a^{-N}.$$

Thus, if we set $u = e^{-z}$, we have¹³

$$Z_G = K \left\{ \int_0^{\infty} u^{(P/akT)-1} \exp[-D(u-1)^2/kT] du \right\}^N \equiv K I^N. \quad (5a)$$

If we write $v = u - 1$, and integrate by parts, then

$$\begin{aligned} I &= \frac{2aD}{P} \int_{-1}^{\infty} (1+v)^{P/akT} v \exp(-Dv^2/kT) dv \\ &= \frac{2D}{kT} \int_{-1}^{+1} \exp(-Dv^2/kT) \left\{ v^2 + \left(\frac{P}{akT} - 1\right) \right. \\ &\quad \times \left. \left(\frac{P}{akT} - 2\right) \frac{v^4}{3!} + \cdots \right\} dv \\ &\quad + \frac{2aD}{P} \int_1^{\infty} v^{P/akT+1} \exp(-Dv^2/kT) dv \\ &\quad + \frac{2D}{kT} \int_{+1}^{\infty} v^{P/akT} \exp(-Dv^2/kT) \\ &\quad \times \left\{ 1 + \left(\frac{P}{akT} - 1\right) \frac{1}{2!v} + \cdots \right\} dv \quad (6) \\ &\equiv \frac{2D}{kT} (I_1 + I_3) + \frac{2aD}{P} I_2. \quad (6a) \end{aligned}$$

It should be noted that so far no approximations have been made. In (6a) it may now be shown that I_3 is certainly entirely negligible in comparison with I_1 except for $(P/akT) \gg 1$. For the compressible metal sodium at $\sim 300^\circ\text{K}$, the equivalent pressure corresponding to the equality $P/akT = 1$ is about 3000 atmos. We shall therefore assume meanwhile that $P/akT < 1$ and so ignore I_3 . Now as $P \rightarrow 0$ it is evident that the first term converges uniformly to a finite limit while the second term does not; in fact, then

$$I \approx (\pi kT/D)^{1/2} + (akT/P) e^{-D/kT}. \quad (7)$$

The second term is then only comparable with the first for

$$P \lesssim (a^2 D kT)^{1/2} e^{-D/kT}. \quad (7a)$$

For sodium again at room temperature, this value of P corresponds to an equivalent pressure of about 10^{-16} atmos, and consequently from this standpoint we may entirely neglect the second term in (7) at normal temperatures and pressures. The second term in (7) corresponds to a gas-like behavior as we shall see later. We might regard (7a) as corresponding to a vapor-pressure equation, and, although in the linear chain the thermo-

¹² R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 254.

¹³ We are grateful to Dr. H. C. Schweinler for suggesting this transformation.

dynamic functions remain continuous and consequently no discontinuity presents itself, we shall see that there is, in general, a sharp maximum in the specific heat when the two terms in (7) are comparable.

3. CONDENSED STATE

Thus, except under the extreme conditions discussed, we have $I = (2D/kT)I_1$, corresponding to a condensed state. Assuming that $D/kT \gg 1$ (e.g., $D/kT \sim 45$ for sodium at room temperature, with D interpreted as the latent heat of vaporization at absolute zero), we may replace the limits (± 1) in I_1 by ($\pm \infty$). The presence of the exponential factor with the large index ensures that we then make negligible errors by this approximation in the constituent integrals until we reach terms containing very high powers of v which are already of no physical interest.¹⁴ Thus,

$$Z_G = K \left(\frac{\pi k T}{D} \right)^{N/2} \left\{ 1 + \frac{1}{4} \left(\frac{P}{akT} - 1 \right) \right. \\ \left. \times \left(\frac{P}{akT} - 2 \right) \frac{kT}{D} + \dots \right\}^N. \quad (8)$$

Now $G = -kT \ln Z_G$ and hence, after some reduction,

$$G = -NkT \ln \left(\frac{2\pi^2 m k^2}{a^2 D} \right)^{1/2} - NkT \ln T + PNA_0 \\ - \frac{1}{2} \frac{N(kT)^2}{D} - \frac{5}{8} \frac{N(kT)^3}{D^2} - \dots \\ + \frac{P}{aD} \left\{ \frac{3}{4} NkT + \frac{19}{16} \frac{N(kT)^2}{D} + \dots \right\} \\ - \left(\frac{P}{aD} \right)^2 \left\{ \frac{1}{4} ND + \dots \right\}. \quad (9)$$

Although [following (6a)] we confined ourselves to $P/akT < 1$, it may be shown that this equation remains applicable for the less restrictive condition $P/aD \ll 1$, so long as $kT/D \ll 1$. Thus

$$C_P \equiv -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P = Nk \left\{ 1 + \frac{kT}{D} + \frac{15}{4} \left(\frac{kT}{D} \right)^2 + \dots \right. \\ \left. - \frac{P}{aD} \left(\frac{19}{8} \frac{kT}{D} + \dots \right) + \dots \right\}. \quad (10)$$

¹⁴ This approximation is, of course, not imperative.

Also,

$$\left(\frac{\partial L}{\partial P} \right)_T \equiv \left(\frac{\partial^2 G}{\partial P^2} \right)_T \\ = -\frac{N}{a^2 D} \left\{ \frac{1}{2} + \frac{11}{8} \frac{kT}{D} + \dots - \frac{3}{4} \frac{P}{aD} \dots \right\}, \quad (11)$$

essentially the compressibility;

$$\left(\frac{\partial L}{\partial T} \right)_P = \frac{Nk}{aD} \left\{ \frac{3}{4} + \frac{19}{8} \frac{kT}{D} + \dots - \frac{11}{8} \frac{P}{aD} \dots \right\}, \quad (12)$$

essentially the thermal expansion;

and

$$C_{L(P=0)} = Nk \left\{ 1 - \frac{1}{8} \frac{kT}{D} - \frac{9}{32} \left(\frac{kT}{D} \right)^2 - \dots \right\}. \quad (13)$$

Damköhler, using his first analytical method (based on the partition function at constant length) obtained the leading terms of Eqs. (11) and (12), and Eqs. (10) and (13) as far as the terms linear in (kT/D) . Since, however, he felt unable to extend this approach to give the higher terms in the expansions, he used a second method to obtain results intended to be valid at higher temperatures, which involved a numerical computation of the partition function at constant pressure which we have here evaluated analytically. These results differed appreciably from those he obtained by his first method, presumably because of inaccuracy in computations, and consequently those conclusions which he bases solely on his second method are incorrect.

The foregoing analysis may also be carried through with the inclusion of second-neighbor interaction if we neglect the repulsive part of the potential for these neighbors and ignore end effects on the assembly. Under these conditions, Eq. (7) becomes:

$$I = \left(\frac{\pi k T}{D(1+\Lambda)^2} \right)^{1/2} + \frac{akT}{P} \exp \left[-\frac{D}{kT} (1-\Lambda)^2 \right], \\ \text{where} \quad \Lambda = 2e^{-aA_0}, \quad (7')$$

and Eqs. (10) to (13) retain the same form with D replaced by $D(1+\Lambda)^2$.

Since the electrical resistivity in a solid at classical temperatures is approximately proportional to the mean-square amplitude of atomic vibrations, we shall assume that in this model the resistance would correspondingly be proportional to $\langle (x-\bar{x})^2 \rangle_{Av}$. Then, in general,

$$\langle (x-\bar{x})^2 \rangle_{Av} = -kT \frac{\partial^2}{\partial P^2} \left(\frac{G}{N} \right),$$

which from (11) gives

$$\langle (x-\bar{x})^2 \rangle_{Av} = \frac{kT}{2a^2 D} \left\{ 1 + \frac{11}{4} \frac{kT}{D} + \dots - \frac{3}{2} \frac{P}{aD} \dots \right\}. \quad (14)$$

TABLE I. Morse constants derived from molecular data.

Element	A_0 (A)	D (kcal/mole)	a (A ⁻¹)	$10^6\alpha$ [lin. exp. calc. from (12)]	$10^6\alpha$ (exptl.)	Ratio: $\frac{\alpha_{exptl.}}{\alpha_{calc.}}$
Li ₂	2.67	26.4	0.83	2.52	5.6	2.2 ₂
Na ₂	3.07	17.6	0.84	3.24	7.2	2.2 ₂
K ₂	3.91	11.8	0.78	4.08	8.3	2.0 ₄

Under the condition that the length is maintained at the equilibrium value at $T=0$ (i.e., $L=NA_0$) we have, therefore,

$$RT, L=L_0 = B \left\{ \frac{kT}{2a^2D} \left(1 + \frac{1}{2} \frac{kT}{D} + \dots \right) \right\}, \quad (15)$$

where B represents the electron-lattice interaction which may be considered constant if L is fixed.

Finally, there is one further relationship which is of value. If the lattice potential were purely harmonic (i.e., expanding only to the quadratic term in x), its characteristic frequency would be proportional to $a\sqrt{D}$. Because of the higher-power (anharmonic) terms, however, this characteristic frequency depends on the compression or extension of the chain and, for an imposed relative atomic displacement x_0 , the characteristic frequency for small vibrations is now proportional to $\sqrt{(a^2D - 3a^3Dx_0)}$. From this it readily follows that the Grüneisen parameter, defined as $\gamma = -d \log \nu_c / d \log L$ (where ν_c is the characteristic frequency),¹⁵ now has the value

$$\gamma = \frac{3}{2} a A_0. \quad (16)$$

It can then be seen, using the leading terms of Eqs. (11), (12), and (13), that the Grüneisen relationship

$$\gamma = \alpha L / \beta C_v,$$

where

$$\alpha = \frac{1}{L} \left(\frac{dL}{dT} \right)_P, \quad \beta = \frac{1}{L} \left(\frac{dL}{dP} \right)_T,$$

is valid as a first approximation.

Equations (10) to (13) then represent the chief thermodynamic properties of what we may call the "condensed" state of the linear chain. Any comparison between these properties and those of a real solid must, at best, be very tentative. The solid inert gases very closely satisfy the condition of short-range forces which we have assumed, and if the transition from one to three dimensions introduces no qualitative features which are completely absent in the linear chain then these equations should indicate the kind of behavior which is to be expected when account is taken of an anharmonic potential function. Unfortunately, the data on such solids are at present meager in the region of temperatures where classical statistics are valid.

¹⁵ For a discussion of the significance of γ in 1, 2 and 3 dimensions, see J. S. Dugdale and D. K. C. MacDonald, *Phys. Rev.* **89**, 832 (1953).

In making comparison with metals, the representation of the interatomic forces by a potential is obviously a much grosser approximation. To illustrate that, nevertheless, this model can provide a useful correlation, we compare in Tables I and II the observed thermal expansion coefficients at room temperature for the alkali metals with those derived using Eq. (12).

Qualitatively, it might appear that the foregoing analysis of the linear chain model could account rather well for the observed deviations from classical harmonic behavior. For example, the model predicts a specific heat at zero "pressure" which increases monotonically with temperature [Eq. (10)] and suggests an electrical resistance at zero "pressure" which rises more rapidly than linearly [Eq. (14)]—features found in a number of metals (for example, see MacDonald² for data on sodium). If, however, we make a closer examination, serious discrepancies arise. Taking sodium as probably the "best-behaved" of the monovalent metals—at least in an electronic sense (see MacDonald and Mendelssohn¹⁶ and MacDonald and Pearson¹⁷)—one finds that C_p is already rising much more rapidly than linearly with T in the room-temperature region where the factor $(15/4)(kT/D)^2$ in Eq. (10) should still be very small compared with (kT/D) . Furthermore, C_p also increases with temperature (a feature common to sodium, potassium, and rubidium¹⁸) while in the present model C_L diminishes with rising temperature. In making comparison with the electrical resistance it is perhaps even more vital to do so under constant-volume conditions, since it is not yet known with certainty how the electron-lattice interaction energy [characterized by B in (15)] varies with volume. For sodium, the temperature variation of electrical resistance is significantly less rapid than linear when corrected to the

TABLE II. Morse constants derived from bulk metal data.*

Element	A_0 (A)	D (kcal/mole)	a (A ⁻¹)	$10^6\alpha$ [lin. exp. calc. from (12)]	$10^6\alpha$ (exptl.)	Ratio: $\frac{\alpha_{exptl.}}{\alpha_{calc.}}$
Li	3.03	36.0	0.80	1.68	5.6	3.3 ₃
Na	3.72	26.2	0.67	2.25	7.2	3.2
K	4.50	21.9	0.53	2.82	8.3	2.9 ₄
Rb	4.9*	20.6	0.47	3.10	9.0	2.9 ₀
Cs	5.2*	18.7	0.44	3.44	9.7	2.8 ₂

* Sources of data: Morse constants (except those marked*): See J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York and London, 1939), pp. 454-455; Morse constants (marked*): See W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (Institute of Metals, London, 1946), p. 216; Experimental expansion coefficients: See A. E. van Arkel, *Reine Metalle* (Springer, Berlin, 1939).

¹⁶ D. K. C. MacDonald and K. Mendelssohn, *Nature* **161**, 972 (1948); *Proc. Roy. Soc. (London)* **A202**, 103 (1950).

¹⁷ D. K. C. MacDonald and W. B. Pearson, *Proc. Roy. Soc. (London)* **A219**, 373 (1953).

¹⁸ See, for sodium and potassium, F. E. Simon and W. Zeidler, *Z. Physik Chem.* **123**, 383 (1926); for sodium, Dauphinee, MacDonald, and Preston-Thomas, *Proc. Roy. Soc. (London)* **A221**, 267 (1954); for rubidium, H. Preston-Thomas in *Proceedings of the Third International Congress on Low Temperature Physics*, Houston, 1953 (unpublished).

volume at absolute zero by using Bridgman's data.¹⁹ The linear model, on the other hand, still predicts a positive deviation under these conditions [see Eq. (15)].

As we have already emphasized, it is not easy to say immediately whether such discrepancies are an intrinsic consequence of a one-dimensional model, or whether in fact one ought already to seek other sources than anharmonicity for the behavior observed. In anticipation of later work we may, however, mention that the falling specific heat at constant L appears to be a very general prediction of the one-dimensional model [see also Damköhler⁶].

Nevertheless, two relationships of interest can be derived which, because of their form, we may expect to translate into three dimensions without essential change. If dB/dV is neglected,

$$\left(\frac{d \log R}{d \log V}\right)_{p=0} = 2\gamma, \quad (17a)$$

and

$$\left(\frac{d \log R}{d \log T}\right)_{p=0} \doteq 1 + 2 \cdot 4\alpha\gamma T. \quad (17b)$$

Mott and Jones²⁰ derive analogous relations starting from the expression $R \propto T/M\theta^2$; their first is in agreement with ours, while they give essentially $1 + 2\alpha\gamma T$ for the second.²¹ The small difference arises because the relationship $R \propto T/M\theta^2$ is only strictly valid for harmonic vibrations, while a part of the resistance variation in (17b) is due to the anharmonicity.

4. THE GAS-LIKE STATE AND THE TRANSITION REGION

It is clear from Eq. (7) that as $P \rightarrow 0$ the second term will ultimately become dominant, and if this term alone is considered, the partition function yields the free energy of a perfect linear "gas" whose specific heat at constant pressure is $\frac{3}{2}Nk$ and whose equation of state is $PL = NkT$. Let us therefore examine the behavior when the two terms of Eq. (7) are comparable. We have now

$$G = -NkT \ln \left(\frac{2\pi^2 mk^2}{a^2 D} \right)^{\frac{1}{2}} - NkT \ln T + PNA_0 - NkT \ln \left(1 + \left(\frac{a^2 D k T}{\pi} \right)^{\frac{1}{2}} \frac{1}{P} e^{-D/kT} \right). \quad (18)$$

Writing $p = P\sqrt{\pi}/aD$, $t = kT/D$, we have for the

¹⁹ P. W. Bridgman, *The Physics of High Pressure* (Bell Publishing Company, London and New York, 1946).

²⁰ N. F. Mott and H. Jones, *Theory of Properties of Metals and Alloys* (Oxford University Press, London, 1936), pp. 268, 271.

²¹ In fact, on their assumptions, Mott and Jones's Eq. (66) should read

$$\frac{R}{T} = \frac{R_0}{T_0} \{1 + 2\alpha\gamma(T - T_0)\},$$

where T_0 is some arbitrary reference temperature within the "classical" region. Their previous equation is of course correct.

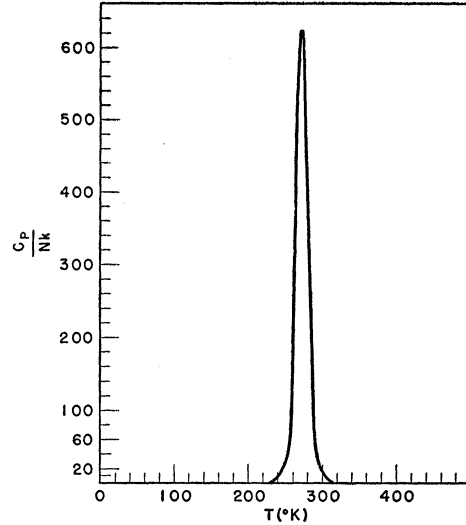


FIG. 2. Specific heat at constant force showing transition region from condensed to gas-like state. This figure shows the third term of Eq. (20); the first two terms are negligible on this scale.

entropy

$$S = Nk \left\{ \ln \left(\frac{2\pi^2 mk^2}{a^2 D} \right)^{\frac{1}{2}} + \ln t + 1 + \ln \left(1 + \frac{\sqrt{t}}{p} e^{-1/t} \right) + \left(\frac{1}{(p/\sqrt{t})e^{1/t} + 1} \right) \left(\frac{1}{2} + \frac{1}{t} \right) \right\}, \quad (19)$$

and

$$C_P = Nk \left\{ 1 + \left[2 \left(1 + \frac{p}{\sqrt{t}} e^{1/t} \right) \right]^{-1} + \frac{p}{\sqrt{t}} e^{1/t} \left(\frac{1}{2} + \frac{1}{t} \right) / \left(1 + \frac{p}{\sqrt{t}} e^{1/t} \right)^2 \right\}. \quad (20)$$

From this equation it can be seen immediately that as $t \rightarrow 0$, $C_P \rightarrow Nk$ and as $t \rightarrow \infty$, $C_P \rightarrow \frac{3}{2}Nk$. When, however, $(p/\sqrt{t})e^{1/t} = 1$, i.e., on what we may term the vapor-pressure curve,

$$P = \left(\frac{a^2 D k T}{\pi} \right)^{\frac{1}{2}} e^{-D/kT} \quad \text{and} \quad C_P = \frac{Nk}{4} \left\{ 5 + \left(\frac{1}{2} + \frac{1}{t} \right)^2 \right\}.$$

In the region for which the expression is valid, i.e., for $t \ll 1$, this gives very nearly $C_P = Nk/4t^2$, so that for $t = 1/50$ (corresponding to about 0°C for sodium), $C_P = 625Nk$. In Figs. 2 and 3 the specific-heat curves are shown for a force such that the transition is centered on 0°C, and it is evident that this specific-heat anomaly approximates to a latent heat. Correspondingly, from (19), we can see readily that as the temperature is increased through this critical range, the entropy rises rapidly by about ND/T , and hence that the equivalent latent heat is ND .

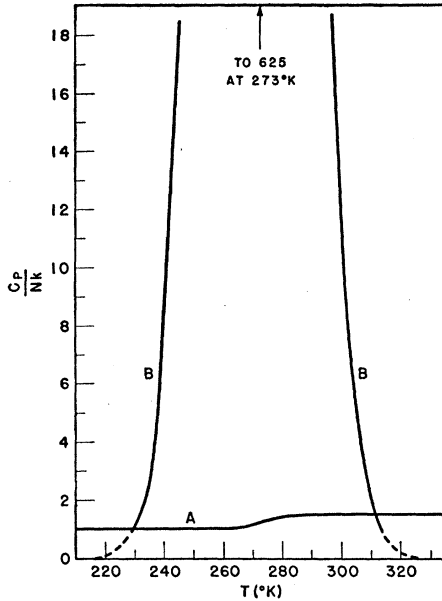


FIG. 3. Specific heat at constant force showing transition region from condensed to gas-like state. Curve A shows the first two terms of Eq. (20). Curve B shows the third term.

From Eq. (18) it also follows that the length is given by

$$L = NA_0 + \frac{NkT}{P} \left\{ 1 / \left(1 + \frac{p}{\sqrt{t}} e^{1/t} \right) \right\}, \quad (21a)$$

which may also be written as an equation of state,

$$P(L - NA_0) = NkT / \left\{ 1 + \frac{P\sqrt{\pi}}{\sqrt{(a^2 DkT)}} e^{D/kT} \right\}. \quad (21b)$$

While it is evident from (21a) that L changes isothermally from NA_0 (characteristic of the condensed state) to NkT/P (characteristic of the gas-like state) as p runs from high to low values, it should be noted that the compressibility increases monotonically, showing no anomaly at the transition, in contrast to the striking behavior of the specific heat.

We are grateful to Professor J. C. Slater for helpful discussions and to Dr. S. K. Roy for help in checking the calculations. We are also indebted to Drs. C. Domb, R. B. Dingle, and A. B. Bhatia for useful criticisms.

APPENDIX

Since it has been suggested in the past (e.g., Peierls,⁸ Domb²²) that a linear chain would be inherently unstable due to thermal vibrations, we append an elementary proof that this is not the case.

Consider the propagation of a wave of thermal

motion through any lattice of particles such that the displacement of the i th particle from its equilibrium position is given by

$$\xi_i = A \sin\{\omega(t + x_i/v)\}, \quad (A1)$$

where x_i is the equilibrium position of the i th particle, v the velocity of sound, and ω the angular frequency. Then the mean square relative displacement of any two particles is given by

$$\langle (\xi_i - \xi_j)^2 \rangle_{Av} = 2A^2 \sin^2 \left(\frac{2\pi \Delta x}{\lambda} \right), \leq \frac{2\pi^2 A^2 \Delta x^2}{\lambda^2} \quad (A2)$$

for $\Delta x \leq \lambda/2$,

where

$$\Delta x \equiv x_i - x_j.$$

If (A1) be a normal mode of the lattice, ignoring anharmonicity, then

$$\left(\frac{1}{2} m N \omega^2 \right) \left(\frac{1}{2} A^2 \right) = \frac{1}{2} k T,$$

where m is the mass of a particle and N is the number of particles in the lattice. Therefore,

$$\langle \Delta \xi^2 \rangle_{Av} / \Delta x^2 \leq 4\pi^2 k T / m N \omega^2 \lambda^2 = k T / m N v^2. \quad (A3)$$

If we now ignore dispersion so that v is not a function of frequency it is clear that (A3) is independent of frequency, and since the individual displacements due to each normal mode are themselves uncorrelated, the total fluctuation due to all normal modes, say \mathfrak{N} in number, is given by

$$\langle \Delta \xi_{\text{tot}}^2 \rangle_{Av} / \Delta x^2 \leq \mathfrak{N} / N (k T / m v^2). \quad (A4)$$

In the case of a one-dimensional lattice, $\mathfrak{N}/N \approx 1$, while for a three-dimensional lattice $\mathfrak{N}/N \approx 3$, and thus in general

$$\langle \Delta \xi_{\text{tot}}^2 \rangle_{Av} / \Delta x^2 \sim k T / m v^2$$

and the total relative displacement of neighboring atoms (setting $\Delta x = a$, the lattice constant) is given by

$$\langle \Delta \xi_{\text{tot}}^2 \rangle_{Av} \sim k T a^2 / m v^2 \sim h^2 T / m k \theta^2.$$

It may be of interest (see also Frenkel²³) to recall that the Lindemann theory of melting corresponds essentially to setting the dimensionless parameter $kT/mv^2 \sim \frac{1}{10}$ at the melting point. However, the factor kT/mv^2 may also be considered immediately as the ratio $(V_t/v)^2$, where V_t is the thermal agitation velocity of the atoms; consequently the general success of the Lindemann theory could also thus be interpreted as evidence of a critical velocity (-ratio) involved in the melting process equally well with its derivation in terms of the displacement of atoms from their equilibrium positions.

²² C. Domb, *Changements de Phase* (Society of Chemical Physics, Paris, 1952), p. 338.

²³ J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), p. 138.