Computational Theory of Warm Condensed Matter

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February 25, 2001

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COMPUTATIONAL THEORY OF WARM CONDENSED MATTER

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98-ERD-052

Abstract. We have developed an improved computational theory of condensed matter in the regime where $T \leq T_{\mathrm{Fermi}}$. Previous methods of calculating the equation of state (EOS) relied on interpolation between low-temperature (solid) and high-temperature (plasma) limits, or employed severe approximations. Recent theoretical and experimental developments have highlighted the need for accurate EOS and opacity data in the intermediate temperature range and offer the opportunity to test theoretical models. We describe our results for EOS and optical properties for temperatures up to 10^6 K, and describe directions for future work.

INTRODUCTION

Laboratory missions such as the stockpile stewardship program (SSP) demand accurate materials-modeling capabilities. Among these, calculations of the equation of state (EOS) and opacity play important roles. SSP programs require knowledge of these properties over an extreme range of densities and temperatures. In the low-density/high-temperature limit, models based on plasma physics are very accurate, whereas models based on condensed-matter physics perform best in the high-density/low-temperature regime. In this project, we are focusing on "warm" condensed matter, i.e., on the region of intermediate temperature and density where the high-temperature or low-temperature approximations may no longer be valid.

Tremendous advances in condensed-matter theory over the past few decades have led to the ability to predict the electronic, vibrational, and superconducting properties of both real and hypothetical materials from "first principles," i.e., using only the atomic number Z and mass A as inputs to the calculation. The vast majority of this theoretical effort has been focused on the low temperature limit and relatively little attention has been given to warm, dense states of matter.

Current models for the EOS of warm, dense matter are primarily based on theoretical models that are most accurate in the low-temperature limit and that treat the effect of finite temperature as a perturbation of the zero-temperature solution. These models are largely untested above the melting point-especially approaching the Fermi temperature T_{Fermi} (the characteristic energy scale for the interacting electrons in a material, typically on the order of a few 10^5 K). Thus, the goal of the current project is to develop rigorous extensions of existing state-of-the-art condensed-matter techniques that are valid in this intermediate-temperature regime. Our approach focuses on three areas: improving theoretical treatments of the thermal contributions to the EOS; calculating optical properties (e.g., opacity) at finite temperature; and developing a new theoretical formalism that can be used to solve the quantum-mechanical, many-electron problem at finite temperature.

RESULTS

Our starting point is the case of a crystalline solid at zero temperature. An excellent description of the formalism for calculating the properties of solids at zero temperature can be found in the review article by Payne et al. [1]. Important features of their treatment include: (1) the use of crystalline symmetry to reduce the simulation cell size to only a few (perhaps only one) atoms, greatly simplifying the calculation; (2) the use of pseudopotentials to eliminate core electrons that do not participate in chemical bonding; and (3) the use of an exchange-correlation potential to model the many-body quantum-mechanical behavior of the electrons.

At finite temperature, this model will begin to break down. First, some of the electrons will occupy excited states due to thermal excitations. At higher temperatures, the solid will melt, resulting in a loss of symmetry, and the thermal motion of the nuclei (or ion cores in the pseudopotential model) will become important. At still higher temperatures, the core electrons will become thermally excited, and will have to be included in the calculation. Additionally, the exchange-correlation potentials V_{xc} used in nearly all condensed matter calculations are based on a zero-temperature model of the electron gas and may not be accurate at high temperatures.

At temperatures below and near the melting temperature (on the order of 10^3 K for most solids), the motion of the ions is the most significant factor, and quantum molecular dynamics has been extremely successful in describing the properties of condensed matter up to $T \leq 10^4$ K. Above this temperature, excitation of core electrons will occur at a temperature near 10^5 K, although this is strongly dependent on the material. The use of a $T = 0$ model for V_{xc} will begin to fail as T approaches T_{Fermi}, also in the range of 10^5 K.

We began by modifying our existing codes to consider a finite electron temperature. This improvement allowed us to model experiments [2] in which a semiconductor crystal heated by a femtosecond-pulse laser exhibited thermally induced structural instabilities within a few picoseconds (10^{-12} s) of heating. On this short a time scale, the electrons remain hot while the ions are relatively cold; therefore, melting of the crystal cannot explain the experimental results. It has been proposed that heating the electrons into excited states alters the forces that act on the nuclei, resulting in the observed structural instability. To simulate the experimental conditions, we used the codes we developed to calculate the vibrational properties of a silicon crystal with cold (stationary) ions and hot electrons, simulating the experimental conditions. Figure 1 shows that at a sufficiently high electron temperature (a few eV), the crystal lattice becomes unstable–as reflected by a negative force constant. This calculated result agrees with what was seen in the experiment.

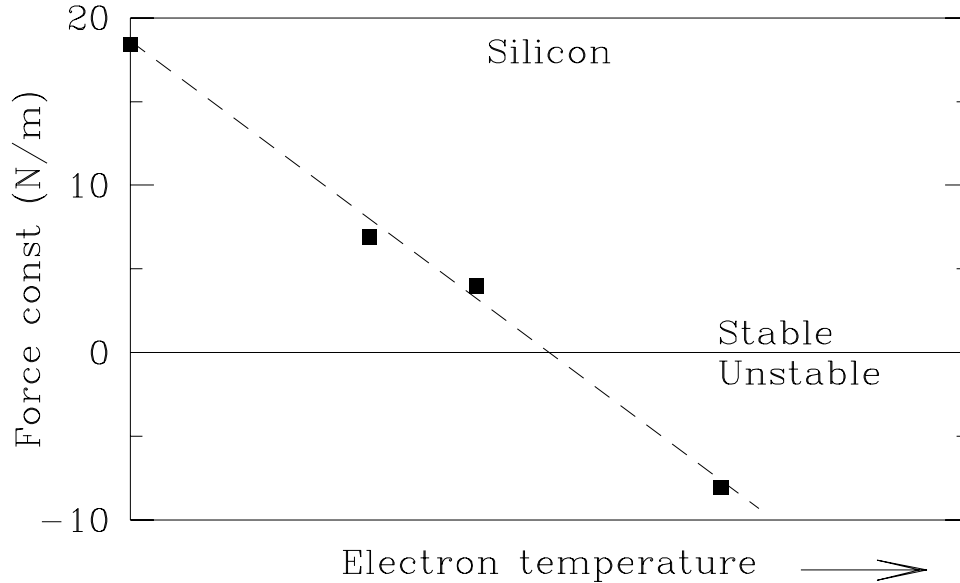Figure 1. Calculated force constants in silicon as a function of electron temperature. With increasing temperature, the force constant becomes negative, indicating a lattice instability, as seen in ultrashort-pulse laser experiments. The squares are calculated values, and the dashed line is a guide to the eye.

Our first effort at calculating the EOS of an element at $T \sim T_{\mathrm{Fermi}}$ (typically 10^5 K) was a

calculation of the Hugoniot of beryllium. These calculations were performed without the use of a pseudopotential, so thermal excitation of the 1s core electrons was automatically included. We did not perform molecular dynamics simulations, but instead calculated the free energy of a beryllium crystal with hot electrons and cold nuclei, and used an ideal gas model to calculate the contribution of ion motion to the EOS. We found that the neglect of ion motion resulted in poor agreement with existing theories, as shown in Figure 2.
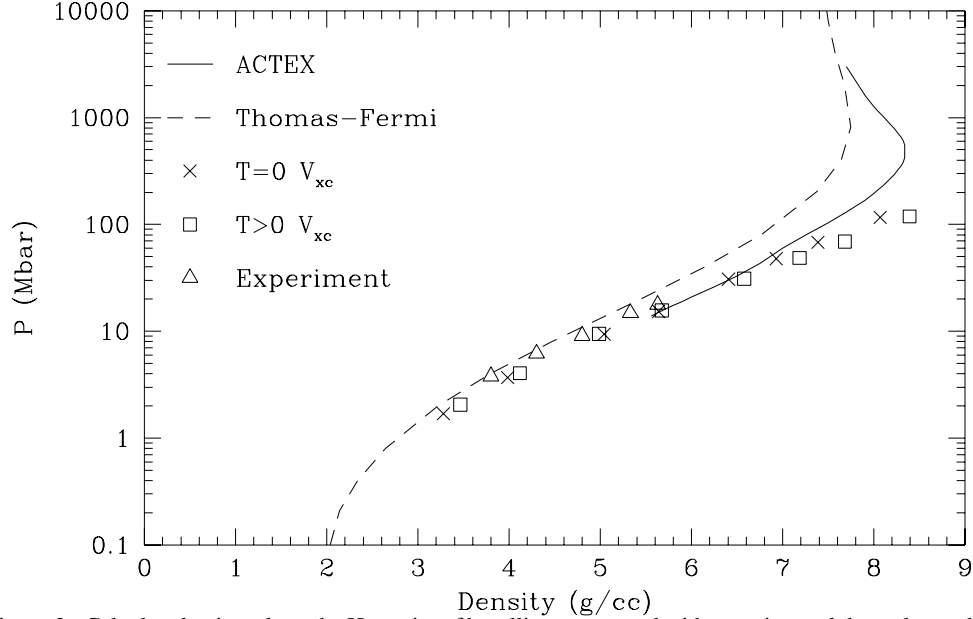

Figure 2. Calculated points along the Hugoniot of beryllium compared with experimental data, plasma-based theory (ACTEX), and simple Thomas-Fermi theory. The inclusion of a finite-temperature model for the exchange-correlation potential V_{xc} moves the Hugoniot to higher density at a given pressure.

We then decided to include the effects of ion disorder on the EOS by performing molecular dynamics (MD) simulations at high temperatures. For all but the lightest elements, thermal excitation of core electrons must be included to obtain reliable results; however, including all of the core electrons in MD is computationally infeasible. We have developed a new pseudopotential formalism, derived from photoemission calculations, which we have adapted to treat atom-electron scattering at extreme temperatures. Our results, as described in [3], indicate that the calculations should be reliable for temperatures up to and exceeding one million Kelvin. This new formalism was employed to calculate the shock Hugoniot of aluminum. At the highest temperatures, we discovered that the molecular dynamics simulations can be performed with very small simulation cells, encompassing just four atoms. This is sufficient to describe the ion-ion pair correlation function out to the average nearest neighbor separation, permitting calculations up to 3×10^6 K. As described in our paper [3], the results are in excellent agreement with experimental data and also with the previous low-temperature calculations, and approach the high-temperature plasma-based theory at high density and temperature.

We also pursued a second line of inquiry focused on the effects of including a finite temperature quantum-mechanical description of the electron gas (as modeled by the exchange and correlation potential $V_{xc)}$. We found that the predicted density of extremely strongly shocked beryllium(see Fig. 2) and aluminum [3] (at $T \geq T_{\mathrm{Fermi}}$) changed by several percent when a finite-T model was used for V_{xc}, indicating that inclusion of finite-T effects is needed for accurate results at $T \geq T_{\mathrm{Fermi}}$.
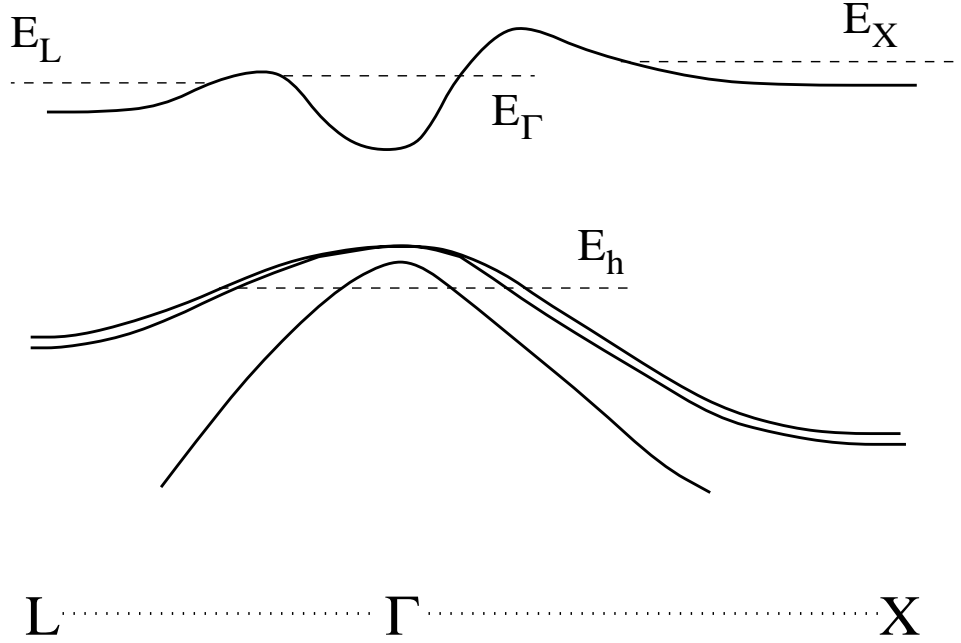
Figure 3. Schematic drawing of the GaAs band structure near the band gap for **k** from L→ Γ →X. The dashed lines indicate quasi-Fermi levels for electrons (conduction band) and holes (valence band).

We also found that for $T << T_{\mathrm{Fermi}}$, finite-T effects were insignificant, as we expected.

Our study of the optical properties of warm dense matter proceeded along two fronts: calculation of visible and near-UV absorption in optically pumped GaAs, and the calculation of excited state (including optical) properties of solid-density Al near the Fermi temperature. In both of these studies, we deepened our physical insight while developing the computational machinery needed to address the problem in a more general context.

Our calculations of absorption in laser-excited GaAs, published in [4], were meant to address the experiments of Mazur [5]. In these experiments, a 70 fs pump pulse containing 1.9 eV photons excites a GaAs crystal. A few hundred fs later, the reflectivity is probed from 1.5 to 4.0 eV (in the vicinity of the so-called E_1 peak at 3.0 eV). The pump fluence is high enough so as to excite in excess of 10^{21} carriers/cm^3 (see Figs. 3,4). At these short pump-probe delay times, the ions are thought to be close to their equilibrium lattice positions. A fundamental result of these measurements is the reduction in E_1 peak height following the excitation. Our calculations using the Bethe-Salpeter equation with a screened electron-hole interaction reproduce these features, at least qualitatively (see Fig. 4). We have shown that the peak reduction results from a combination of Pauli blocking (altered probability of interband excitation) and increased screening of the electron-hole attraction (excitonic effect). However, it is possible that the excited charge responds too slowly to contribute to the screening. Unable to go beyond the static screening approximation to the Bethe-Salpeter equation (in an ab initio calculation) we posited a "quasi-static" screening approach, wherein the excited carriers are assumed to respond too slowly to contribute to the screening. The results are similar to those of Fig. 4, but with slightly larger intensity in the peak at 3 eV for each density. The true results are likely to lie somewhere between those of the static and quasi-static cases.

The Al calculations are being performed to address thin foil measurements in V division at LLNL. Here we simulate the Al fluid at solid densities and temperatures of several eV using our quantum molecular dynamics scheme described in [3]. Electron and ion temperatures are independently var-
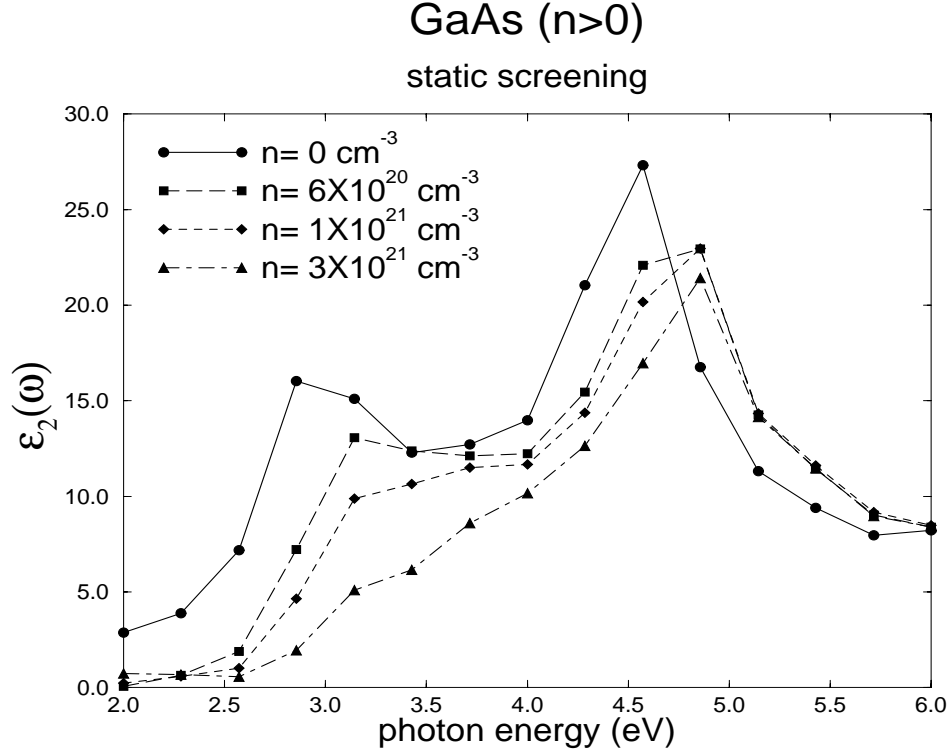
GaAs (n>0)

static screening

$\epsilon_2(\omega)$

photon energy (eV)

n= 0 cm^{-3}
n= 6X10^{20} cm^{-3}
n= 1X10^{21} cm^{-3}
n= 3X10^{21} cm^{-3}

Figure 4. $\epsilon_2(\omega)$ vs photon energy ω for four occupation number distributions (each characterized by excited carrier density n) in the static screening approximation. As the excited carrier density n increases, the E_1 peak in the absorption is strongly screened (see text).

ied. Excitonic effects are ignored in this study, due to the strong screening in (even un-pumped) Al. We find that the frequency-dependent conductivity resembles that of the Drude model for the $T_{\mathrm{electron}} = T_{\mathrm{ion}} =$ several eV cases, even at solid densities. However, the spectral broadening we have used is entirely phenomenological. The true broadening may result from the strong electron-electron scattering expected when $T \sim T_{\mathrm{Fermi}}$. In order to address this problem, we have collab-orated with the Louie group at UC Berkeley to compute the energy-dependent lifetime $\tau(E)$ of an electron in hot dense Al using the GW approximation. Results suggest that $1/\tau(E = E_{\mathrm{fermi}})$ is proportional to T^2, as suggested long ago by Landau. In addition, we have learned that the amount of spectral weight in the quasiparticle peak in the electron spectral function is a very weak function of T (at least within the GW approximation), suggesting that the quasiparticle concept is still mean-ingful at these conditions, even if the lifetime is short. Calculations of the AC conductivity for the crystalline ($T_{\mathrm{ion}} = 0$) case are currently underway. These may be the most relevant for comparing to the V division experiment, for their pump-probe delay time is under a ps, and the thickness of their foils is only 100 Angstroms.

SUMMARY AND FUTURE WORK

We have developed a method for calculating the equation of state for simple materials at temperatures ranging from zero Kelvin to in excess of 10^6 K. Crucial elements of this method include (1) the use of molecular dynamics to account for the motion of atoms in the fluid, (2) pseudopotentials incorporating excited core states to accurately reflect atom-electron scattering at high temperature, and (3) a finite- temperature treatment of the quantum-mechanical properties of the electron gas. This method has been successfully applied to the EOS of aluminum. We have also extended zero-temperature theory for the optical properties of solids to handle the case where the electrons in the solid are in excited states, either due to elevated temperature or laser-driven excitation. We found that it was necessary to include both (1) the screening of the electron-hole interaction and (2) the modified probability of interband transitions for accurate results. Future extensions of this work will focus on the optical properties of disordered materials (e.g., hot fluids) and on the EOS of higher Z elements containing localized orbitals (e.g., d and f orbitals).

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