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Equation of state, phonons, and lattice stability of ultrafast warm dense matter

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Using the two-temperature model for ultrafast matter (UFM), we compare the equation of state, pair-distribution functions g(r), and phonons using the neutral pseudoatom (NPA) model with results from density functional theory (DFT) codes and molecular dynamics (MD) simulations for Al, Li, and Na. The NPA approach uses state-dependent first-principles pseudopotentials from an “all-electron” DFT calculation with finite-T exchange-correlation functional (XCF). It provides pair potentials, structure factors, the “bound” and “free” states, as well as a mean ionization ˇZ unambiguously. These are not easily accessible via DFT+MD calculations which become prohibitive for \( T/T_F \) exceeding \( \sim 0.6 \), where \( T_F \) is the Fermi temperature. Hence, both DFT+MD and NPA methods can be compared up to \( \sim 8 \) eV, while higher \( T \) can be addressed via the NPA. The high-\( T \) phonon calculations raise the question of UFM lattice stability and surface ablation in thin UFM samples. The ablation forces in a UFM slab are used to define an “ablation time” competing with phonon formation times in thin UFM samples. Excellent agreement for all properties is found between NPA and standard DFT codes, even for Li where a strongly nonlocal pseudopotential is used in DFT codes. The need to use pseudopotentials appropriate to the ionization state ˇZ is emphasized. The effect of finite-\( T \) XCF is illustrated via its effect on the pressure and the electron-density distribution at a nucleus.

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1. INTRODUCTION

The equation of state (EOS) of common thermodynamic phases of matter is well understood. However, recent laser and shock-wave experiments have accessed novel ultrafast regimes of density and temperature which are of great theoretical and technological interest. The same physics appears during the injection of hot carriers in field-effect transistors and other nanostructures. Topics such as inertial-confinement fusion [1], Coulomb explosions [2], space reentry shielding, laser machining, and ablation [3] involve such regimes of warm dense matter (WDM). However, elementary approaches cannot be applied since the Coulomb coupling constant \( \Gamma \), i.e., the ratio of the Coulomb energy to the kinetic energy, is larger than unity. The electrons may range from degenerate to Boltzmann type, with \( T/E_F \sim 1 \) or larger, while \( E_F \) is the Fermi energy. This causes a prohibitive increase in basis sets that span the many excited electronic states. WDMs pose a theoretical challenge for rapid accurate computations of properties such as pressure, heat capacity, phonons, and conductance needed even for equilibrium WDMs.

A class of WDMs known as ultrafast matter (UFM) is produced when energy is deposited using an ultrafast pulsed laser on a metal surface [4]. The light couples strongly to the mobile electrons which equilibrate on femtosecond time scales, to a temperature \( T_e \) (as high as many eV) while the much heavier ions and their strongly bound core electrons remain essentially at their initial temperature \( T_i \), i.e., usually the room temperature \( T_r \). This two-temperature WDM (2T-WDM) phase with \( T_e > T_i \) remains valid for time scales \( t \) such that \( \tau_{ee} < t < \tau_{ei} \), where \( \tau_{ee} \), \( \tau_{ei} \), and \( \tau_{ii} \) are the electron-electron, ion-ion, and electron-ion temperature relaxation times, respectively. It has been shown for near-solid densities that \( \tau_{ei} \) is of the order of picoseconds, and orders of magnitude longer than \( \tau_{ee} \) and \( \tau_{ii} \) [5,6]. For WDMs with \( \theta = T/E_F < 0.6 \), small, similar relaxation times hold as seen in calculations for typical systems [7]. Experiments using femtosecond pump-probe techniques [8,9] provide data for quasi-equilibrium analogs of free energy and pressure, transport, and relaxation processes. While many UFM samples do not conform to the \( 2T \) model (e.g., as in Medvadev et al. [10]), the \( 2T \) model provides a great simplification when it holds. Even for UFMs, theory and experiment are quite challenging as the system transits rapidly from a solid to a plasma depending on the pump energy. Hence, a theoretical model that encompasses a wide range of material conditions is needed to describe the time evolving system as a series of static \( 2T \) systems. The “quasi-equilibrium” theory is applied to each static picture of the time evolving system.

In this work, we use the neutral pseudoatom (NPA) model, in the form given by Perrot and Dharma-wardana [11–16], to study the \( 2T \)-WDM regime of a few nominally simple metals, viz., aluminum, lithium, and sodium. These are “simple” at ambient conditions since their valence electrons are “free-electron like” and energetically separated from the core electrons. The number \( \bar{Z} \) of valence electrons per atom (mean ionization) for Al, Li, and Na is 3, 1, and 1, respectively. Furthermore, if the matter density is \( \rho \), each ion can be assigned a spherical volume with the Wigner-Seitz (WS) radius \( r_{WS} = (3/4\pi \rho)^{1/3} \), and it can be shown for Al, Li, Na that the bound-electron core has a radius \( r_c \) such that it is well inside the WS sphere for the temperatures studied here (see Sec. IV D). In such cases, the definition of \( \bar{Z} = N - n_b \), where \( n_b \) is the number of bound electrons in the core, is unambiguous, clear, and is a physically measurable quantity, e.g., using x-ray Thomson scattering [17]. In the case of equilibrium WDM, the NPA calculated \( \bar{Z} \) for Al and Li remains 3 and 1 in the range \( 0 < T_e < 8 \) eV whereas in the case of sodium, \( \bar{Z} \) rises to 1.494 by \( T = 8 \) eV and 1.786 by 10 eV. The case of
Na provides us an example of a typical variation of $\bar{Z}$ very common in equilibrium WDM systems and handled without any ambiguity and with thermodynamic consistency by the NPA approach coupled with determinations of the ion-ion $g(r)$ using the NPA pair potentials. However, in the case of UFM, which is the scope of this work, $\bar{Z}$ is kept unchanged for all three elements through the 0 $< T_e < 8$ eV temperature range.

The NPA model replaces the interacting many-nuclear and many-electron problem by an effective noninteracting single-nuclear and single-electron formulation where the many-body problem is reduced using finite-$T$ density functional theory (DFT) [18,19]. The NPA charge densities are used to construct 2T pseudopotentials and effective ion-ion pair potentials. The method takes into account particle correlations at the pair-density level and beyond using density functional methods via exchange-correlation functionals for electrons, and ion-correlation functionals for ions in a decoupled step which uses a classical integral equation or molecular dynamics. The NPA framework is well adapted to treating metallic systems ranging from solids to liquids or plasmas at very high or low compressions, and from $T = 0$ to several keV. The importance and relevance of the NPA lies in its accuracy, flexibility, and computational rapidity compared to DFT coupled to molecular dynamics (MD) methods (DFT+MD). However, the NPA, as used here, is inapplicable when inner-shell electrons (e.g., $d$ electrons) play a role in the ion-ion interactions (e.g., as in transition metals). A simple metal becomes “complex” when its electronic bound states extend beyond its WS radius $r_{\text{WS}}$. This is not a shortcoming but a strength of the model which determines the ion-ion structure factor $S(k)$ with the simulations of Kietzmann et al. Having confirmed the accuracy of the pseudopotentials and pair potentials, the 2T-thermodynamic properties, such as the quasipressure, are also presented. These are compared with the values for systems in thermal equilibrium. Discussions about phonon formation times in 2T systems, the role of finite-$T$ XC contributions in the 2T-EOS calculation, and the choice of suitable pseudopotentials in ab initio finite-$T$ simulations are also presented.

II. NEUTRAL PSEUDATOM MODEL

A. General description of the model

Several average-atom models and NPA models have been proposed, even in the early literature [31]. Many of these are intuitive cell models and are not true DFT models. A rigorous DFT formulation of a NPA model at $T = 0$ was first used for solids by Dagens [11,12]. There, the treatment of the ion distribution was developed in the traditional manner as providing a fixed external potential; Dagens showed that the NPA results at $T = 0$ agree closely with the band-structure codes available at the time. A finite-$T$ version was given in several papers by Perrot [13] and Dharma-wardana [27,32,33]. In Ref. [32], the ion distribution $\rho(r)$ itself was treated within DFT using the property that the free energy $F[n,\rho]$ is a functional of both $n(r)$ and $\rho(r)$ simultaneously. A classical DFT equation for the ions and an ion-correlation functional $F_{\text{ion}}(\rho)$, approximated as a sum of hypernetted-chain (HNC) diagrams plus bridge diagrams, was introduced, without invoking a Born-Oppenheimer approximation or treating the ions as providing a fixed external potential [34]. Exchange-correlation functionals $F_{\text{xc}}(\rho)$ for electron-ion interactions were also introduced although negligible in common materials. This puts the NPA approach on a very rigorous DFT footing where approximations enter in modeling the ion-correlation functional, just as in the case of the electron DFT problem for the electronic XCF.

However, in the following, we present the theory in terms of the more familiar superposition picture. We consider a system...
of ions located at sites \( \mathbf{R}_i \), at temperature \( T_e \), and average density \( \rho \), interacting with a system of electrons at temperature \( T_e \) and average density \( n \). The multicenter problem is reduced to a simplified single-center problem where the total electron density \( n(r) \) is regarded as the superposition of single-site densities such that \( n(r) = \sum n_i(r - \mathbf{R}_i) \). In contrast to ion-sphere (IS) models like those used in Purgatorius [35], or Piron and Blenski [36], Starrett and Saumon [37], the single-site free-electron density \( n_f(r) \) extends over the whole of space, approximated by a correlation sphere [32] of radius \( R_s \) which is of the order of 10 ionic Wigner-Seitz radii. All particle correlations are assumed to have died out when \( r \to R_s \). This \( R_s \) is similar to the linear dimension of the simulation box of a DFT+MD simulation which has to be as big as possible. However, in practice the charge distribution used in DFT+MD simulations spreads over a volume of about 100 ions. In contrast, the NPA correlation sphere with \( R_s \approx 10 R_{WS} \) extends over \([R_s/R_{WS}]^3\), i.e., the volume covered by \( \sim 1000 \) ions. The calculation of course uses only one nucleus, but its charge density overlaps the space of some 1000 atoms, and this is crucial to getting the right pair potentials with long-range Friedel oscillations, and to satisfy the Friedel sum rule [32]. The IS models cannot satisfy the Friedel sum rule. At higher temperatures where particle correlations are weak, \( r_s \) may be reduced to, e.g., \( 5 R_{WS} \), but the results are independent of \( R_s \), and \( R_s \) is not an optimization parameter.

The ion distribution \( \rho(r) = \rho g(r) \) contains the full ion PDF, \( g(r) \), when seen from any site taken as the origin. It is found that in most cases it is sufficient, as far as the bound-electron structure is concerned, to approximate \( g(r) \) by a spherical cavity \( c(r) \) of radius \( r_{WS} \) and total charge \( Z \) centered on the ion, followed by a uniform positive density \( \rho \) for \( r > r_{WS} \). As mentioned below, unlike in IS models, its effect will be subtracted out (as a “cavity correction”) to obtain the response of a uniform electron gas to the nucleus. Thus, we have

\[
 c(r) = n[H(0) - H(r - r_{WS})],
\]

where \( H(r) \) is the Heaviside step function. Initially \( Z \) is unknown but its value is obtained self-consistently from the iterative Kohn-Sham procedure. The single-site electron density is written as \( n_i = \Delta n_i + m_i \) where \( m_i \) is the cavity correction and \( \Delta n_i \) is the electron pileup obtained by the DFT calculation for the electrons in the external potential \( V_{ext} \) given by

\[
 V_{ext}(r) = \frac{Z}{r} + \frac{1}{|r - \mathbf{r}|} \star c(\mathbf{r}),
\]

where the symbol \( \star \) means integration over all space. Here, \( Z = Z_o \) is the nuclear charge. The positive background with the WS cavity, the nucleus at its center, and the free-electron charge density filling the whole correlation sphere constitute the neutral pseudopotam [27,33]. The WDM system is made up of superpositions of such neutral pseudopotam correlated to give the ion-ion \( g(r) \), with the cavity contributions subtracted out.

For simple metallic systems, this cavity model that defines the extent of the bound states is sufficient to produce physically accurate results and is mathematically convenient, as shown in the papers by Dagens or those of Perrot and Dharma-wardana cited above. Thus, to compute the cavity correction \( m(q) \), we assume that the electrons respond linearly to the cavity \( c(r) \), viz., in Fourier space,

\[
 m(q) = -V(q)c(q)\chi_{ee}(q, n, T_e).
\]

Here, \( V(q) = 4\pi/q^2 \) is the Coulomb potential and \( \chi_{ee} \) is the interacting-electron response function at the electron density \( n \) and temperature \( T_e \). To go beyond the random phase approximation (RPA), we use the following finite-\( T \) response function:

\[
 \chi_{ee}(q, n, T_e) = \frac{\chi(0, n, T_e)}{1 - \frac{q^2}{q^2_{TF}} \chi(0, n, T_e)}
\]

with \( \chi_0 \) the finite-\( T \) Lindhard function and \( G(q) = G(q, T_e) \) a local-field correction (LFC) defined as

\[
 G(q) = \left( 1 - \frac{\gamma_0}{\gamma} \right) \left( \frac{q}{q_{TF}} \right)^2.
\]

In the above, the Thomas-Fermi wave vector \( k_{TF} = \sqrt{6\pi n/\alpha E_F} \) is defined by the Fermi energy of the system \( E_F = 1/(\alpha r_s) \) where \( r_s \) is the electron WS radius and \( \alpha = (4/9\pi n)^{1/3} \). The finite-\( T \) interacting electron compressibility \( 1/\gamma = n^2/\alpha^2 [n f(r_s, T_e)]/\partial n^2 \) is determined from the homogeneous electron gas free energy per electron \( f(r_s, T_e) \), as given in Eq. (13), which include a finite-\( T \) XC interaction \( f_{XC} \).

The noninteracting electron compressibility \( \gamma_0 \) is obtained by setting \( f_{XC} = 0 \).

The simplicity of the NPA model rests on decomposing the total charge distribution into a superposition of single-center distributions. If the ion-ion structure factor \( S_{11}(q) \) is known, any total electron charge distribution \( n_i(q) \) can always be written as a convolution of the \( S_{11}(q) \) with some effective single-center charge distribution \( n(q) \), even for transition metals or systems with resonant levels; but, partitioning the electron contributions from states that extend beyond their WS cells without correctly including the physical interactions is not sufficient. Furthermore, a “simple metal” at one temperature may behave as a “transition metal” at another temperature when a shell of electrons begins to transit to the continuum, and vice versa. If the system is of such low density that \( r_{WS} \) is larger than the bond length of a possible dimer (e.g., Li\(_2\)), then the dimer itself will be contained within the WS sphere, and in such cases the NPA model fails; a more elaborate “neutral-pseudomolecule” approach or the use of suitable electron-ion XC potentials \( F_{XC}^e(n, \rho) \) is then needed.

We do not examine such nonsimple WDMs in this study. Similarly, at high densities, WDM-Li shows complex phases [4], and the simple NPA model needs modifications. In the present case, a single-center decomposition is physically transparent if the bound-electron core is unambiguously confined within the WS sphere of the ion. We discuss in the results section (Sec. IV D) the variation of the \( Z \) of Na which changes from unity at low \( T \) to 1.49 by \( T = 8 \) eV. The occupation number in the 2\( p \) level begins to decrease, while its radius slightly decreases, and hence there is no ambiguity in estimating \( Z = Z - n_f \), where \( n_f \) are all the bound electrons compactly contained well inside the WS sphere. That is, the electron density pileup \( \Delta n_i \) can be clearly divided into bound and free parts such that \( \Delta n_i = n_b + n_f \).
Once this division is achieved, the interaction of an electron with the nucleus plus its core can in most cases be replaced by a pseudopotential \( U_{el} \) which is a weak scatterer because it is constructed using linear response; this is given by

\[
U_{el}(q) = n_f(q)/\chi_{ee}(q,x,T_e),
\]

where \( \chi_{ee} \) is provided by Eq. (4).

Even though linear response is used, the resulting pseudopotential includes nonlinear effects since \( n_f(q) \) is the fully nonlinear free-electron density obtained from DFT. Only a range of \( q \) between zero to slightly above \( 2k_F \) (depending on \( T_e \)) needs to be included as the large-\( q \) behavior (short range in \( r \), i.e., inside the core) is not relevant. The resulting pseudopotential is valid only if it satisfies the relation \( U_{el}/(-ZV(q)) \leq 1 \). Unlike the pseudopotentials used in VASP, ABINIT, and similar DFT codes, this linear-response pseudopotential does not require solving a Schrödinger equation. It is a state-dependent local pseudopotential that can be fitted to, say a Heine-Abaranov form for convenience (see Shaw and Harrison [39]). This has a constant core potential \( V_{\text{HIA}} = D \) for \( r < r_c \) and it is Coulomb type, \( V_{\text{HIA}} = -Z/r \) for \( r > r_c \). However, such a fitting is not needed except to conveniently report the pseudopotential and to quantify the core radius associated with the potential. In our NPA calculations we use the numerical form of \( U_{el}(q) \) directly.

The pseudopotential calculated at \( T_e \) can be used to form a 27 ion-ion pair potential (27PP) with ions at \( T_e \) and electrons at \( T_e \) since it is a sum of the direct Coulomb interaction and the indirect interaction via the displaced-electron charge, viz.,

\[
U_{ii}(q,T,T_e) = -\bar{Z}^2(T) V(q) + |U_{el}(q)|^2 \chi_{ee}(q,T_e).
\]

This procedure is valid because \( \bar{Z} \) remains unchanged in UFM since the bound core of electrons remains at the initial ion temperature for times \( t < t_d \). If \( T_e \) is large enough to change \( \bar{Z} \), be it for UFM or equilibrium systems, then the pseudopotential has to be recalculated using an NPA calculation at the needed temperature.

At low \( T_e \), the Friedel oscillations in the electron density resulting from the sharp discontinuity at \( k = 2k_F \) in \( \chi_{ee}(q) \) produce oscillations in the pair potential \( U_{ii}(q) \). These lead to multiple minima in the ion-ion energy which contribute to the maxima in \( g(r) \). Such physically important features are not found in “Slater-sum” approaches [40] to finite-\( T \) potentials, in “Yukawa-screening” models [7, 41], or in Gordon-Kim models [42]. Furthermore, the charge densities restricted to the WS sphere used in IS models cannot capture such long-range effects. Our NPA pair potential can be used to study phonons in the system or to generate the ion-ion \( g_{ii}(r) \) and corresponding structure factor \( S_{ii}(k) \) when necessary. The ion subsystem in a UFM is clamped at \( T_e \sim 300 \text{K} \) when Al, Li, and Na are crystalline metals. Hence, the ion-ion pair distribution function is simply given by the relation

\[
g_{ii}(r) = \frac{1}{4\pi \rho} \sum_{|i|} \delta(r - R_i).
\]

The summation is over the crystal lattice, permitting a simple computation of the ion contribution to the quasi-free energy and pressure from the 27 pair potential.

### B. NPA quasithermodynamic relations

The total free energy \( F \) of the 27 system given by the NPA is

\[
F = F_{\text{emb}} + F_{\text{cav}} + F_{\text{heg}} + F_{\text{ion}},
\]

where \( F_{\text{heg}}, F_{\text{emb}}, F_{\text{cav}}, \) and \( F_{\text{ion}} \) are, respectively, the free-energy contribution of the interacting homogeneous electron gas (HEG), the embedding free energy of the NPA into the electron gas, the correction from the cavity, and the ion-ion free energy. The only parameters of this model are the nuclear charge \( Z \), electron temperature \( T_e \), and the HEG density \( n \) such that the average ion density \( \rho = n/Z \), itself determined by the ion temperature \( T_e \). We discuss these four terms below, using Hartree with \( \hbar = m_{e}v = |e| = 1 \).

(i) The embedding energy \( F_{\text{emb}} \) is the difference between the free energy of the electron gas containing the central ion and the unperturbed HEG; thus,

\[
F_{\text{emb}} = T[n + \Delta n(r)] - T[n] - \int \frac{Z}{|r|} \cdot [\Delta n(r) + c(r)] dr + \frac{1}{2} \int \frac{|\Delta n(r) + c(r)|}{|r - r'|} \cdot |\Delta n'(r') + c'(r')| dr dr',
\]

with \( T[n] \) the electron kinetic energy.

(ii) The cavity correction \( F_{\text{cav}} \) is computed from the total screened Coulomb potential \( V(r) \) resulting from the total electron displacement \( \Delta n(r) \):

\[
V_{\text{cav}}(r) = \int \frac{[c'(r') + \Delta n(r') - \bar{Z}\delta(r' - R_e)]}{|r - r'|} dr'.
\]

Since each cavity involves a charge deficit \( \eta(r) = n - c(r) \), the cavity correction is

\[
F_{\text{cav}} = -\frac{1}{2} \int \frac{\eta(r) \cdot [c'(r') - m'(r')]}{|r - r'|} dr dr' + \int \eta(r) \cdot V_{\text{cav}}(r) dr.
\]

(iii) The free energy of the HEG \( F_{\text{heg}} \) is written as

\[
F_{\text{heg}} = \bar{Z} f_{\text{heg}}(n,T_e) = \bar{Z} [f_{0}(n,T_e) + f_{\text{sc}}(n,T_e)],
\]

where \( f_{0} \) and \( f_{\text{sc}} \) are, respectively, the noninteracting and exchange-correlation free energies per electron at the density \( n \) and temperature \( T_e \). To compute \( f_{0} \), we use the thermodynamic relation \( f_{0} = \Omega_{0}/nV + \mu_{0} \), where \( \Omega_{0} \) and \( \mu_{0} \) are the noninteracting grand potential and the chemical potential, respectively.

We emphasize that the NPA correlation-sphere model uses the noninteracting \( \mu_{0} \) associated with the mean electron density \( n \) as required by DFT theory. In IS models, the known matter density defines the Wigner-Seitz cell, and the free electrons are confined in it, and the corresponding \( \mu \) is determined by an integration within the WS sphere [e.g., see Eq. (1) of Faussurier [43], leading to a value of \( \mu \neq \mu_{0} \). In contrast, the mean electron density \( n \), the nuclear charge \( Z_n \), and the temperature \( T \) are the only inputs to the NPA code. The computation outputs the corresponding mean ion density \( \rho \) and \( \bar{Z} = n/\rho \). A series of calculations are done in a range of \( n \) and the specific \( n \) which gives the physical ion density, viz.,
The explicit electron-density dependence of the ion-ion pair potential is given by the virial equation

\[ P = n^2 \frac{\partial}{\partial n} (F_{\text{heg}} + F_{\text{emb}} + F_{\text{cav}}) - \int g_{ii}(r) \left( \frac{3}{r} \frac{\partial}{\partial r} - n^2 \frac{\partial}{\partial n} \right) U_{ij}(r) d\mathbf{r}. \]  

The explicit electron-density dependence of the ion-ion pair potential is taken into account in computing the pressure [44]. Analytical results can be obtained for the terms

\[ P_{\text{emb}} = - \int \eta(r) \cdot V^*(r) d\mathbf{r}, \]  

\[ P_{\text{cav}} = - \tilde{Z} V^*(r_{\text{WS}}), \]

whereas other derivatives have to be done numerically.

### III. RESULTS

We used the NPA model to determine the properties of 2T-WDM as produced by femtosecond laser pulses interacting with three common metals in their usual solid state, viz., aluminum, lithium, and sodium, with electron densities such that \( r_s \) is 2.07, 3.25, and 3.93 a.u., corresponding to \( \tilde{Z} = 3, 1, \) and 1, respectively. Note that the \( \tilde{Z} \) for Na deviates from unity for \( T > 3 \text{ eV} \). The ion density is kept constant in the calculations for isochoric sodium. We present the 2T ion-ion pair potentials, nonequilibrium phonon dispersion curves, and pressures for varying \( T_e \), while the ions remain cold at \( T_i = 0.026 \text{ eV} \) (300 K).

#### A. Ion-ion pair potentials

The first step within our UFM model is to compute the equilibrium (at room temperature, \( T_e = T_i = 0.026 \text{ eV} \)) free-electron density \( n_f(q) \) from the NPA calculation. The pseudopotential \( U_{f}(q, T_e) \) at \( T_e = T_i \) can then be obtained using Eq. (6). This pseudopotential is an atomic property that depends on \( \tilde{Z} \) and on the core radius given the ionic \( r_{ws} \), which is then used to construct ion-ion pair potentials \( U_{ij}(q, T_e) \) at any \( T_e \) via Eq. (7). For this, the electron response at \( T_e \neq T_i \) is used. This method is simpler and numerically almost indistinguishable from calculating the pseudopotential from a full 2T-NPA procedure where the core electrons are held frozen at \( T_i \) and \( n_f(q, T_e) \) is calculated from the Kohn-Sham equation, with \( \tilde{Z} \) remaining unchanged. The agreement between the two different ways of calculating the 2T potentials provides a strong check on our calculations. Furthermore, while pair potentials cannot be easily extracted from \textit{ab initio} calculations, the NPA model provides this physically important quantity.

Examples of NPA ion-ion pair potentials at different temperatures are presented in Fig. 1. At equilibrium or sufficiently low \( T_e \), all three pair potentials display Friedel oscillations as discussed in Sec. II. Hence, it requires many neighbor shells to compute the total pairwise ion-ion interaction energy with sufficient precision. For Li and Na, we used 8 shells whereas 30 shells were necessary for the Al-Al interaction. As \( T_e \) increases, the sharp Fermi surface breaks down, the discontinuity in \( f(k) \) at \( k = k_F \) broadens, and oscillations disappear, yielding purely repulsive Yukawa-screened potentials [41].

#### B. 2T quasiequilibrium phonon spectra

As the electrons get heated, the screening weakens and interionic forces become stronger; hence, there is an interest

![FIG. 1. Two-temperature ion-ion pair potentials for electrons at three different temperatures and ions at \( T_i = 0.026 \text{ eV} \) (300 K), for (a) Al, (b) Li, and (c) Na.](image)
in computing the phonon spectra although in many cases the phonon oscillation times may be comparable to the lifetime of the UFM system. Once the 2TPP is constructed for the desired \( T_e \), the phonon spectra are easily calculated by the diagonalization of the dynamical matrix \[ D(k) = \sum_i D(R_i) e^{-i k R_i}, \] (20) where the elements of the harmonic matrix \( D(R) \) are given by \[ D_{\mu\nu}(R) = \frac{1}{2} \sum_j \frac{\partial^2 U_{\mu\nu}(R_j)}{\partial u_{\mu}(R) \partial u_{\nu}(0)} \] (21) with \( R_j \) the position of the \( j \)th atom and \( U_{\mu\nu} \) the pair potential of Eq. (7). From the \( s \) eigenvalues \( \lambda_s(k) \) of \( D(k) \), the phonon frequencies are given by \( \omega_s(k) = \sqrt{\lambda_s(k) / M} \) with \( M \) the mass of the ion. The resulting phonons are compared with the results from \textsc{abinit}-DFT simulations employing density functional perturbation theory \[46,47\] (DFPT), which determines the second derivative of the energy using the first-order perturbation wave functions. We used the common crystal structure for each metal, i.e., face-centered cubic (fcc) for Al and body-centered cubic (bcc) for Li and Na, with their room temperature lattice parameters \( a = 4.05, 3.49, \) and \( 4.23 \) Å, respectively.

Quasiequilibrium phonon dispersion relations at \( T_e = 6 \) eV using the two methods are presented in Fig. 2 with the NPA equilibrium phonons as reference to illustrate important modifications in the spectra. In addition, the NPA quasiequilibrium phonon spectrum at \( T_e = 12 \) eV are also presented; at this temperature DFPT becomes prohibitive. The excellent accord between the NPA and experimental equilibrium phonon spectra at low temperatures has already been demonstrated and shows the meV accuracy of the NPA calculations even at low temperatures \[48\]. It is not possible to get good accord with experiment in this regime if the free electron density is constrained to be within the Wigner-Seitz sphere, as found by Blenski \textit{et al.} \[49\] within their ion-sphere model for Al at normal density and at low \( T \).

For the three systems in this study, the two methods (NPA and DFPT) predict very similar 2\( T \) phonon spectra, thus reconfirming the 2\( T \) NPA calculations and corroborating the DFPT calculations at finite \( T \). This is important as there are as yet no experimental observations of UFM phonon spectra. In the case of Al, we observe a large increase in frequencies, as high as 32\% for longitudinal (L) modes, which supports the "phonon hardening" theory. However, we notice that transverse (T) branches in the \( \Gamma - L \) region are barely affected by the electron heating, as was also noted by Recoulès \[50\]. In the case of Li and Na, we find that the spectral modifications are more complex than the "homogeneous" increase found for Al; here, we find an important increase in the L branch in the middle of the \( \Gamma - H \) region takes place, whereas there is no change at the symmetry point \( H \). No modifications to T branches are noticed in this region. In the region \( H - \Gamma \), the L-branch frequencies increase in the middle of the region \( H - P \) but remain unchanged at the symmetry point \( H \). For the T branch, an increase is noticeable at the maximum in the region \( P - \Gamma \) whereas no change affects the minimum in the region \( H - P \). In the region \( \Gamma - N \) and for the L branch, we observe the overall largest increase of 29\% and 37\% for Li and Na, respectively, whereas frequencies of T modes are only slightly modified.

C. 2\( T \) quasiequilibrium equation of state

A system in its initial equilibrium configuration \((T_f = T_e)\) rapidly reaches a new UFM state with \( T_f \) remaining near \( T_e \) while \( T_e \) increases. However, since the ion motion within the time of arrival of the probe pulse is negligible, the pressure builds up essentially isochorically due to electron heating.

In Fig. 3, we compare the pressure calculated with the NPA model with \textsc{abinit} and \textsc{vasp} simulations. In the latter, we used an energy cutoff of 1630 eV for the plane-wave basis, with 60 energy bands to capture finite-\( T \) effects. In \textsc{abinit} simulations, we used norm-conserving (NC) pseudopotentials with the
and heat up to $T$ very high as discussed in Sec. IV D. Intensive computations with DFT calculations to generate accurate results which require long few minutes on a desktop computer are sufficient in NP A pair potentials, and structure factors are readily obtained. As the system evolves with time since mean ionization, properties, opacities, energy-relaxation times, etc., are needed breaks down. However, in all other cases, the pressure goes needed for such lattice motion is available before the UFM simulations do not, the effect of such finite-\(T\) corrections will be reviewed in Sec. IV D.

We find that, for all three metals, calculations using NPA, ABINIT, and VASP predict nearly identical pressures with small deviations only at high \(T_e\). At \(T_e = 8\) eV, the maximum difference between all models is 9, 4, and 3 GPa for Al, Li, and Na, respectively. Thus, the results from the extension of the NPA model to the \(2T\) regime confirms the usability of the solid-state codes at least up to 6 eV on the one hand, and on the other hand the validity of the NPA approach. However, since NPA uses a finite-\(T\) XC functional whereas \textit{ab initio} simulations do not, the effect of such finite-\(T\) corrections will be reviewed in Sec. IV.

The computational efficiency and accuracy of the NPA approach make it a valuable tool for studying WDM and other complex systems where iterative computations of materials properties such as 2\(T\) EOS, 2\(T\) specific heat, transport properties, opacities, energy-relaxation times, etc., are needed as the system evolves with time since mean ionization, pair potentials, and structure factors are readily obtained. A few minutes on a desktop computer are sufficient in NPA calculations to generate accurate results which require long and intensive computations with DFT+MD.

**IV. DISCUSSION**

**A. Crystal-lattice stability**

As electrons absorb the laser energy (within fs time scales) and heat up to \(T_e\), the internal pressure of the system becomes very high as discussed in Sec. III C. In metals, the thermal expansion is also caused by the free-electron pressure. We studied the crystal stability of the solids as a function of lattice expansion; the results are presented in Fig. 4.

For Al at \(T_e = 2\) eV, we find that a moderate expansion \(a/a_0 = 1.24\) is sufficient to reduce the pressure back to zero, indicating that the crystal may appear stable if the time scale needed for such lattice motion is available before the UFM breaks down. However, in all other cases, the pressure goes to zero only asymptotically with increasing lattice parameter, suggesting that such UFM crystals are unstable. Such thermal expansions or spontaneous fluctuations lead to the “explosive” breakdown of the solid on ps time scales. However, since UFM conditions are reached in fs time scales, the ions remain essentially in their initial positions and (as already noted) no net linear forces act upon them due to crystal symmetry. They remain trapped in a stronger harmonic potential leading to hardening of most of the phonon branches. The physical reason for the hardening at increased \(T_e\) is the decreased screening of ion-ion interactions by the hotter electron gas.

**B. “Phonons” and surface ablation**

The UFM system is under very large pressure and the ion-ion 2\(T\)PP is purely repulsive unless \(T_e\) is small (cf. Fig. 1). The discussion in terms of phonons may become inapplicable at higher \(T_e\) due to nonzero ablation forces acting on ions in typical UFM samples (0.1–1 \(\mu\)m thick). An ideal periodic lattice implies that the linear derivative of the total potential is zero because the crystal is isochorically constrained by the external pressure. The phonons of UFM “exist” only within this artifice. Small thermal “Debye-Waller”–type ionic displacements \(u\) (with a mean value \(\langle u\rangle = 0.2\) Å) at 300 K for Al, retained in the UFM do not render the periodic

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**FIG. 3.** Quasiequilibrium pressures obtained with the NPA (lines), ABINIT (circles), and VASP (triangles) for Al, Li, and Na.

**FIG. 4.** Total pressure of the solids as a function of the lattice parameter of the crystal relative to the room-temperature value \(a_0\) for (a) Al, (b) Li, and (c) Na.
TABLE I. The “ablation force” $F_{abl}$ and the “ablation time” $\tau_{abl}$ for the (100) surface of an Al slab from \textsc{vasp} and \textsc{npa} at three different electron temperatures $T_e$ and lattice temperature $T_l = 0.026$ eV. The fastest [100] phonon oscillation time $\tau_{io}$ is also given for each $T_e$.

\begin{tabular}{|c|c|c|c|c|c|}
\hline
$T_e$ (eV) & $F_{abl}^{\text{npa}}$ (eV/Å) & $F_{abl}^{\text{vasp}}$ (eV/Å) & $\tau_{abl}^{\text{npa}}$ (fs) & $\tau_{abl}^{\text{vasp}}$ (fs) & $\tau_{io}$ (fs) \\
\hline
2.00 & 0.91 & 0.90 & 111 & 111 & 105 \\
4.00 & 2.75 & 2.70 & 63.9 & 64.2 & 92.6 \\
6.00 & 5.03 & 4.70 & 47.1 & 48.6 & 80.6 \\
\hline
\end{tabular}

However, pump-probe experiments use very thin metal films. Crystal symmetry is broken and large uncompensated forces act at the surface of the films; as a result, the surface layer and successive layers ablate. We calculated the ablation force $F_{abl}^{\text{npa}}$ on an fcc-(100) Al surface and the two inner layers using the \textsc{vasp} code with the Al surface reconstructed as happens for the cold surface at 0 K. Five layers of Al and five layers of vacuum were used for evaluating the Hellmann-Feynman forces on the surface atoms. The \textsc{npa} model is beyond its regime of validity since the charge density at a surface is not uniform. However, the \textsc{npa} pressure is the force per unit area at the bounding (100) surface, with one ion per unit area. This is used as the \textsc{npa} estimate of the ablation force $F_{abl}^{\text{npa}}$. The forces on the inner neighbor and next-neighbor layers calculated from \textsc{vasp} at $T_e = 6$ eV were 3% and 0.02%, respectively, of the force on the surface layer. The surface force $F_{abl}$ determines an approximate “ablation time” $\tau_{abl}$, the time needed for the surface plane to move by an interplane distance ($a/2$ in the case of Al). This $\tau_{abl}$ estimate makes some assumptions, e.g., $F_{abl}$ to be constant over $a/2$, with no movement of inner layers. To verify if phonons can form within such time scales, we compare $\tau_{abl}$ with the shortest time for an ion oscillation $\tau_{io}$ at the highest phonon frequency for the [100] direction; the results are presented in Table I.

As $T_e$ increases, phonons “harden” and $F_{abl}$ increases. In order to observe the “hardening” of phonons on any measurement, a probe time $t_{pr}$ such that $\tau_{io} < t_{pr} < \tau_{abl}$ is required. However, for sufficiently high $T_e$ (e.g., above $\sim 2$ eV for Al), the $F_{abl}$ are strong enough to make $\tau_{abl} < \tau_{io}$. Hence, the ion oscillations have no time to build up and it is probably impossible to satisfy the time constraint enabling the observation of hardened phonons. The phonon concept itself becomes misleading for thin UFM films. Interpreting experiments when $t_{pr} > \tau_{abl}$ may require explicit inclusion of surface ablation corrections in the theory used for analyzing optical data (e.g., in the Helmholtz equations).

C. Finite-$T$ exchange and correlation

In the \textsc{npa} model, we used the finite-$T$ \textsc{xcf} of \textsc{pdw} and assessed the importance of such corrections in the temperature regime studied here. The valence density, or “free” -electron density $n_f(r)$, of the solid at $T_e > T_l$ is the key quantity for the \textsc{npa} model. In Fig. 5, we present the $n_f(r)$ obtained using the \textsc{pdw} finite-$T$ \textsc{xcf} with that obtained from the zero-$T$ \textsc{xcf}. Even though the correction is small, it may be of importance in some circumstances, e.g., x-ray Thomson scattering spectra, and hence there is no reason to neglect it. The difference between the $T = 0$ XCF and the finite-$T$ XCF increases with $\theta = T/E_F$ at first, and it rapidly and asymptotically goes to zero as $\theta > 1$ and as $T \to \infty$. Hence, the more important consequences of using finite-$T$ XCF should occur in the partially degenerate regime $0 < \theta < 1$.

The finite-$T$ XCF is present in two contributions to the pressure, namely, the electron-electron interacting linear response function $\chi(k,T_e)$, which is used to construct the pseudopotential and the pair potential, and the HEG electron kinetic pressure. Although the finite-$T$ XCF has noticeable effects on the pair potentials or on the energy spectrum of bound states, we observe that overall thermodynamic effects are only slightly sensitive to such finite-$T$ corrections as can be seen in Fig. 6. In fact, at $T_e = 8$ eV, the finite-$T$ XCF only decreases the pressure in Al by 4%. Since individual finite-$T$ contributions are considerable, this insensitivity to XCF comes from the interplay of several terms. For instance, the electron pressure by itself differs by about 10% in the regime $\theta \sim 0.8$, of importance in some circumstances, e.g., x-ray Thomson scattering spectra, and hence there is no reason to neglect it. The difference between the $T = 0$ XCF and the finite-$T$ XCF increases with $\theta = T/E_F$ at first, and it rapidly and asymptotically goes to zero as $\theta > 1$ and as $T \to \infty$. Hence, the more important consequences of using finite-$T$ XCF should occur in the partially degenerate regime $0 < \theta < 1$.

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but the overall pressures obtained from \( T = 0 \) and finite-\( T \) NPA calculations differ by less than 4%.

### D. Pseudopotential and mean ionization

Here, we discuss the importance of choosing the proper pseudopotential for \textit{ab initio} simulations of UFM systems in the 2\( T \) model. The pump-laser frequency is normally chosen such that core electrons are not excited and remain strongly bound to the “cold” nuclei at temperature \( T_e \). Thus, only the \( Z \) valence electrons on each ion are heated to \( T_e \) during the irradiation. In DFT calculations, the electron temperature is used in a Fermi-Dirac distribution for the occupation numbers of all electrons in the simulation. Thus, if the chosen pseudopotential includes more of the core electrons as free electrons, i.e., exceeding the appropriate number of valence electrons, then they too will be “heated” even if they should not be. Then, wrong predictions may result, e.g., for the 2\( T \) pressure of the given UFM and its electronic specific heat.

To illustrate this point, we carried out \textsc{ABINIT} simulations using PAW pseudopotentials which include \( Z = 3 \) and 9 valence electrons for Li and Na, respectively. We also did NPA-DFT calculations with \textit{all} electrons at \( T_e \). In the NPA model, the mean ionization \( Z = Z_{\text{a}} - n_0 \) can be computed as in Ref. [27]. The \( Z \) as a function of \( T_e \) is not an integer in the NPA but represents an average over different ionization states as discussed in Ref. [14].

In the case of Al and Li, the NPA predicts that \( Z \) is unaffected for \( T_e < 8 \) eV, relevant to UFMs. Pressure should also be unchanged, which is exactly what we obtain with the \textsc{ABINIT} simulations of Li using the all-electron PAW pseudopotential. However, in the case of Na, \( Z \) starts to increase around \( T_e = 3 \) eV up to \( Z = 1.49 \) at \( T_e = 8 \) eV (see Table II). The increase in \( Z \) is accompanied by a decrease in the occupation of the 2\( p \) level as electrons are promoted to the continuum. The decreased screening in the core (both due to increase of \( T \) and due to the decrease in the number of core electrons) leads to a decrease in the radius of the \( n = 2 \) shell. Hence, the increase of \( Z \) and the modification of the core levels do not lead to any ambiguity in specifying \( Z \).

We computed the pressure with the NPA model including the changed \( Z \) and compared it with the \textsc{ABINIT} simulations of Na using the nine-electron PAW pseudopotential. Results are presented in Fig. 7.

We find that, at \( T_e = 8 \) eV, the pressure, when heating of some core electrons is included, is 54\% higher than the correctly calculated value. The use of “all-electron” codes for the study of UFM in the 2\( T \) state suffers from this pitfall of not selecting the physically appropriate \( Z \) and the corresponding pseudopotential. When suitable pseudopotentials are not available for DFT+MD calculations, one possibility is to use only the relevant part of the electron density of states (DOS) that is assigned to the free electrons on the basis of \( Z \), when pressure and related properties are computed. For instance, when calculating the specific heat of “free electrons” for use in UFM studies, the free-electron DOS used in the calculations should be consistent with the number of actual free electrons that couple with the laser. In a metal such as gold (not studied here), even though a pseudopotential with 11 valence electrons is needed, the DOS used for evaluating the electron specific heat for \( T_e < 2 \) should be only for \( Z = 1 \). The optical properties of gold (see Ref. [51]) show that the \( d \) shell couples to light only when the interband threshold energy (\( \sim 2 \) eV) is exceeded. In the case of gold, the \( 5d \) shell hybridizes with the continuum electrons (nominally made up of 6\( s \) electrons) and extends outside the Au-Wigner-Seitz sphere until the \( s - d \) transition threshold (\( \sim 2 \) eV) is reached. Hence, at low temperatures the NPA model with its “one-center” formulation cannot be used for gold at normal density. Similarly, WDM systems with bound states extending outside the Wigner-Seitz sphere cannot be treated unless explicit multicenter electron-ion correlation terms are included.

### E. Local pseudopotential for Li

The Li pseudopotential used in the NPA is a \textit{local} pseudopotential, whereas it is widely found in the context of large DFT codes that Li almost always needs a nonlocal pseudopotential. Even in early studies of phonons, a nonlocal pseudopotential was used by Dagens, Rasolt, and Taylor [52], and yet the Li phonons at room temperature they obtained were less satisfactory than for, say, sodium. We have already shown that the NPA pair potential based on a local pseudopotential quite adequately reproduces the Li phonons at room temperature and high temperature at normal density, but not as accurately as for aluminum or sodium. Hence, it is of interest to test the robustness of the Li pseudopotential and pair potential at higher compression by calculating the Li-Li \( g(r) \) using the NPA potentials. Here, we use the modified hypernetted chain...
(MHNC) method where a bridge term is included using the Lado-Foiles-Ashcroft (LFA) criterion \[53\] which is based on the Gibbs-Bogoliubov inequality for the free energy of the system. The MHNC assumes radial symmetry and limits us to “simple-liquid” structures.

Since Li becomes a complex liquid with clustering effects at high compressions \[38\], we consider a compression of \(\sim 1.6\) and compute the PDF for Li at 0.85 g/cm\(^2\) and at 2000 K (0.173 eV) for which results are available from Kietzmann et al. \[54\]. The LFA criterion yields a hard-sphere packing fraction \(\eta = 0.371\) to model the bridge function. The resulting NPA-MHNC \(g(r)\) is displayed together with the \(g(r)\) of Ref. \[54\] in Fig. 8. We find that the simple but state-dependent local pseudopotential constructed from the free-electron charge pileup at a Li nucleus is adequate to calculate phonons (i.e., requiring an accuracy of meV energies), as well as the Li-Li PDFs up to moderate compressions and high coupling constants \(\Gamma\).

**F. Comparison between equilibrium WDM and UFM EOS**

In UFM, the internal pressure mainly results from the hot electron subsystem since ions remain close to their initial temperature \(T_i\). Here, we investigate the difference in the pressure between the quasiequilibrium UFM regime \((T_i \neq T_e)\) and the equilibrium WDM regime which will usually be in a liquid or plasma state with \(T_i = T_e\). In DFT codes it is possible to simulate liquids by computing forces among ions and the MD evolution of the positions of the \(N\) ions in the simulation cell. However, to obtain reasonable statistics, one needs to reduce considerably the first Brillouin zone and increasing the number of bands in DFT codes is computationally very demanding, it becomes prohibitive at higher temperatures. Such a problem does not occur in the NPA model as only one DFT calculation at a single nucleus is required to construct the ion-ion pair potential. The structure factors may be computed using MD, or with MHNC equation for simple liquids.

The comparison of the pressure from UFM and equilibrium WDM is presented in Fig. 9. The equilibrium WDM pressure is much higher than the UFM value. Furthermore, the DFT-NPA calculation is in agreement with NPA up to \(T_e = 5\) eV (the limit of our DFT+MD simulation). This mutually reconfirms the validity of the NPA as well as DFT+MD approaches in the WDM regime.

Since \(Z\) reaches \(\sim 7\) at \(T_e \sim 100\) eV, codes for simulating Al should employ pseudopotentials that include more electrons than the three valence electrons valid at low temperatures. Simulations with high \(Z\) values will greatly increase the computational load and such calculations become prohibitive. Hence, NPA methods or orbital-free Hohenberg-Kohn methods become relevant \[55\]. The latter do not, however, provide energy spectra and details of the bound electrons.

**V. CONCLUSION**

In order to describe physical properties of UFM, we examined applications of the NPA model within the two-temperature quasiequilibrium model. We computed phonons, as well as the pressure resulting from the heating of free electrons. The excellent accord between such NPA calculations and DFT simulations using the ABINIT and VASP codes reconfirms the use of the NPA in this regime. As the internal pressure increases due to the heating of electrons by the ultrafast laser pulses, we explicitly showed that the phonon picture does not have much physical meaning, especially for thin WDM samples, even if frequencies could be computed using the harmonic approximation. As the NPA approach has negligible computational cost compared to standard DFT codes, it is a valuable tool for swiftly and accurately calculating important WDM properties such as mean ionization, pair potentials, structure factors, phonons, x-ray Thomson scattering spectra, electron-ion energy relaxation, conductivity, etc.
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