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Liquid dynamics theory of high-temperature specific heat

Duane C. Wallace
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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The potential-energy surface underlying the liquid dynamics Hamiltonian is supposed to consist of a large number of intersecting, macroscopically similar, nearly harmonic random valleys. The statistical mechanics replaces each valley with an infinitely extended harmonic potential surface and then corrects for (a) the anharmonic distortion of the potential surface and (b) the boundary condition that limits the extent of the potential surface along lines where neighboring valleys intersect. The ion-motional specific heat then consists of the main quasiharmonic contribution $C_H = 3Nk$ plus the anharmonic correction C_A and the boundary correction C_B. Here we analyze available specific-heat data for monatomic liquids, at temperatures T up to three times the melting temperature T_m, and suggest the following interpretation of the data: (a) C_A is about the same for both the crystal and liquid at the melting point and C_A tends toward zero as T increases above T_m and (b) C_B is a roughly universal function of T/T_m, running from around zero at $T = T_m$ to around $-0.6Nk$ at $T = 3T_m$. The quintessential liquid property, the primary difference between a liquid and a crystal, is that the liquid ions move through a vast number of random potential valleys and this property is directly responsible for the boundary specific heat C_B. A physically based model for C_B agrees with experiment for mercury to high temperatures. [S1063-651X(98)08602-4]

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I. INTRODUCTION

We have recently presented a theory of liquid dynamics of monatomic liquids [1]. The theory is based on an approximate description of that part of the many-particle potential energy surface that is significant for the statistical mechanics of the liquid state. The potential surface is composed of a large number of intersecting nearly harmonic valleys, each valley corresponds to a random arrangement of the N ions in the system, and all random structural valleys have the same macroscopic average properties in the large-N limit. For motion within one valley, the system has $3N$ nearly harmonic normal modes, giving rise to a total ionic specific heat of approximately $3Nk$. The random structural valleys are all accessible to the liquid state and are supposed to number w^N for an N-particle system, hence they give the universal contribution $Nk \ln w$ to the entropy of the liquid relative to the crystal. Calibration of this constant, from experimental data [2], is $\ln w = 0.80$. Finally, we noted that the many-particle potential-energy valleys might require some nonzero kinetic energy to stabilize them [1], so that the Hamiltonian is based on a self-consistent potential, but this will not alter the consequent statistical mechanics studied here.

The liquid dynamics theory allows a straightforward evaluation of the partition function and the free energy [1]. Of interest here is the theoretical expression for the entropy of a liquid metal, in classical statistics for the ion motion,

$$S = Nk\{\ln w + 3[\ln(T/\theta_0) + 1]\} + S_{AB} + S_E. \tag{1}$$

For a representative random structural valley, the harmonic normal modes of the ion motion have frequencies ω_λ, $\lambda = 1, \ldots, 3N$, and the characteristic temperature θ_0 is defined by

$$\ln k\theta_0 = \langle \ln \hbar\omega_\lambda \rangle, \tag{2}$$

where $\langle\,\rangle$ indicates an average over the normal mode spectrum [3]. The term in curly brackets in Eq. (1) is the quasiharmonic contribution and for elemental liquids it accounts for nearly all of the entropy. Two small corrections are the anharmonic entropy S_A, resulting from anharmonicity of the many-particle potential valleys, and the boundary contribution S_B, resulting from truncation of the potential valleys at the places where two valleys intersect. The sum of these small terms is denoted S_{AB} in Eq. (1),

$$S_A + S_B = S_{AB}. \tag{3}$$

Finally, the entropy contribution resulting from thermal excitation of electrons from their ground state, important for metals, is denoted S_E.

For all the normal melting elements for which the necessary data can be found (six elements) and to temperatures as high as the data are available (to $T = 3T_m$), the quasiharmonic contribution in Eq. (1), plus the electronic excitation term, gives an excellent account of the experimental entropy [1]. The remaining theoretical term S_{AB} is of the same magnitude as the combined errors of the entropy analysis. In the present paper, in order to magnify the anharmonic and boundary contributions to the thermodynamic functions, we study the constant-volume specific heat C_V. This is defined by $C_V = (\partial S/\partial \ln T)_V$ and from Eq. (1) it follows that

$$C_V = 3Nk + C_{AB} + C_E. \tag{4}$$

Our technique is to evaluate C_V from the measured constant-pressure specific heat C_P and to calculate C_E from theory to obtain the ion-motional specific heat $C_I = C_V - C_E$. We then try to understand the character of C_I through its liquid-dynamics expression

$$C_I = 3Nk + C_A + C_B, \tag{5}$$

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where $3Nk$ is the quasiharmonic contribution and is the major part of C_I. This analysis and interpretation of experimental specific-heat data is carried out in Sec. II.

The anharmonic specific heat expresses that the many-particle potential valleys are not perfectly harmonic, but have an anharmonic distortion. In principle, C_A can be of either sign. The boundary contribution expresses that the many-particle potential valleys do not extend to infinity in all directions, but are truncated along lines of intervalley intersection (the boundary). Hence part of the infinite-valley potential surface is removed and C_B is necessarily negative. A simple model expressing this picture of the boundary effect is constructed in Sec. III and the model is shown capable of fitting experimental data. A brief summary of conclusions is presented in Sec. IV.

For normal melting elements, where crystal and liquid have approximately the same electronic structure, the melting temperature plays the role of a characteristic temperature and liquid thermodynamic functions are expected to exhibit regular behavior when considered as functions of T/T_m. However, such behavior cannot be expected for the anomalous melting elements, where the crystal and liquid have substantially different electronic structures [4]. In Si and Ge, for example, the interionic potential in the metallic liquid bears no resemblance to that in the covalent diamond crystal and the melting temperature cannot serve as a characteristic temperature [4]. For this reason, our first liquid-dynamics analysis was limited to normal melting elements [1]. In the present specific-heat analysis, the two least anomalous elements Sn and Ga appear to rationalize well and so are included, while the more strongly anomalous Sb, Bi, Si, and Ge do not rationalize well and are omitted. These four elements aside, the specific-heat data analyzed here include every classical monatomic liquid for which sufficient accurate data currently exist.

II. ANHARMONIC AND BOUNDARY CONTRIBUTIONS TO LIQUID SPECIFIC HEAT

To calculate C_E reliably, we consider only the nearly free-electron elements, where C_E is quite small and the low-temperature expansion for independent electrons can be used for crystal and liquid alike. The low-temperature expansion requires the electron density of states at the Fermi energy and this is obtained from band-structure calculations where possible [5,6], corrected for density changes, and otherwise from free-electron theory. The expression for C_E may be found in [1].

We have already observed that $C_I \approx 3Nk$ at the melting temperature T_m for both crystal and liquid phases [1]. But the experimental data contain more information than this because the departure of C_I from $3Nk$ is generally larger than experimental error. The main additional correlation within the data is shown in Fig. 1, a graph of C_I/Nk for the liquid, against the same quantity for the crystal. Estimated errors of the data in Fig. 1 are ±0.05 (except for compressed Ar, see below). Since the ion-motional specific heat for a crystal is also given by Eq. (5), with the boundary term C_B omitted, we have attributed the difference $C_I - 3Nk$ for the crystal at melt to anharmonicity [4,7,8] and have been able to verify this attribution quantitatively for sodium, through computer simulations [9]. With this information in mind, the conclusion we draw from Fig. 1 is that $C_B \approx 0$ for the liquid at melt and C_A is approximately the same for the liquid at melt as for the crystal at melt.

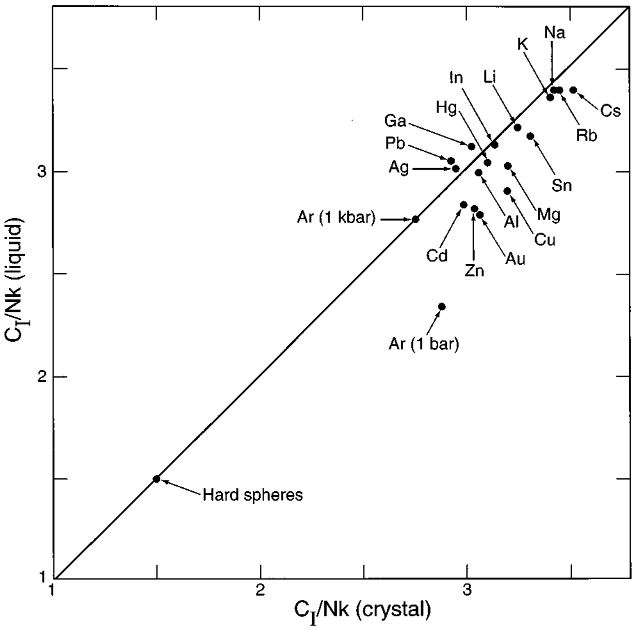

FIG. 1. Ion-motional specific heat for the liquid at the melting point, against the same quantity for the crystal at the melting point. The line represents equality of liquid and crystal values.

Figure 1 shows two examples requiring clarification. For Ar at 1 bar, C_I for the crystal is not unusual, but C_I for the liquid is quite low. We have previously observed that liquid Ar at 1 bar is noticeably gaslike [4] and that compressed liquid Ar behaves more like an ordinary liquid [10,11]. Experimental estimates of C_V at 1 kbar pressure were extracted from the data of Crawford, Lewis, and Daniels [12] for the crystal and from the data of Gosman, McCarty, and Hust [13] for the liquid. The results for C_I/Nk have estimated errors of ±0.1 and the point plotted in Fig. 1 puts Ar at 1 kbar on the line with the liquid metals. Finally, we plotted the data point for a hard-sphere system to demonstrate that this system does not provide a realistic approximation for the motion of ions in a crystal or a liquid.

Considering now the temperature dependence of liquid specific heat, it has long been known that C_I decreases as temperature increases at atmospheric pressure [14–16]. Grimvall [15] graphed C_I/Nk vs T/T_m for three metals and we can now extend that graph to the nine metals shown in Fig. 2. For these nine metals, the thermodynamic data required to obtain C_I at T_m, as well as references providing the experimental data at elevated temperatures, are listed in Table I. Errors in C_I/Nk are expected to be around ±0.05 at T_m, increasing to around ±0.1 at the highest temperature graphed for each element.

The following qualitative interpretation of Fig. 2 appears reasonable at this time. Leaving aside Pb, the metals fall into two groups: (a) the four alkali metals, having $C_A/Nk \approx 0.4$ and $C_B \approx 0$ at T_m, and (b) the remaining four metals for which both C_A and C_B are approximately zero at T_m. With increasing temperature, C_A for the alkali metals decreases

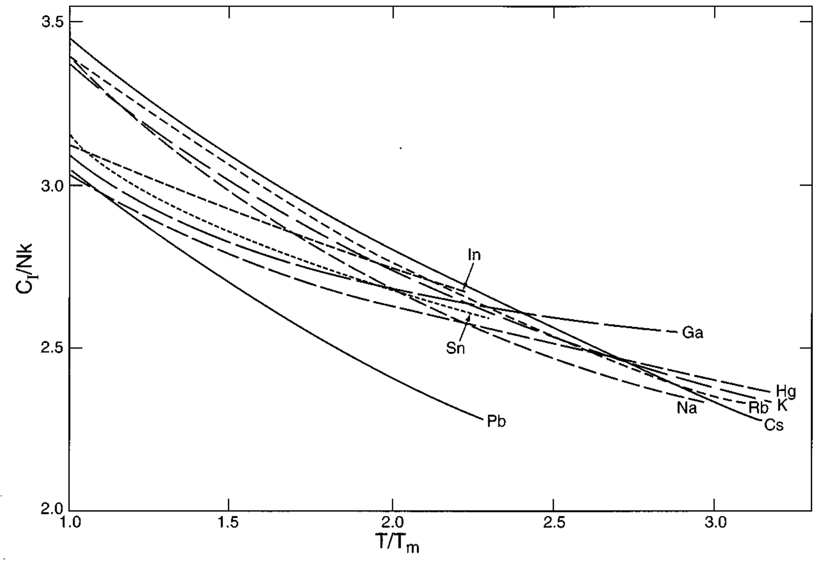

FIG. 2. Ion-motional specific heat as a function of T/T_m.

and is approximately zero for $T \gtrsim 2T_m$. C_B/Nk is roughly a universal function, running from 0 at T_m to -0.6 at $3T_m$.

The curve for Pb falls below the other metals at the higher temperatures and it does not appear possible to attribute this difference to errors in the analysis. Without further information, we cannot interpret the special behavior of Pb. The weakly anomalous Sn and Ga are rather similar to the normal melting In and Hg. We also note that Fig. 2 shows data at 1 bar pressure and the decrease in C_I with temperature includes both the explicit temperature dependence, and some volume dependence as well, through the thermal expansion with increasing temperature.

III. MODEL FOR THE BOUNDARY CONTRIBUTION TO SPECIFIC HEAT

We will outline evaluation of the liquid-dynamics classical partition function, first for harmonic normal modes and then with a correction for the boundary effect. For a single one-dimensional harmonic oscillator, with mass M and frequency ω, the partition function is

$$\frac{1}{h}\int_{-\infty}^{\infty}\exp(-\beta p^2/2M)\,dp\int_{-\infty}^{\infty}\exp\left(-\frac{1}{2}\beta M\omega^2q^2\right)dq = \frac{kT}{\hbar\omega}, \tag{6}$$

where $\beta = 1/kT$. For the liquid system of N ions confined to a single harmonic valley in the potential-energy surface, the normal modes have frequencies ω_λ, $\lambda = 1, \ldots, 3N$, and the corresponding partition function is [3]

$$\Pi_\lambda(kT/\hbar\omega_\lambda).$$

Finally, extending the liquid configuration space to include w^N similar valleys and setting the static structural potential energy Φ_0 for each valley yields the ion-motional partition function in the quasiharmonic approximation

$$Z_H = w^N \exp(-\beta\Phi_0)\Pi_\lambda \frac{kT}{\hbar\omega_\lambda}. \tag{7}$$

The corresponding Helmholtz free energy is

TABLE I. Data for the high-temperature specific heat analysis. Columns 2–5 are experimental data for the liquid at melt, where β is thermal expansion coefficient and B_S is adiabatic bulk modulus. References provide the experimental data at elevated temperatures.

Element	ρ (g/cm^3)	β (10^{-4}/K)	B_S (kbar)	C_P/Nk	C_E/Nk	Refs.
Na	0.925	2.57	59.4	3.828	0.053	[17–20]
K	0.829	2.9	29.4	3.865	0.080	[17,19–21]
Rb	1.479	3.0	23.5[a]	3.886	0.089	[17,19,22]
Cs	1.84	3.0	17.2[a]	3.896	0.136	[17,19,22]
Pb	10.68	1.12	358	3.684	0.089	[23–26]
Ga	6.09	1.20	491[a]	3.428	0.036	[23,27]
In	7.03	1.11	378	3.549	0.065	[23,28]
Sn	7.00	0.87_6	442	3.574	0.087	[23,24,26]
Hg	13.69	1.80	299	3.426	0.029	[23,29]

[a] B_S calculated from experimental B_T.

$$F_H = \Phi_0 - NkT \ln w - 3NkT \ln(T/\theta_0), \tag{8}$$

where θ_0 is given by Eq. (2).

Suppose now that the one-dimensional harmonic oscillator, described by Eq. (6), moves in a well extending only up to the amplitude a. The partition function is then

$$\frac{1}{h}\int_{-\infty}^{\infty} \exp(-\beta p^2/2M)dp \int_{-a}^{a} \exp\left(-\frac{1}{2}\beta M\omega^2 q^2\right)dq$$

$$= \frac{kT}{\hbar\omega} \operatorname{erf} b, \tag{9}$$

where $b = +\sqrt{\frac{1}{2}\beta M\omega^2 a^2}$. Extending this description to the entire set of normal modes and counting the multiplicity of valleys, the partition function including the boundary effect is

$$Z_{HB} = w^N \exp(-\beta\Phi_0)\Pi_\lambda \frac{kT}{\hbar\omega_\lambda} \operatorname{erf} b_\lambda, \tag{10}$$

where

$$b_\lambda = +\sqrt{\tfrac{1}{2}\beta M\omega_\lambda^2 a_\lambda^2}. \tag{11}$$

The corresponding free energy is $F_{HB} = F_H + F_B$, where the boundary contribution takes the form

$$F_B = -kT\sum_\lambda \ln(\operatorname{erf} b_\lambda). \tag{12}$$

Finally, the ion-motional specific heat may be written

$$C_I = C_H + C_B = 3Nk + C_B, \tag{13}$$

where the boundary contribution is

$$C_B = -k\sum_\lambda B_\lambda(b_\lambda^2 + \tfrac{1}{2} + B_\lambda), \tag{14}$$

$$B_\lambda = \frac{b_\lambda \exp(-b_\lambda^2)}{\sqrt{\pi} \operatorname{erf} b_\lambda}. \tag{15}$$

Let us now introduce a simple model for the above description of the boundary effect. Take $0 \leqslant \zeta \leqslant 1$ and for the fraction $1-\zeta$ of normal modes let the amplitude a_λ be infinite, so the boundary contribution vanishes for these modes. For the remaining fraction ζ, set all the normal mode parameters the same, i.e., set $\omega_\lambda = \omega$ and $a_\lambda = a$. Then the total boundary contribution to F [Eq. (12)] becomes

$$F_B = -3NkT\zeta \ln(\operatorname{erf} b). \tag{16}$$

We shall make the temperature dependence explicit by writing b, from Eq. (11), in the form

$$b = +\sqrt{T_a/T}, \tag{17}$$

$$kT_a = \tfrac{1}{2}M\omega^2 a^2. \tag{18}$$

It is then convenient to write the specific heat in the form

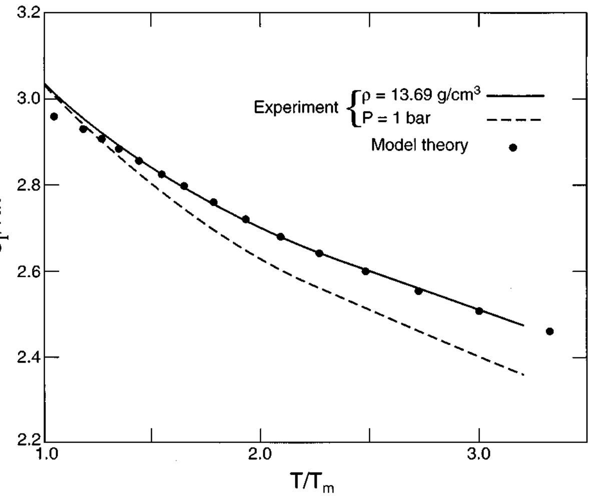

FIG. 3. Ion-motional specific heat vs T/T_m for mercury, comparing experimental data at constant pressure (1 bar), and at the constant density of the liquid at the melting point (13.69 g/cm^3), and the model for harmonic plus boundary contributions appropriate for constant density.

$$C_I = 3Nk[1 - \zeta B(b^2 + \tfrac{1}{2} + B)], \tag{19}$$

where

$$B = \frac{b^2 \exp(-b^2)}{\sqrt{\pi} \operatorname{erf} b}. \tag{20}$$

To compare this model with experiment, we note the parameters a and ζ are expected to depend on volume, so to isolate the explicit temperature dependence, the comparison should be made at constant volume. The correction of C_V measured at 1 bar to C_V at the fixed volume of the liquid at the melting point follows well-known thermodynamic equations [7]. The references listed in Table I provide the data to make this correction for liquid mercury and mercury is an appropriate example because it appears to have no significant anharmonic specific heat. As shown in Fig. 3, the correction from constant pressure to constant volume is quite significant in C_I vs T for mercury. By choosing the parameter values

$$\zeta = 0.56, \quad T_a/T_m = 6, \tag{21}$$

Eq. (19) provides a rather good fit to C_I vs T at fixed volume for mercury, also as shown in Fig. 3.

We believe that the above physical picture of the boundary effect in liquid dynamics is approximately correct, namely, that each many-particle potential valley effectively extends to infinity in some directions, while in other directions it is truncated at the intersection with another valley. The above parameters then suggest that the truncation takes up roughly half the perimeter of each valley and that a single normal mode with energy $6kT_m$ and moving in the appropriate direction will carry the system to an intervalley intersection.

IV. CONCLUSIONS

At classical temperatures for the ion motion, lattice dynamics theory gives $C_I = 3Nk + C_A$ and liquid dynamics theory gives $C_I = 3Nk + C_A + C_B$. We have experimental data for C_I for both the crystal and liquid at the melting point for 15 normal melting metals, plus the weakly anomalous Sn and Ga, and Ar at 1 kbar pressure. One existing data point only, namely, that for the strongly anomalous Si [1], is omitted from consideration here. In view of the theoretical expressions and the strong correlation of crystal and liquid data shown in Fig. 1, the following conclusions appear justified, up to errors of roughly $\pm 0.1Nk$: (a) $C_B \approx 0$ for the liquid at the melting point and (b) C_A is approximately the same for the crystal and liquid at the melting point.

Experimental data for temperature dependence of C_I exist for ten liquid metals, of which the anomalous-melting Bi is omitted, and the other nine are graphed in Fig. 2. For so few examples, our conclusions cannot be supposed general, but are restricted to the nine elements considered. (a) For the alkali metals (Na,K,Rb,Cs), C_A is a roughly universal function of T/T_m, running from around $0.4Nk$ at $T = T_m$ to around zero for $T \geqslant 2T_m$. (b) For a second group of four metals (Hg,In,Sn,Ga), $C_A \approx 0$ at all T. (c) For both groups, C_B is a roughly universal function of T/T_m, running from zero at T/T_m to $-0.6Nk$ at $T = 3T_m$. (d) Pb falls below the other metals at the higher temperatures for reasons remaining to be learned.

Compared to the harmonic specific heat $C_H = 3Nk$, the anharmonic contribution C_A is apparently always small, in agreement with our predominantly quasiharmonic liquid-dynamics Hamiltonian [1]. The present analysis allows a more detailed conclusion for the case where C_A is actually significant, namely, for the alkali metals. Since C_A decreases as T increases, for $T > T_m$, the anharmonic distortion must lie at potential energy per ion small compared to kT_m, i.e., near the bottom of the many-particle potential-energy valley. Notice that this property is then consistent with C_A being nearly the same in both the crystal and liquid at the melting point, a strong characteristic of the alkali metals (Fig. 1).

The essential difference between a crystal and a liquid is that while the ions in a crystal move almost entirely within a single highly ordered many-particle potential valley, the liquid ions move through a vast number of disordered valleys. The essential property of the liquid state, which allows this intervalley motion, is truncation of the potential surface at the intersection of neighboring valleys. The experimental boundary specific heat C_B reveals this property of the liquid state. A simple but physically realistic model for C_B can be made to agree with experiment for mercury, to $T = 3.2T_m$, at constant volume (Fig. 3). The parameters of the fit [Eq. (21)] then suggest that the liquid ions move easily from valley to valley. We shall attempt to make this notion quantitative in future research.

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