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Recent developments and outstanding challenges in theory and modeling of liquid metals

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Abstract

We review recent progress in accurately modeling properties related to liquid metals and alloys. In particular, we examine the ability to provide true material specific models, and to use those models to examine real quantities of interest. This includes properties such as equilibrium melting lines for pure systems, alloy phase diagrams, and crystal-melt interfacial properties. We also discuss the role of such calculations in relation to understanding crystal nucleation and solidification. As an example of the type of phenomena that we would like to be able to understand (and ultimately predict), we discuss recent experiments on the 'simple' eutectic system Al–Si, which has a complex solidification behavior, due to the facetted interfaces that occur in this system. Recent neutron scattering experiments suggest that there can be inhomogeneities in the melt, on the order of 10 nm in size, depending on the thermal history of the melt. Understanding this type of behavior requires more accurate descriptions of alloy systems than have been previously available, as well as new techniques and approaches similar to those developed in recent years for simpler systems.

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1. Introduction

The purpose of this paper is to review selected developments in the theory and modeling of liquid metals. This has become a popular topic for some time, and in the last five years there has been a dramatic increase in interest in the area. Thus, there is a vast amount of recent literature, and we do not attempt to provide a full summary of all of this. The subjects discussed in the paper below represent some of what we feel is new and interesting, or what presents specific challenges to the modeling area.

Simulations of liquids can provide much information to the community; not only supplementing experimental data, but providing new tests of theories and ideas, making specific predictions that require experimental tests, and ultimately helping to lead to the deeper understanding and better predictive behavior. The information can be very specific, such as calculations of structure, diffusion or viscosity in specific systems at specific temperature [1–5]. On the other hand, simulations can provide more 'generic' behavior: for example, there has been significant interesting recent work in nucleation and crystal-melt interfaces in model systems such as hard-spheres and Lennard-Jones systems [6–20].

What, specifically, would we like to understand and predict? While the liquids are interesting in their own right,

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much of the interest is related to phase transitions: for example, nucleation and growth of crystal phases, the glass transition and glass formability, liquid–liquid phase transitions. (Again, there are many related, interesting questions that are not addressed here, including pattern formation during solidification, devitrification behavior, and deformation of metallic glasses.) Much of this really requires detailed knowledge of *non-equilibrium* behavior. However, we stress that there is little predictive capability even in the *equilibrium* behavior, and that without this, the non-equilibrium behavior will remain elusive.

More specifically, in equilibrium, we would like to be able to predict structure, viscosity, and diffusive behavior, in both pure metals and alloy systems. Phase diagrams, including melting curves [21–28], solidus and liquidus lines [29–35], are difficult to predict accurately without experimental input, even for simple binary systems [30–33]. Some of this review will specifically focus on equilibrium properties of solid–liquid interfaces [3,9,12,16–18,35–54], including their free energies and mobilities. All of these quantities affect the non-equilibrium properties we would like to predict: nucleation rates (both homogeneous and heterogeneous), growth rates, and glass formability.

We choose to focus primarily (though not exclusively) on atomistic modeling, primarily utilizing molecular dynamics or Monte Carlo techniques. We will do little to discuss these techniques, though we will stress their calculation. We will make some brief mention of theoretical techniques that are being used to address some of the issues, and how they can be compared with simulation or experimental results.

The paper is organized as follows. In Section 2, we will discuss the methods used to calculate energies and forces between atoms. Section 3 will describe developments in the calculation of bulk equilibrium properties. Section 4 will review recent developments in crystal-melt interfaces, which have received significant attention in the last four years, and also crystal nucleation from the melt. Section 5 will demonstrate the challenges facing the community, using the ‘simple’ case of eutectic Al–Si. A brief final discussion follows in Section 6.

2. Real materials: from pair potentials to first-principles calculations

Ultimately, we would like to understand both *generic* properties of liquid metals, as well as *material specific* properties. Early work simulating liquids relied upon simple potentials, in particular hard-sphere and Lennard-Jones interactions (for example, see [47–52,55,56]). To some extent, it may be surprising that 40 years later, these are still of interest [7,14,16,40,57–60], and are still relevant to the properties of liquid metals. For material specific properties, pair potentials used to dominate, but these fail to capture certain properties (such as elastic anisotropies). More recently, the literature has been dominated by the use many-body potentials that may be written as a functional of pair potentials [12,21,41–43,45,46,61,62], specifically:

$$E(\{r_i\}) = \sum_i F(\rho_i) + \sum_{<ij>} \phi(r_{ij}), \tag{1}$$

where

$$\rho_i = \sum_{j \neq i} f(r_{ij}). \tag{2}$$

Thus, the energy of an atom depends only on the sets of distances of neighboring pairs, as in a pair potential. Potentials of this type include the embedded atom model (EAM) [63–66], Finnis–Sinclair (FS) models [67], ‘glue’ models [54,68], and effective medium models [69,70]. For convenience, we will simply refer to these as EAM models. By including many-body terms, the potentials become more accurate, in particular under conditions where the atomic density or coordination changes significantly. However, the accuracy is limited, and for bulk liquid properties, it is not apparent that these add significantly to pair potential descriptions. It is useful to note that the energy can be expanded around the average density, to approximate this by an effective (density-dependent) potential [62,64]. Of course, such an approximation will not work well in locations where the density is significantly different from the average density.

Recently, the ready availability of sufficient computational power has led to increased use of *ab initio* simulations of liquids [1–5,9,71–76], utilizing density functional theory (typically with the local-density approximation [LDA] or generalized gradient approximation [GGA]) to calculate the total energies and forces including the electronic structure. Such methods are, in principle, significantly more accurate than empirical potential, and do not require fitting potentials. However, they are more computationally intensive, and thus the simulations tend to be small (almost always less than 500 atoms, and often under 100), with short simulation times. The use of such methods has been encouraged by the availability of commercial codes (for example, the ‘Vienna Ab initio Simulation Package,’ a.k.a. VASP [4,5,77]) and also freely available codes (such as the ‘Spanish Initiative for Electronic Simulations with Thousands of Atoms,’ a.k.a. SIESTA [78]). In all cases, the accuracy can be limited by the choice of energy cut-offs and *k*-point sampling, but generally these are useful for examining material specific properties.

We note that there are approaches that bridge between the classical potentials (such as EAM and pair potentials) and full electronic structure based methods. These include the related tight-binding (TB) and bond-order potential (BOP) methods, which includes an empirical electronic structure calculation. These schemes can be more accurate than the classical potentials, by including the electronic structure explicitly, while being significantly faster than *ab initio* calculations (by a factor of ~100) by including only a limited basis. The use of these has been limited by the difficulty of developing accurate potentials; however,