PHYSICAL REVIEW E VOLUME 56, NUMBER 4 OCTOBER 1997

Statistical mechanics of monatomic liquids

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

(Received 28 March 1997)

Two key experimental properties of elemental liquids, together with an analysis of the condensed-system potential-energy surface, lead us logically to the dynamical theory of monatomic liquids. Experimentally, the ion motional specific heat is approximately $3Nk$ for N ions, implying the normal modes of motion are approximately $3N$ independent harmonic oscillators. This implies the potential surface contains nearly harmonic valleys. The equilibrium configuration at the bottom of each valley is a ''structure.'' Structures are crystalline or amorphous, and amorphous structures can have a remnant of local crystal symmetry, or can be random. The random structures are by far the most numerous, and hence dominate the statistical mechanics of the liquid state, and their macroscopic properties are uniform over the structure class, for large-N systems. The Hamiltonian for any structural valley is the static structure potential, a sum of harmonic normal modes, and an anharmonic correction. Again from experiment, the constant-density entropy of melting contains a universal disordering contribution of $Nk\Delta$, suggesting the random structural valleys are of universal number w^N, where $\ln w = \Delta$. Our experimental estimate for Δ is 0.80. In quasiharmonic approximation, the liquid theory for entropy agrees with experiment, for all currently analyzable experimental data at elevated temperatures, to within 1–2% of the total entropy. Further testable predictions of the theory are mentioned. [S1063-651X(97)01810-2]

PACS number(s): 65.50.+m, 64.10.+h, 05.70.Ce

I. INTRODUCTION

More than 50 years ago, noting that fusion has only small effects on the volume, cohesive forces, and specific heat, Frenkel [1] reached the conclusion that ''the character of the heat motion in liquid bodies, at least near the crystallization point, remains fundamentally the same as in solid bodies, reducing mainly to small vibrations about certain equilibrium positions.'' Twenty years earlier still [2] he argued that these equilibrium positions are irregular in a liquid, just as in an amorphous solid, but while the equilibrium positions are permanent in a solid, they are not so in a liquid; rather each liquid atom oscillates for a time about the same equilibrium position, then jumps to a new one. In the present work, Frenkel's qualitative picture will not be abandoned, but will only be refined.

From computer simulations of the motion of atoms in small systems, containing 32 and 108 particles, Stillinger and Weber [3–6] isolated mechanically stable arrangements of the particles, called amorphous packings. They suggested that the equilibrium properties of liquids result from vibrational excitations within, and shifting equilibrium between, these stable molecular packings. Again from computer simulations for 500 particle systems, LaViolette and Stump [7] observed a wide variety of packing symmetry when the system density was varied.

We have constructed an expansion of the liquid entropy in a multiparticle correlation series, and, using measured pair-correlation functions, have shown that keeping only correlations up to two particles gives an excellent account of the experimental entropy for most liquid metals [8–10], for liquid argon [11], and for the hard-sphere liquid [12]. For those few liquids where theory and experiment do not agree at the pair-correlation level, the experimental entropy is always smaller than theory, suggesting the presence of higher-order correlations in the liquid [9].

In spite of the long history of insightful contributions to the nature of the liquid state, we do not yet possess a theory for the motion of particles in a liquid. What is needed is a Hamiltonian which is approximately solvable for its energy levels, a partition function which sums over those energy levels, and a comparison of the statistical-mechanical free energy with the experimental thermodynamic properties of liquids. This latter comparison will give some indication of the validity of the theory, and will point the way toward theoretical improvements. This program will be carried out in the present paper, for the case of monatomic liquids.

Experimental properties of elemental liquids give a fairly definite picture of the liquid state, as described in Sec. II. With unwavering faith in this simple picture implied by experiment, we analyze the potential energy landscape, construct the Hamiltonian in Sec. III, and evaluate the partition function and free energy in Sec. IV. Our comparison with experiment in Sec. V comprises two parts: (a) the relation to the experiment of principal theoretical quantities whose theoretical calculation is beyond the scope of this work, and (b) a detailed comparison of theory and experiment for the entropy of elemental liquids as function of temperature. Section VI presents a brief descriptive summary of the liquid theory, and some of its predictions, and a discussion of some technical points.

The liquid state of an element has the same theoretical description, whether the liquid evolves from the crystal by the normal melting process, or by anomalous melting. However, since we are going to infer liquid properties from information on the melting process, we have to keep in mind the existence of these two melting categories. Here is a brief summary of our findings on the melting of elements [13,14].

(a) In normal melting there is no significant change in the

TABLE I. Ion motional specific heat C_I^c for the crystal at melt, and C_I^l for the liquid at melt, for 19 elements.

Element	C_I^c/Nk	C_I^l/Nk	Element	C_I^c/Nk	C_I^l/Nk
Li	3.25	(3.21)	Mg	3.20	3.02
Na	3.43	3.39	Zn	3.04	2.81
K	3.41	3.36	Cd	2.99	2.83
Rb	3.45	3.39	Ga	3.03	3.12
Cs	3.52	3.39	In	3.14	3.13
Al	3.06	2.99	Sn	3.31	3.17
Pb	2.93	3.05	Hg	3.11	3.04
Cu	3.20	2.90	Si	3.47	(2.05)
Ag	2.95	3.01	Ar	2.88	2.33
Au	3.06	(2.79)			

electronic structure, as, for example, metal crystal to metal liquid. Experimental data for the entropy of melting at constant density lie in the narrow range $(0.64-0.97)Nk$, and has mean and variance given by $(0.80\pm 0.10)Nk$.

(b) In anomalous melting there is a significant change in the electronic structure, as for example polar crystal to metal liquid. The entropy of melting at constant density is much higher than the normal value, being $(1.48-3.85)Nk$ for the six anomalous elements we have studied, and apparently contains the normal contribution, plus an amount due mostly to the increase in potential energy in going to the new electronic structure.

From these findings, we formulated the hypothesis that the liquid contains a universal ion-motional disordering entropy of $Nk\Delta$, relative to the crystal, where $\Delta = 0.80$ [14].

II. NATURE OF THE LIQUID STATE

The constant-volume specific heat C_V is obtained by a well-known thermodynamic correction [15] from the experimental constant-pressure specific heat C_P. We assume for the liquid, just as for the crystal, that C_V is comprised of an ion-motional contribution C_I, and an electron excitation contribution C_E,

$$C_V = C_I + C_E. \tag{1}$$

To obtain accurate values of C_I, from the experimental C_V, we consider only the nearly-free-electron elements, where C_E is quite small, and where in addition we can apply the low-temperature expansion with confidence to crystal and liquid alike:

$$C_E = \tfrac{1}{3}\pi^2 Nk^2 T n(\varepsilon_F), \tag{2}$$

where $n(\varepsilon_F)$ is the electron density of states per atom at the Fermi energy ε_F. For all the elements for which we are currently able to evaluate C_I accurately, for both crystal and liquid at melt, the results are listed in Table I. Errors in C_I of $\pm 0.05\,Nk$ are expected, with larger errors likely in several cases. Our data sources for C_P are Hultgren *et al.* [16] and the JANAF (Joint Army–Navy–Air Force) tables [17], and the electron density of states was obtained from band-structure calculations where possible [18,19], approximately corrected for density changes, otherwise from free-electron theory.

The data of Table I reveal the nearly universal property $C_I \approx 3Nk$ for both crystal and liquid at melt. Since we know in general that $C_I = 3Nk$ is a property of $3N$ independent harmonic oscillators, and in particular that we have an excellent theory of ion motion in crystals in terms of $3N$ independent harmonic oscillators [20,15], we assume the ion motion in elemental liquids can be resolved to good approximation into $3N$ independent harmonic oscillators. Consistent with this assumption, we picture the ions moving primarily within one or more nearly harmonic valleys in the potential energy surface.

For monatomic liquids, the general behavior of C_I is to decrease as temperature increases at constant density, and to decrease as density decreases at constant temperature. Though the density dependence can be complicated by the presence of phase transitions on an isotherm, the system always becomes a gas at sufficiently low density, and also at sufficiently high temperature [21], and $C_I = 1.5Nk$ for a gas. Grimvall [22] showed that C_I for liquid metals decreases as temperature increases at atmospheric pressure, and this decrease reflects both the increasing temperature and decreasing density.

From the viewpoint of harmonic oscillators as liquid behavior, let us examine some finer details of the data in Table I. For the alkali metals, C_I is larger than $3.0Nk$; in fact it is around $3.4Nk$ for both crystal and liquid. We know this larger value is due to anharmonicity in the crystal [23,24], and we believe it is due to the same kind of anharmonicity in the liquid as well. For Ar, the crystal shows ordinary behavior, with a little anharmonicity, but the liquid is far from ordinary, with $C_I = 2.33Nk$. This is because liquid Ar at 1 bar is greatly expanded from the crystal, is very weakly bound, and the ion motion takes on some of the gas character. We have previously noted this character of liquid argon [13], and found some evidence that sufficiently compressed Ar behaves like an ordinary liquid [11,25]. In Si, the large anharmonicity of the crystal presumably results from the strongly directional covalent bonds of the diamond structure, while the very low liquid $C_I = 2.05Nk$ reflects the quite extraordinary nature of liquid Si. First, because of anomalous melting, metallic liquid Si is at a temperature far above the normal melting temperature of the metallic form [13]. Second, while the number of neighbors in the first peak of the pair-correlation function is around 9–11 for most liquid metals [26], for Si and Ge it is respectively 6.4 and 6.8 [26], and, in this connection, Ashcroft [27] suggested the presence of dynamical clustering of the ions in liquid Ge. Finally, though it is a small effect, the free-electron value $C_E = 0.22Nk$ for Si might be an overestimate. The remaining 12 elements of Table I show remarkably uniform behavior, with $C_I = (2.9-3.3)Nk$ for the crystals, and $C_I = (2.8-3.2)Nk$ for the liquids. Note that this group includes two more anomalous melting elements, Sn and Ga, whose liquid C_I values are not at all unusual, perhaps because these two elements are only weakly anomalous in their melting.

To complete the qualitative picture of the liquid state, one more issue needs to be addressed. For harmonic oscillators, the specific heat is independent of the number of structures a system possesses. On the other hand, the entropy measures that number, for if a system has w^N accessible structures, the entropy contains the term $Nk \ln \omega$. Our hypothesis of a universal disordering entropy $Nk\Delta$ of the liquid relative to the crystal, mentioned in Sec. I, and noting that the crystal has only one structure, now suggests the number of accessible structures in a monatomic liquid is the universal number w^N, where $\ln w = \Delta$. We will now proceed to a mathematical description, which makes more precise this qualitative picture of the liquid state.

III. HAMILTONIAN

We consider a condensed-matter system of N-like atoms distributed more or less uniformly in a volume V. Each atom is separated into an ion core and valence electrons, where the ion can be the bare nucleus, or can include some electron shells, and for abbreviation we refer to the complete set of valence electrons simply as ''the electrons.'' The ions are labeled $K=1,\ldots,N$, have positions $\mathbf{r}_K$, and the energy of the system when the ions are held fixed and the electrons are in their ground state is the adiabatic potential $\Phi(\{\mathbf{r}_K\})$. If now the ions are allowed to move in this potential, with momenta $\mathbf{p}_K$, the motion is described by the ionic Hamiltonian H_I,

$$H_I = \sum_K \frac{\mathbf{p}_K^2}{2M} + \Phi(\{\mathbf{r}_K\}), \tag{3}$$

where M is the ion mass. When the Born-Oppenheimer approximation holds, the electrons remain in their ground state, and H_I is the complete system Hamiltonian [20]. In reality, however, the motion of the ions causes excitation of the electrons from their ground state, and this is especially important for metals, where the electrons have excited states of very low energy. The excitation of electrons, including its coupling to the motion of the ions, will be represented by H_E, so the total Hamiltonian is

$$H = H_I + H_E. \tag{4}$$

In this paper, we concentrate on the ionic motion, and will not worry about the details of H_E, though we will have to estimate its contribution to the total free energy, in order to compare the liquid theory with experiment.

The set $\{\mathbf{r}_K\}$ spans the $3N$-dimensional configuration space, which contains a number of nearly harmonic valleys in the potential-energy surface. The equilibrium configuration at the bottom of each valley is a ''structure.'' A ridge is formed at the intersection of neighboring valleys, and a line along the ridge top denotes the intervalley boundary. We can allow that all the valleys, plus a large number of intervalley boundaries, are accessible to the liquid state. The collection of all accessible intervalley boundaries is called simply ''the boundary.'' The entire collection of structural valleys, plus the boundary, is denoted the ''liquid configuration space,'' and contains all configurations important for the equilibrium statistical mechanics of the liquid state. This latter conclusion follows from the specific-heat analysis of Sec. II.

In perspective, the great majority of configuration space is inaccessible to the liquid state. The main restriction, revealed in the pair correlation function [26], is that the liquid is virtually never found in a configuration in which two ions are closer than r_c, where r_c is around 75% of the mean nearest-neighbor separation.

The structures are labeled γ, where $\gamma=1,\ldots,w^N$, and w is to be determined. The positions of the ions in structure γ are $\mathbf{R}_K(\gamma)$. For a proposition limited to configurations lying within the valley of structure γ, we use the terminology ''in γ.'' When the system is in γ, the position of ion K is measured by $\mathbf{u}_K(\gamma)$, its displacement from equilibrium, where

$$\mathbf{u}_K(\gamma) = \mathbf{r}_K - \mathbf{R}_K(\gamma). \tag{5}$$

Again when the system is in γ, the adiabatic potential is denoted Φ_γ, and is considered a function $\Phi_\gamma(\{\mathbf{u}_K(\gamma)\})$ of the displacements. Then when the system is in γ, the ionic Hamiltonian is H_γ, given by

$$H_\gamma = \sum_K \frac{\mathbf{p}_K^2}{2M} + \Phi_\gamma(\{\mathbf{u}_K(\gamma)\}). \tag{6}$$

It is useful to expand Φ_γ in powers of the displacements,

$$\Phi_\gamma = \Phi_0(\gamma) + \Phi_H(\gamma) + \Phi_A(\gamma). \tag{7}$$

Here $\Phi_0(\gamma)$ is the static structure potential,

$$\Phi_0(\gamma) = \Phi_\gamma(\{\mathbf{u}_K(\gamma)=0\}) = \Phi(\{\mathbf{R}_K(\gamma)\}). \tag{8}$$

The harmonic potential $\Phi_H(\gamma)$ expresses terms of second order in displacements,

$$\Phi_H(\gamma) = \tfrac{1}{2}\sum_{KL} \mathbf{u}_K(\gamma)\cdot\mathbf{\Phi}_{KL}(\gamma)\cdot\mathbf{u}_L(\gamma), \tag{9}$$

where the potential coefficients $\mathbf{\Phi}_{KL}(\gamma)$ are merely second displacement derivatives of Φ_γ, at equilibrium. The anharmonic potential $\Phi_A(\gamma)$ is all terms higher than second order in displacements, and since we already know the ion motion consists approximately of $3N$ independent harmonic oscillators, then $\Phi_A(\gamma)$ is a small contribution. Now H_γ can be written so as to emphasize the importance of harmonic motion,

$$H_\gamma = \Phi_0(\gamma) + H_H(\gamma) + \Phi_A(\gamma), \tag{10}$$

where the important dynamic term is $H_H(\gamma)$,

$$H_H(\gamma) = \sum_K \frac{\mathbf{p}_K^2}{2M} + \Phi_H(\gamma). \tag{11}$$

This is diagonalized in terms of $3N$ normal modes labeled $\lambda=1,\ldots,3N$, with momenta p_λ, coordinates $q_\lambda(\gamma)$, and frequencies $\omega_\lambda(\gamma)$, so that $H_H(\gamma)$ becomes

$$H_H(\gamma) = \sum_\lambda \left[\frac{p_\lambda^2}{2M} + \frac{1}{2}M\omega_\lambda^2(\gamma)q_\lambda^2(\gamma)\right]. \tag{12}$$

The Hamiltonian H_γ applies to any structure in configuration space. Let us consider first the nature of various structures, and then the corresponding boundary conditions imposed on the Hamiltonian. For most elemental systems, at any density in the condensed phase, there are crystalline structures having long-range order, some of which lie at the lowest energies. Above these are an array of structures without long-range order and generally called amorphous. Here it will be necessary to divide amorphous structures into two classes.

(a) Structures with a remnant of crystal symmetry, at least among nearest neighbors, which we call ''symmetric'' structures. These range from the microcrystalline structures observed in computer simulations [3,4,7], to the tetrahedrally coordinated amorphous carbon made experimentally by ion implantation [28], and studied theoretically by local-density-approximation techniques [29]. This class, though large in number, is still *relatively* few, because of the symmetry restriction. In addition, the structure potential $\Phi_0(\gamma)$, and the set of normal mode frequencies $\{\omega_\lambda(\gamma)\}$, are sensitive to near-neighbor symmetry, so these important quantities have significant variations over the class of symmetric structures.

(b) Structures with a wide distribution of nearest-neighbor orientations, where near-neighbor symmetry is frustrated [30], as in the random close-packed hard-sphere model reviewed by Finney [31]. We call these ''random'' structures, and the random character leads to two important properties, for large-N systems. First, they constitute the great majority of all structures, and hence dominate the statistical mechanics of the liquid state. Second, each macroscopic structural property is narrowly distributed over the class of structures. It follows that the structure potential $\Phi_0(\gamma)$, and the set of normal mode frequencies $\{\omega_\lambda(\gamma)\}$, are essentially independent of γ for large-N random structures, and one can define the liquid structure potential Φ_0^l, and the liquid frequency set $\{\omega_\lambda\}$, by

$$\Phi_0^l = \Phi_0(\gamma), \tag{13}$$

$$\{\omega_\lambda\} = \{\omega_\lambda(\gamma)\}, \tag{14}$$

where γ is a random structure in the thermodynamic limit.

We now consider the boundary condition on H_γ, requiring that the system is in γ. In the theory of lattice dynamics, negligible error is introduced by extending the crystal-structure valley to infinity, thus eliminating the boundary condition. The same procedure will constitute an acceptable approximation for the random structural valleys, but the error in ignoring the intersections of neighboring valleys will not be negligible in the liquid theory. The correction of this error is called the ''boundary'' contribution, because it results from the presence of the intervalley boundaries.

Let us use the above arguments to write a simple approximation for H_γ for random structures. We first neglect the boundary condition, so the normal coordinates $q_\lambda(\gamma)$ are given infinite extent. We then use Eqs. (13) and (14) to omit γ dependence of $\Phi_0(\gamma)$ and $\hbar\omega_\lambda(\gamma)$, and finally we neglect anharmonicity, to write

$$H_\gamma \approx \Phi_0^l + \sum_\lambda \left[\frac{p_\lambda^2}{2M} + \frac{1}{2} M\omega_\lambda^2 q_\lambda^2(\gamma) \right]. \tag{15}$$

In this quasiharmonic approximation, H_γ depends on γ only through the configuration-space location of structure γ, and the error is specifically the neglect of anharmonic and boundary contributions. The latter can be expressed as a set of interactions $H_{\gamma\gamma'}$, which cause transitions between valleys γ and γ'.

IV. PARTITION FUNCTION

We first evaluate the canonical partition function Z_I for the ion motion alone, and since the motion of ions in practically all monatomic liquids is classical, we use classical statistics. Z_I is written

$$Z_I = \frac{1}{h^{3N}N!} \int \cdots \int \exp(-\beta H_I) \Pi_K d\mathbf{p}_K d\mathbf{r}_K . \tag{16}$$

The configuration part of the integral includes all permutations of the ions over each configuration, so division by $N!$ cancels the sum of permutations.

Restricting the configuration integral to the liquid configuration space, the partition function becomes a sum over the random structural valleys,

$$Z_I = \Sigma_\gamma Z_\gamma , \tag{17}$$

where

$$Z_\gamma = \frac{1}{h^{3N}} \int \cdots \int \exp(-\beta H_\gamma) \Pi_K d\mathbf{p}_K d\mathbf{u}_K(\gamma). \tag{18}$$

Here $N!$ has been removed, because when the system is in γ, each ion K is assigned an equilibrium position $\mathbf{R}_K(\gamma)$, and no permutations are allowed. We can use the quasiharmonic approximation (15) for H_γ, to find the equivalent approximation for Z_γ:

$$Z_\gamma \approx \frac{\exp(-\beta\Phi_0^l)}{h^{3N}} \Pi_\lambda \int\int \exp\left[-\beta\left(\frac{p_\lambda^2}{2M} + \frac{1}{2} M\omega_\lambda^2 q_\lambda^2 \right)\right] \times dp_\lambda dq_\lambda . \tag{19}$$

Evaluating the integral gives

$$Z_\gamma \approx \exp(-\beta\Phi_0^l) \Pi_\lambda \frac{kT}{\hbar\omega_\lambda}. \tag{20}$$

Now in Eq. (17) for Z_I, the Σ_γ merely counts the number of random structures, which is w^N, so that

$$Z_I \approx w^N \exp(-\beta\Phi_0^l) \Pi_\lambda \frac{kT}{\hbar\omega_\lambda}. \tag{21}$$

The error in this result is the neglect of anharmonic and boundary contributions.

The Helmholtz free energy for the ion motion is $F_I = -kT \ln Z_I$. We evaluate this from Eq. (21) for Z_I, and add a term F_{AB} to account for the combined anharmonic and boundary contribution. It is also convenient to introduce the liquid characteristic temperature θ_0^l, related to the logarithmic moment of the frequency distribution,

$$\ln(k\theta_0^l) = \frac{\Sigma_\lambda \ln(\hbar\omega_\lambda)}{3N}. \tag{22}$$

Then

$$F_I = \Phi_0^l - NkT\ \ln w - 3NkT\ \ln(T/\theta_0^l) + F_{AB}. \qquad (23)$$

The next step is to calibrate w. As noted in Sec. I, we previously concluded, from experimental data for entropy of melting at constant density, that the ion system has a universal disordering entropy $Nk\Delta$ of liquid relative to crystal, where $\Delta = 0.80$. Let us find the theoretical expression for this melting entropy. From Eq. (23), the ion motional entropy of the liquid is

$$S_I = Nk\ \ln w + 3Nk[\ln(T/\theta_0^l) + 1] + S_{AB}. \qquad (24)$$

The free energy for the crystal is given by Eq. (23) evaluated for one structure only, namely, the appropriate crystal structure, which we denote with a superscript c,

$$F_I^c = \Phi_0^c - 3NkT\ \ln(T/\theta_0^c) + F_A^c, \qquad (25)$$

where the anharmonicity is still present, as indicated, but the boundary effect is negligible for the crystal state. The corresponding crystal entropy is

$$S_I^c = 3Nk[\ln(T/\theta_0^c) + 1] + S_A^c. \qquad (26)$$

Then from Eqs. (24) and (26), the ion-motional entropy of melting at constant density is ΔS_I,

$$\Delta S_I = Nk\ \ln w + 3Nk\ \ln(\theta_0^c/\theta_0^l) + S_{AB} - S_A^c. \qquad (27)$$

The only quantity here which might sensibly be a universal constant is w, so we set

$$\ln w = 0.80, \qquad (28)$$

and then investigate the consequences.

This discussion recalls the melting properties mentioned in Sec. I. First, S_{AB} and S_A^c are usually small at melt. For normal melting elements, where crystal and liquid have qualitatively the same electronic structure, the interionic forces should be approximately the same, so that $\theta_0^c/\theta_0^l \approx 1$. Then the last three terms in Eq. (27) are all small, and Eq. (27) reads $\Delta S_I = 0.80Nk +$ (small scatter), which expresses the nature of the experimental data for normal melting elements. For anomalous melting elements, the crystal and liquid have qualitatively different electronic structures, hence θ_0^c and θ_0^l should differ significantly. Then (27) is $\Delta S_I = 0.80Nk + (\text{a large term})$ depending on the different electronic structures of crystal and liquid, which expresses the nature of the experimental data for anomalous melting elements. The calibration (28) therefore provides a satisfactory rationalization of experimental data for ΔS, and tells us how many random structures are present in the potential-energy landscape.

Finally, let us consider the remaining part of the Hamiltonian, the term H_E which expresses excited states of the electrons, and the coupling of those states to the ion motion. The corresponding contribution to the partition function may be evaluated in quantum statistics for the electrons, and classical statistics for the ions. The work has not been done, as far as the author is aware, and it poses an interesting and useful calculation. In the meantime, we will adopt the same model for the liquid as we have used for the crystal [14], namely, that the presence of H_E gives rise to an additive term F_E in the free energy, and that at temperatures where the ion motion is classical, F_E is the bare independent-electron free energy determined by the electron density of states and Fermi statistics (Sommerfeld model). Hence the total free energy is

$$F = F_I + F_E. \qquad (29)$$

Empirical evidence shows this to be an excellent model for crystals, including transition metals, where the electronic contribution is quite important [32].

V. COMPARISON WITH EXPERIMENT FOR NORMAL MELTING ELEMENTS

Thermodynamic functions for the liquid are calculated from the free energy derived in Sec. IV. Here we will consider the internal energy U, the entropy S, and the constant-volume specific heat C_V, given by

$$U = \Phi_0^l + 3NkT + U_{AB} + U_E, \qquad (30)$$

$$S = Nk\ \ln w + 3Nk[\ln(T/\theta_0^l) + 1] + S_{AB} + S_E, \qquad (31)$$

$$C_V = 3Nk + C_{AB} + C_E, \qquad (32)$$

where Φ_0^l and θ_0^l are functions of V. For the nearly free-electron elements, C_E is given by the low-temperature expansion (2), and in this order we also have

$$TC_E = TS_E = 2U_E. \qquad (33)$$

These equations are not restricted in any way by the melting process. However, the experimental data at T_m, or as a function of T/T_m, requires special consideration when the melting process at T_m is anomalous, and to avoid such complications, which after all are irrelevant to the theory of the liquid state, we restrict attention in this section to the normal melting elements.

From Eq. (32), the ionic contribution C_I is

$$C_I = 3Nk + C_{AB}. \qquad (34)$$

C_{AB} stands for two terms, the anharmonic contribution, which can be of either sign, and the boundary contribution, which is negative since it results from the limiting of the potential-energy surface, at the intersections of neighboring valleys. From the experimental data for the liquids at melt, Table I, $C_{AB} \approx 0.4Nk$ for the alkali metals, and this was already attributed to anharmonicity in Sec. II. For the rest of the normal melting elements in Table I, $C_{AB} \approx 0$, except for Ar, where the large negative C_{AB} can result from both anharmonic and boundary effects. Finally, C_{AB} is presumably responsible for the general decrease of C_I, with increasing temperature or with decreasing density, as mentioned in Sec. II.

From the crystal free energy, discussed in Sec. IV,

$$U^c = \Phi_0^c + 3NkT + U_A^c + U_E^c. \qquad (35)$$

The change in internal energy upon melting at constant density is $\Delta U = U^l - U^c$, and is written

TABLE II. Data for the liquid entropy analysis. Columns 2–6 are experimental data for the liquid at melt, where β is thermal expansion coefficient and B_S is adiabatic bulk modulus. References provide the same experimental data at elevated temperatures. θ_0^c is evaluated at the density of the liquid at melt. S_E is theoretical electronic entropy at melt.

Element	ρ (g/cm^3)	β (10^{-4}/K)	B_S (kbar)	S/Nk	C_P/Nk	Refs.	θ_0^c	S_E/Nk
Na	0.925	2.57	59.4	7.78	3.83	[36, 37, 17]	102.2	0.053
K	0.829	2.9	29.4	9.06	3.87	[38, 37, 17]	61.9	0.080
Rb	1.479	3.0	23.5[a]	10.26	3.89	[39, 40, 17]	37.7	0.089
Pb	10.68	1.12	358	10.13	3.68	[41, 42, 43, 16]	52.1	0.089
In	7.03	1.11	378	9.11	3.55	[44, 16]	74.4	0.065
Hg	13.69	1.80	299	8.31	3.43	[45, 16]	56.4	0.029

[a] B_S is calculated from experimental B_T for Rb.

$$\Delta U=\Delta\Phi_0+U_{AB}-U_A^c+\Delta U_E, \tag{36}$$

where the last three terms should be small for normal melting. But this quantity can also be evaluated in thermodynamics, by equating the liquid and crystal Gibbs free energies at a common pressure and temperature, with the result [13]

$$\Delta U=T_m\Delta S+\cdots, \tag{37}$$

where $+\cdots$ represents a power series in η, starting at η^2, and where for melting at a constant pressure and temperature,

$$\eta=\frac{\rho_{cm}}{\rho_{lm}}-1. \tag{38}$$

Combining Eqs. (36) and (37),

$$\Phi_0^l(\rho_{lm})-\Phi_0^c(\rho_{lm})=T_m\Delta S(\rho_{lm})+\cdots, \tag{39}$$

where $+\cdots$ represents the small terms in Eqs. (36) and (37). This tells us that the liquid structure potential lies above that of the melting crystal by about $T_m\Delta S$, a result which can be checked by theoretical calculation of these two structure potentials for a normal melting element.

Let us consider the temperature dependence of thermodynamic properties of the liquid at elevated temperatures. The thermodynamic functions, all being derived from the free energy, contain only one independent function of temperature. We choose to analyze the entropy, and will include only elements in all three of the following categories.

(a) Nearly free electron elements, so we have a reliable theoretical evaluation of S_E.

(b) Normal melting elements, so we can approximate θ_0^l by θ_0^c.

(c) Elements for which data exist to find entropy at constant volume, up to temperatures sufficiently high to reveal a meaningful temperature dependence, say up to $T/T_m \gtrsim 2$.

The sum total of elements satisfying these conditions is six. The need for the volume correction is as follows. We have accurate values [33] of θ_0^c at the density ρ_N, from inelastic neutron-scattering measurements on crystals at low temperatures. We correct these θ_0^c to density ρ by means of

$$\theta_0^c(\rho)\approx\theta_0^c(\rho_N)\left(\frac{\rho}{\rho_N}\right)^{\gamma}, \tag{40}$$

where γ is the Grüneisen parameter for the crystal, tabulated in Ref. [13]. Now the liquid at melt is quite expanded from ρ_N, and values of $\theta_0^c(\rho_{lm})/\theta_0^c(\rho_N)$ are in the range 0.81–0.90, which is about as far as we can safely apply the formula (40). But the high-temperature liquid continues to expand, making it impossible to get reliable estimates of θ_0^c at ever lower densities, so instead we correct the measured entropy to the fixed density ρ_{lm}. If ρ_a is the density at atmospheric pressure, the density correction of S at each temperature is given by

$$S(\rho_{lm})=S(\rho_a)-\zeta V\beta B_T, \tag{41}$$

where β is the thermal expansion coefficient, B_T is the isothermal bulk modulus, and

$$\zeta=\frac{\rho_{lm}}{\rho_a}-1. \tag{42}$$

For the six liquids in question, data for the liquid at melt, and our sources for data at elevated temperatures, are listed in Table II.

In Sec. IV we argued the approximation $\theta_0^c\approx\theta_0^l$ for normal melting elements. Let us use this to write the approximation S_{theory},

$$S_{\text{theory}}=Nk\ \ln w+3Nk[\ln(T/\theta_0^c)+1]+S_E. \tag{43}$$

Comparison with Eq. (31) shows the error in this formula is due to using θ_0^c in place of θ_0^l, and in neglecting S_{AB}. But Eq. (43) has no adjustable parameters. The comparison with experiment is shown in Fig. 1 for mercury to $T=3.2T_m$, and is quite striking.

Figure 2 shows the difference $S_{\text{expt}}-S_{\text{theory}}$, for all the high-temperature entropy data we are currently able to analyze. Error estimates are as follows. Original values [33] of $\theta_0^c(\rho_N)$ are accurate to around 1%, and this accuracy might be reduced to say 3% for our values of $\theta_0^c(\rho_{lm})$. Smaller errors, say around ± 0.02 are expected in S_E, so the total error in evaluating S_{theory} is likely to be around $\pm 0.1Nk$. For the experimental data collected here, combined error in the measured entropy and the volume correction ranges from around $0.02Nk$ at T_m, to around $0.1Nk$ at $3T_m$. Hence the theoretical-experimental differences shown in Fig. 2 are hardly beyond the combined expected errors of the analysis. Our conclusion, for temperatures to around $3T_m$, is that approximation (43) has an error not much larger than $\pm 0.2Nk$,

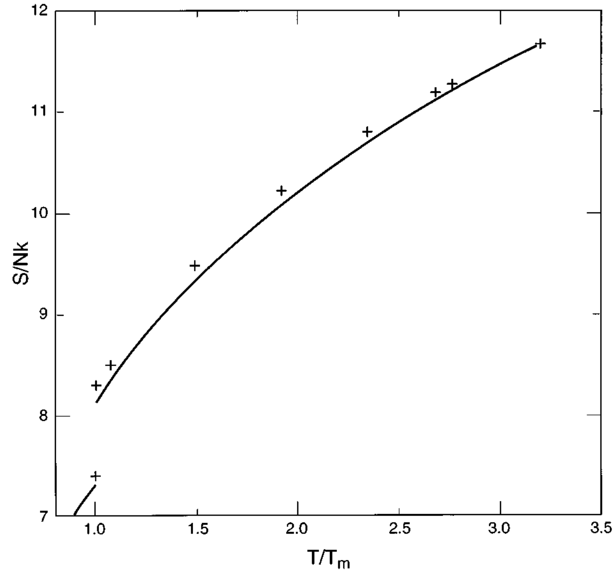

FIG. 1. Theory for the entropy of crystal and liquid mercury (solid line), compared with experimental entropy (crosses), at the fixed volume of the liquid at melt.

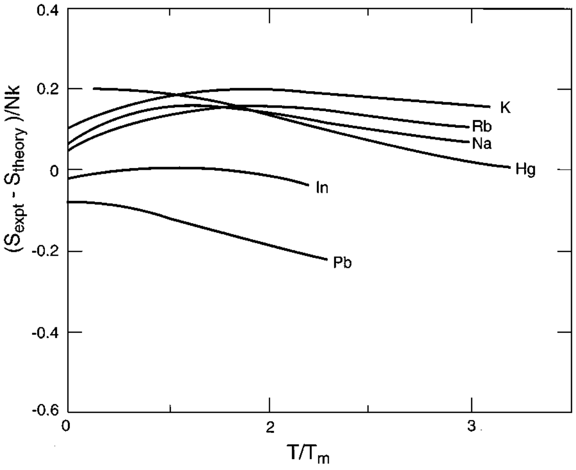

FIG. 2. Difference between experimental and theoretical entropy at elevated temperatures, at the fixed volume of the liquid at melt, for six liquid metals.

which is 1% or 2% of the total entropy, and is only 25% of the difference $0.8Nk$ between liquid and crystal entropies at melt.

VI. SUMMARY AND DISCUSSION

Liquid dynamics theory

Two key experimental thermodynamic properties of elemental liquids, together with an analysis of the many-ion potential-energy surface, lead us logically to the dynamical theory of monatomic liquids. The steps are as follows.

(a) Experimentally, the ionic specific heat of the liquid at melt is approximately $3Nk$ for a system of N ions. This implies the ionic normal modes of motion are approximately a set of $3N$ independent harmonic oscillators, or what is equivalent, the ion motion is mainly confined to nearly harmonic structural valleys in the potential-energy surface.

(b) Structures are either crystalline or amorphous, and amorphous structures are either symmetric or random. The random character gives two properties of random structures for large-N systems: they are the vast majority of all structures, hence they dominate the statistical mechanics of the liquid, and the structure potential and normal mode frequency distribution are essentially the same for all random structures.

(c) The Hamiltonian for the motion of ions is H_γ when the system is in the valley of any structure γ, and is written in Eqs. (10) and (12) as the structure potential, a sum of harmonic normal modes, and an anharmonic correction. All random structures contribute equally to the partition function. The ion motional free energy in Eq. (23) is the sum of four terms: the liquid structure potential, the entropy from summing over structures, the single-structure harmonic vibrational free energy, and the term expressing anharmonic and boundary contributions.

(d) Experimentally, the entropy of melting at constant density contains an ionic disordering contribution of $Nk\Delta$, where Δ is a universal constant. This suggests the number of random structures in the potential energy landscape is w^N, so the entropy of melting contains the term $Nk \ln w$, implying $\ln w = \Delta$. Our estimate of the value of Δ is 0.80.

Testable predictions

The theory applies to any monatomic liquid, hence it covers both normal and anomalous melting. However, to avoid unnecessary complications, we limit our consideration here to normal melting elements.

(a) Reflecting the experimental properties upon which our theory is built, $C_I \approx 3Nk$ for the liquid at melt, and ΔS contains the universal contribution $Nk \ln w$.

(b) At the same density, liquid and crystal characteristic temperatures are expected to be approximately the same: $\theta_0^l \approx \theta_0^c$. This can be tested by direct theoretical calculations of these quantities.

(c) The liquid structure potential Φ_0^l is approximately $\Phi_0^c + T_m \Delta S$, a relation which can be tested by direct theoretical calculations of $\Phi_0(\gamma)$ for crystal and random structures.

(d) The liquid theory for entropy, using approximation (b) and neglecting the anharmonic and boundary contribution, agrees with experimental entropy at elevated temperatures to the remarkable accuracy of $\pm 0.2Nk$.

The comparison of theory with experiment for liquid entropy at T_m is a test of the quasiharmonic approximation for the solid, plus the universal liquid disordering entropy, while the comparison of theory with experiment for liquid entropy at elevated temperatures is a test of the quasiharmonic approximation for the liquid.

Structures and normal modes

As a technical point, it is possible that genuine structures do not exist for some or even many of the potential-energy valleys in configuration space. A structure might be nearly stable, but not exactly so, with some small forces remaining, so that the exact potential surface leads very slightly downward from approximate structure to approximate structure. Nevertheless, in the classical liquid state, the particles have kinetic energy at least on the order of kT_m, and the structures will be dynamically stabilized. Dynamic stabilization can be expressed through a self-consistent potential Φ, as for example in a self-consistent phonon theory [34,35].

Transits

When the liquid system moves across a boundary, from one structural valley to another, we call the motion a ‘‘transit.’’ While the equilibrium statistical mechanics of the liquid has been constructed without explicit consideration of transits, the transit events have an essential role in achieving and maintaining thermodynamic equilibrium. This situation is in strict analogy to the physics of gases, either classical or quantum, where the equilibrium statistical mechanics is merely the statistics of free-particle states, while scattering events provide the irreversible driving force to achieve and maintain equilibrium. An important property of any normal many-particle system, which means to exclude macroscopically correlated states such as superfluid states, is that the irreversible driving force is local. On this ground, we conclude that transits are local, that is, when the N-particle system moves from the structure at $\{R_K(\gamma)\}$ to the structure at $\{R_K(\gamma')\}$, the equilibrium positions R_K change for only a small local group of ions K. We will learn more about transits as we apply the present liquid theory to irreversible processes.

ACKNOWLEDGMENTS

The author appreciates helpful discussions with Bradford Clements and Heinrich Röder.

[1] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946), Chap. III, Sec. 1.

[2] J. Frenkel, Z. Phys. **35**, 652 (1926).

[3] F. H. Stillinger and T. A. Weber, Kinam **3**, 159 (1981).

[4] F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982).

[5] T. A. Weber and F. H. Stillinger, J. Chem. Phys. **80**, 2742 (1984).

[6] F. H. Stillinger and T. A. Weber, Science **225**, 983 (1984).

[7] R. A. LaViolette and D. M. Stump, Phys. Rev. B **50**, 5988 (1994).

[8] D. C. Wallace, Phys. Lett. A **122**, 418 (1987).

[9] D. C. Wallace, Proc. R. Soc. London, Ser. A **433**, 615 (1991).

[10] D. C. Wallace, Int. J. Quantum Chem. **52**, 425 (1994).

[11] D. C. Wallace, Phys. Rev. A **38**, 469 (1988).

[12] D. C. Wallace, Phys. Rev. A **39**, 4843 (1989).

[13] D. C. Wallace, Proc. R. Soc. London, Ser. A **433**, 631 (1991).

[14] D. C. Wallace, Phys. Rev. E **56**, 1981 (1997).

[15] D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).

[16] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, Ohio, 1973).

[17] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985).

[18] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[19] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[20] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

[21] D. C. Wallace, B. L. Holian, J. D. Johnson, and G. K. Straub, Phys. Rev. A **26**, 2882 (1982).

[22] G. Grimvall, Phys. Scr. **11**, 381 (1975).

[23] R. E. Swanson, G. K. Straub, B. L. Holian, and D. C. Wallace, Phys. Rev. B **25**, 7807 (1982).

[24] D. C. Wallace, Phys. Rev. B **46**, 5242 (1992).

[25] D. C. Wallace, Proc. R. Soc. London, Ser. A **439**, 177 (1992).

[26] Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980).

[27] N. W. Ashcroft, Nuovo Cimento D **12**, 597 (1990).

[28] D. R. McKenzie, D. Muller, and B. A. Pailthorpe, Phys. Rev. Lett. **67**, 773 (1991).

[29] H. Röder, R. N. Silver, D. A. Drabold, and J. J. Dong, Phys. Rev. B **55**, 15 382 (1997).

[30] S. Sachdev, in *Bond-Orientational Order in Condensed Matter Systems*, edited by K. J. Strandburg (Springer, Berlin, 1992), p. 255.

[31] J. L. Finney, in *Amorphous Solids and the Liquid State*, edited by N. H. March, R. A. Street, and M. Tosi (Plenum, New York, 1985), p. 31.

[32] O. Eriksson, J. M. Wills, and D. C. Wallace, Phys. Rev. B **46**, 5221 (1992).

[33] H. Schober and P. H. Dederichs, in *Metals: Phonon States, Electron States and Fermi Surfaces*, edited by K.-H. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 13, Pt. a (Springer, Berlin, 1981).

[34] P. Choquard, *The Anharmonic Crystal* (Benjamin, New York, 1967).

[35] N. R. Werthamer, Am. J. Phys. **37**, 763 (1969).

[36] E. I. Gol’tsova, High Temp. **4**, 348 (1966).

[37] Yu. S. Trelin, I. N. Vasil’ev, V. B. Proskurin, and T. A. Tsyganova, High Temp. **4**, 352 (1966).

[38] E. E. Shpil’rain, K. A. Yakimovich, V. A. Fomin, S. N. Skovorodjko, and A. G. Mozgovoi, in *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, London, 1985), p. 435.

[39] G. H. Shaw and D. A. Caldwell, Phys. Rev. B **32**, 7937 (1985).

[40] N. B. Vargaftik, V. F. Kozhevnikov, V. G. Stepanov, V. A. Alekseev, and Y. F. Ryzhkov, in *Seventh Symposium on Thermophysical Properties*, edited by A. Cezairliyan (ASME, New York, 1977), p. 926.

[41] E. A. Brandes, *Smithells Metals Reference Book*, 6th ed. (Butterworths, London, 1983), Table 14.3a.

[42] R. R. Miller, in *Liquid Metals Handbook*, 2nd ed., edited by R. N. Lyon (U.S. GPO, Washington DC, 1952), p. 38.

[43] M. B. Gitis and I. G. Mikhailov, Akust. Zh. **11**, 434 (1965) [Sov. Phys. Acoust. **11**, 372 (1966)].

[44] D. P. Almond and S. Blairs, J. Chem. Thermodyn. **12**, 1105 (1980).

[45] H. A. Spetzler, M. D. Myer, and Tin Chan, High Temp.-High Press. **7**, 481 (1975).