Thermal electronic excitations in liquid metals

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Thermal electronic excitations in metal crystals are calculated by starting with a reference structure for the nuclei: the crystal structure of the appropriate phase. Here we explain the corresponding theory for metal liquids, starting with an appropriate reference structure for a liquid. We explain the significance of these structures, and we briefly review how to find them and calculate their properties. Then we examine the electronic densities of states for liquid structures of Na, Al, and Cu, comparing them to their crystal forms. Next we explain how to calculate the dominant electronic thermal excitation term, considering issues of accuracy that do not arise in the crystal theory. Finally we briefly discuss the contribution from the interaction between excited electrons and moving nuclei.

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I. INTRODUCTION

For metallic crystals, thermal electronic excitation theory is well developed. The leading approximation is to fix the nuclei at a reference structure, namely the appropriate crystal structure, at which we calculate the electronic density of states (DOS) and use statistical mechanics to describe the excitation of electrons across the Fermi level. It then remains to describe the correction due to the vibrational motion of the nuclei. This correction is expressed through electron-phonon interactions, and is treated in perturbation theory to the first order in which its free energy contribution is nonzero. The total crystal free energy then consists of a series of diminishing contributions: the structural potential, nuclear vibrations, electronic excitation, and electron-phonon interactions, where the last contribution is the only truly complicated one, and is negligible for practical equation-of-state applications. The same ordering of terms holds for nearly-free-electron (NFE) metals and transition metals, though the electronic excitation effects are much larger in transition metals.

A similar formulation has not been developed for liquid metals because the first step requires a reference structure, and such a structure has not been available for liquids. However, the needed structure naturally appears in the V-T (vibration-transit) theory of liquid dynamics. In this theory, the potential energy valleys which underlie the liquid motion are divided into symmetric and random classes, where the numerically superior random valleys dominate the liquid motion, and all have the same statistical mechanical properties in the thermodynamic limit. The nuclear motion consists of vibrations in a random valley interspersed with transits which carry the system between random valleys. A transit is accomplished by a small local group of nuclei, and transits are going on at a high rate throughout the liquid. The nuclear configuration at any instant is within a single random valley, so the valley minimum, called a random structure or liquid structure, serves as the reference structure for the nuclear motion.

Our goal is to explain how to use the liquid structure electronic DOS to study the statistical mechanics of thermal electronic excitations in liquids. We start with density functional theory (DFT) results for the liquid structure DOS for Na, Al, and Cu, and we show the close similarity between liquid and crystal DOS. Then we discuss the electronic excitation theory, which is formally the same for crystal and liquid with an important exception: the liquid’s higher temperature range requires the integral formulation. With the theory in hand, we then estimate the size of electronic excitation effects: they are small for the crystal at all temperatures, and are nearly the same for liquid and crystal at melt, but they can become important in the high-temperature liquid. Finally, we observe that the interaction between electronic excitations and nuclear motion will also become non-negligible in the liquid at high temperatures.

II. THE LIQUID STRUCTURE ELECTRONIC DOS

Since the use of the liquid structure DOS is new in liquid dynamics theory, we will describe the procedure for finding these structures and explain how we have validated their application to V-T theory. We also distinguish two classes of melting of elements: normal melting, where liquid and crystal have essentially the same electronic structure, and anomalous melting, where the electronic structures are significantly different. Anomalous melting is rare, and it breaks the rule we commonly apply to metallic systems, that liquid and crystal are similar at melt. For simplicity of discussion here, we shall consider only normal melting metallic systems.

Finding liquid structures proceeds in two steps. First, random structures are found by quenching an N-atom supercell to a potential energy minimum, typically through direct minimization of the total energy (using e.g. a DFT code such as VASP). Because of the dominance and
uniformity of the random valleys, quenches almost always arrive at random structures, and these structures possess very narrow distributions\textsuperscript{15} of the Hamiltonian parameters: the structural potential $\Phi_0$ and the vibrational characteristic temperatures $\theta_n$ for $n = 0, 1, 2$. In our experience, a set of 10 or more DFT quenches from independent stochastic configurations\textsuperscript{14,15} will have a distribution of $\Phi_0$ lying above the crystal potential by roughly $k_B T_m$, and of width $\lesssim 0.04 k_B T_m$ for $N \gtrsim 150$. The $\theta_n$ are likewise narrowly distributed. These properties will verify the structures are random. Second, the electronic properties associated with the random structure must be checked. For systems considered here, the liquid is metallic, so the electronic structure should be the correct metallic structure. Random structures having the proper liquid electronic structure are called liquid structures.

Because the nuclear motion in elemental liquids poses an intricate mechanical problem, V-T theory has been developed primarily through comparison of statistical mechanical models with experimental data. This development has provided a level of verification of the role of the liquid structure in liquid dynamics theory\textsuperscript{19}. The most convincing validation of the liquid structure is now provided by DFT calculations which, together with a statistical mechanical model for the small contribution from transits\textsuperscript{14,15} yield highly accurate thermodynamic properties of the liquid at melt for Na and Cu\textsuperscript{18}.

Finally, there are independent theoretical arguments that apply to the liquid DOS. In pseudopotential perturbation theory, the electronic DOS is free electron in zeroth order, and the presence of the ions makes a small correction\textsuperscript{18} this theory applies to Na and Al. Moreover, for normal melting elements, which include Na, Al, and Cu, the electronic structure is the same for liquid and crystal at the same volume, so the DOS are very similar. Small differences arise because variations in the crystal DOS are smoothed out of the liquid DOS by its disordered nuclear arrangement (see Figures below).

The DFT calculations employ VASP, use the PW91 generalized gradient approximation\textsuperscript{19} (GGA), and treat the valence electrons in a plane-wave basis with element-specific projector-augmented wave potentials.\textsuperscript{20} The calculations employ first order Methfessel-Paxton smearing\textsuperscript{21} with width 0.2 eV and an energy cutoff of 102 eV (Na), 301 eV (Al), and 342 eV (Cu). The self-consistent field cycles are converged to within $10^{-6}$ eV. The crystal DOS in the figures were calculated with a $40 \times 40 \times 40$ k-point mesh. The liquid DOS for Na and Al were calculated with a $12 \times 12 \times 12$ mesh, while a $7 \times 7 \times 7$ mesh was used for Cu. For Na, $N = 500$, while $N = 150$ for Al and Cu.

Figure\textsuperscript{1} shows that the calculated electronic DOS for Na agrees with the free electron result to high accuracy for the crystal at $\epsilon \lesssim \epsilon_F$, and for the liquid at all energies, as expected. Effects from Brillouin zone band gaps appear in the crystal at $\epsilon > \epsilon_F$, and similar but smoothed effects appear in the liquid.

In Figure\textsuperscript{2} for Al, the free electron DOS is in good overall agreement with DFT for crystal and liquid alike. More precisely, the free electron DOS is slightly wider than DFT, and averages around 5% lower at energies within 2 eV of $\epsilon_F$. Brillouin zone band gaps appear below $\epsilon_F$ in the crystal, but are absent in the liquid.
In Figure 3 for Cu, the crystal shows the well-known d-band structure with bonding and antibonding states separated by a pseudogap. The liquid shows the same form with the same width, but noticeably smoothed. We have also used the free electron approximation for electronic excitation effects in the liquid noble metals, a notion that goes back to the Mott and Jones model of a filled d band overlapped by a broad partially filled s band (Figure 80 of Ref. [23]). The free electron DOS in Figure 3 represents the Mott and Jones result, which agrees with the crystal and liquid DOS to within 30% at the Fermi energy. This shows that the free electron approximation is adequate when the temperature is not too high and the thermal electronic contribution is not needed to very high accuracy.

![Diagram of Cu electronic DOS](image)

**FIG. 3.** (Color online) The electronic density of states for crystal and liquid Cu at an atomic volume of 13 Å³. (For comparison, the volume of the crystal and liquid at melt are, respectively, 13.05 and 13.54 Å³.) The bonding and antibonding states separated by a pseudogap are clearly visible, although the gap is smoothed in the liquid. The free-electron DOS with one electron per atom is also shown, agreeing approximately at \( \epsilon = \epsilon_F \).

### III. STATISTICAL MECHANICS

To examine the statistical mechanical role of the liquid DOS, we shall discuss the thermodynamic internal energy \( U(V,T) \). The estimates we find for the energy hold approximately for the entropy and free energy as well. In V-T theory the internal energy is

\[
U = \Phi_0 + U_{\text{vib}} + U_{\text{tr}} + U_{\text{el}} + \delta U_{\text{el}}
\]  

where \( \Phi_0(V) \) is the structural potential energy introduced earlier, \( U_{\text{vib}}(V,T) \) and \( U_{\text{tr}}(V,T) \) express respectively the nuclear vibrational and transit motions, and \( U_{\text{el}}(V,T) \) and \( \delta U_{\text{el}}(V,T) \) express respectively the electronic excitation with nuclei fixed at the structure, and the correction to this due to the nuclear motion. The zero of energy appears in \( \Phi_0(V) \), while the remaining thermal excitation contributions are each measured from \( \Phi_0(V) \). This decomposition is analogous to the standard decomposition for crystals, with the additional term \( U_{\text{tr}} \) representing an additional type of nuclear motion.

For a monatomic liquid at \( T_m \), by far the largest thermal energy contribution is \( U_{\text{vib}} \). \( U_{\text{tr}} \) makes a significant contribution around 0.1 \( U_{\text{vib}} \), while \( U_{\text{el}} \) is around 0.01 \( U_{\text{vib}} \) for NFE metals, around 0.1 \( U_{\text{vib}} \) for transition metals, and is easily evaluated from the liquid DOS, Figures [13]. The smallest and most difficult term to evaluate is \( \delta U_{\text{el}} \). We shall therefore concentrate first on \( U_{\text{el}} \) and consider \( \delta U_{\text{el}} \) for the high-temperature liquid in the last section.

For liquid theory, the Sommerfeld expansion is not efficient due to rapid fluctuations in the DOS around the Fermi energy, so we use the DOS integral formulation for thermodynamic functions. In this formulation,

\[
U_{\text{el}} = \int_{-\infty}^{\infty} n(\epsilon) \left[ \tilde{f}(\epsilon) - g(\epsilon) \right] \epsilon \, d\epsilon
\]  

where

\[
\tilde{f}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}.
\]  

Here \( \mu \) is the chemical potential and \( g(\epsilon) \) is the ground state evaluation of \( \tilde{f}(\epsilon) \). The term in \( g(\epsilon) \) subtracts the electronic ground state energy, which has already been included in \( \Phi_0 \) (Section 3 of Ref. [9]). Volume dependence is contained in \( n(\epsilon) \) and \( \mu \), and we shall estimate temperature effects at constant volume. This is the formulation used by Ref. [7] to calculate the electronic excitation entropy for transition metal crystals to \( T_m \).

### IV. THE LIQUID TO HIGH TEMPERATURES

At a fixed volume \( V \), the liquid persists as the stable phase from \( T_m(V) \) to an upper limit which we estimate as roughly \( 4T_m(V) \). As temperature increases further, the system enters the broad liquid-to-gas transition where neither liquid theory nor gas theory is accurate. We believe that current V-T theory will be a decent approximation to \( T \approx 4T_m \), but that it will require modification to remain highly accurate to such a temperature.

Necessity of the integral formulation, Eq. (2), is shown by estimating the range of \( \epsilon - \mu \) that contributes to the integral. In the approximation that \( n(\epsilon) \) is constant, calculation of \( U_{\text{el}} \) to an accuracy of 2% requires \( \beta|\epsilon - \mu| \) from 0 to 6. The corresponding range of \( |\epsilon - \mu| \) at \( T = 4T_m \) is listed in Table I. We conclude that a significant part of the valence electron DOS contributes to \( U_{\text{el}} \) for liquid metals at high temperatures.

We have listed in Table I our estimates of the ratio \( U_{\text{el}}/U_{\text{expt}} \) to high temperatures, starting from the crystal...
TABLE I. The melt temperature and range of $|\varepsilon - \mu|$ needed for accurate evaluation of $U_{el}$ for each material in this study.

| Quantity | Na | Al | Cu |
|----------|----|----|----|
| $T_m$ (K) | 371.0 | 933.5 | 1358 |
| $|\varepsilon - \mu|$ range at $4T_m$ (eV) | 0 – 0.8 | 0 – 2.0 | 0 – 2.8 |

TABLE II. The relative contributions of the thermal electronic excitation energy to the total energy for NFE and transition metals at two temperatures. (The high-temperature value for transition metals depends on where the Fermi energy lies with respect to the $d$ band; we give an upper bound.)

| Quantity | NFE metals | Transition metals |
|----------|------------|------------------|
| $U_{el}/U_{expt}$ at $T_m$ | $0.014 \pm 0.005$ | $0.13 \pm 0.02$ |
| $U_{el}/U_{expt}$ at $4T_m$ | $0.07$ | $\gtrsim 0.40$ |

and liquid data tables of Ref. 3 for the class of liquid NFE elements and the class of liquid transition metals. They show us that for NFE metals $U_{el}$ is small enough that one can use the free electron DOS for reliable estimates, but for transition metals the liquid DOS is required. At the high temperature of $4T_m$, $U_{el}/U_{expt}$ for NFE metals approaches the level exhibited by transition metals at $T_m$, while $U_{el}$ for transition metals can become a major part of $U_{expt}$.

V. INTERACTION BETWEEN ELECTRONIC EXCITATION AND NUCLEAR MOTION

The term $\delta U_{el}$ in the internal energy, Eq. (11), expresses the interaction between electronic excitation and nuclear motion. In liquid and crystal alike, the formal theory for this term has a nonadiabatic contribution dominant at low temperatures and an adiabatic contribution dominant at high temperatures. Practically, the adiabatic term dominates in the liquid at $T \geq T_m$. We have $\delta U_{el} \propto TU_{el}$ in the crystal, but the $T$-dependence should weaken in the liquid. Our estimate is that the magnitude of $\delta U_{el}$ will surpass that of $U_{el}$ in the range $T_m \leq T \leq 4T_m$. Hence in contrast with crystal theory, both $\delta U_{el}$ and $U_{el}$ will become at least significant, and in some cases important, in the high temperature liquid.

In the absence of a liquid reference structure for $n(\varepsilon)$, Hafner, Kresse, and coworkers25–30 presented the average DOS $\langle n(\varepsilon) \rangle_{MD}$, averaged over nuclear configurations taken from an $ab\ initio$ molecular dynamics (MD) trajectory. This average DOS is temperature-dependent and contains nuclear motion effects, hence is quite different from the liquid structure DOS presented here. Indeed, the two formulations are to a certain extent complementary because $\langle n(\varepsilon) \rangle_{MD}$ contains information on $\delta U_{el}$, the last term in Eq. (11). We shall examine the interrelation of the two formulations and shall present a detailed study of the theory for $U_{el}$ and $\delta U_{el}$ in a forthcoming paper.

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