

Letter

A molecular dynamics method to identify the liquidus and solidus in a binary phase diagram

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ABSTRACT

A method is presented adopting the phase coexistence technique within molecular dynamics simulations to identify the liquidus and solidus of binary systems. The Compositional Moving Interface method is applied to the case study of the Cu–Ni system and compared against a thermodynamic end-point model where the input parameters are determined using the same MD potential. This is a simple and powerful method to predict the solidus and liquidus boundary of a binary phase diagram for mixed systems calculated from the dynamics of a simulation.

The melting temperature of simple (unary) systems can be calculated using computational techniques based on molecular dynamics (MD) simulations, such as the Z-method [1–4] and the moving interface (or phase coexistence) method [5–9]. However, binary systems will not have one melting point, but a two-phase region bound by a liquidus and a solidus. When those methods are applied to a binary mixture a “pseudo-unary” melting point is found [10–12], but it is not clear whether these melting points correspond to the solidus, the liquidus or somewhere in between. On the other hand, current methods to predict solidus and liquidus of binary systems from atomic scale simulations rely on assumptions of ideal mixing to extrapolate the results from the end members.

A previous attempt in the literature to predict the phase boundaries from two-phase MD simulation proved successful on oxygen-carbon-selenium plasma mixtures [13]. However, the method is cumbersome, sensitive to a choice of local order parameter, and computationally intensive compared to the proposed method. Further, work by Coura et al. [14] use MD to study directional growth of binary mixtures by investigating an equilibrium crystal-fluid interface. Here a variant of the moving interface method is presented that can predict the liquidus and solidus boundaries and thereby construct a binary phase diagram. We call this method the compositional moving interface or CMI.

The proposed CMI method has been developed to predict the melting behaviour of solutions that do not follow ideal laws of mixing. It has been previously used, along with other approaches, to show

deviation from ideal behavior in U, Th and Pu oxide systems [15]. However, it is not possible to test the validity of the approach against systems that deviate strongly from ideal mixing as there are no computational predictions for such systems that can be validated to a high degree of certainty. Direct comparison with experiments for strongly non-ideal systems, on the other hand, is hindered by the additional uncertainties introduced by the quality and transferability of the empirical potentials used. Instead, here we test the validity of the proposed method against ideal mixing laws, in a self-consistent manner. More specifically, we use the Cu–Ni system as a case study, as it is a well studied system and for which reliable empirical potentials exist. Cu–Ni is an isomorphous system that displays complete solid state miscibility at high temperatures, with small enthalpy of mixing [16–22], and where the radii differ only slightly. Under these conditions, mixing behaviour is well approximated by that of a regular or ideal solution. Therefore, the predictions of liquidus and solidus made assuming ideal mixing, and informed by parameters obtained through MD simulations, are directly comparable with the CMI predictions made using the same empirical potentials and simulations parameters.

MD simulations were conducted using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [23]. The study employed the embedded atom potential model by Sheng et al. [24].¹ For all simulations a Nosé-Hoover barostat with a relaxation time of 0.5 ps was used to control the pressure while the system temperature was controlled with a Nosé-Hoover thermostat and a relaxation time of

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0.1 ps. An MD timestep of 1 fs was used in all calculations unless otherwise stated.

First the melting temperature (T_m) of the end members were calculated using the conventional moving interface method. The moving interface simulation cell is constructed by joining two equilibrated simulation cells, one constituting a solid phase and the other a liquid phase both at the same temperature and conventionally of the same composition. Depending on the simulation temperature, the interface between the two phases will move. If the system energy is too low to maintain the liquid phase the interface will move into the liquid and the system will progressively solidify. Likewise, if the system energy is sufficiently high the solid will melt into the liquid. In the current study, the temperature range in which neither phase grows by an appreciable amount (up to three atomic planes) in 1 ns, is only 5 K.

The simulation cell was constructed as follows. A $10 \times 10 \times 60$ cell, containing 24,000 atoms, was heated to a target temperature at 0 GPa and allowed to equilibrate for 20 ps. After this, the cell was split into two adjacent regions: the solid region, in which the atoms' positions were frozen in place (i.e. no integration of trajectories), and the liquid region, which was heated to 2500 K (above the melting points of Cu and Ni) over 20 ps, held at that temperature for another 20 ps to establish a true liquid distribution, and cooled back down to the test temperature. During this process the system pressure was relieved by applying a barostat in the z-direction only (the direction normal to the interface). Following this, the atoms in the solid region were unfrozen and using NPT dynamics with the barostat acting in all directions the whole simulation cell was equilibrated at the target temperature for 1 ns.

Using the moving interface approach described above, the T_m of Cu and Ni were calculated as 1385 ± 2.5 K for Cu and 1760 ± 2.5 K for Ni, respectively. The error associated with the MD melting points are determined as the range in which melting occurs (i.e. the minimum and maximum refer to a simulation that did not and did melt, respectively). These temperatures are in close agreement with experimental T_m observations of 1358 K and 1728 K [25]. A small difference between MD and experimental melting temperatures is expected, and a difference of only ~ 30 K provides confidence in the potentials. The predicted enthalpy of fusion values², ΔH_m , at those temperatures are $12.23 \text{ kJ mol}^{-1}$ and $17.64 \text{ kJ mol}^{-1}$ for Cu and Ni respectively, also in close agreement with experiment [26] ($12.93 \text{ kJ mol}^{-1}$ and $17.04 \text{ kJ mol}^{-1}$).

For an ideal solution (i.e. one that has zero enthalpy of mixing and zero volume change on mixing) the liquidus and solidus can be calculated from their heats of fusion and melting temperatures with the following relations [27], where it has been assumed that the heat capacity difference between the liquid and solid phases is zero.

$$\ln \frac{x_s^A}{x_l^A} = \frac{\Delta H_m^A}{R} \left(\frac{1}{T_m^A} - \frac{1}{T} \right) \quad (1)$$

$$\ln \frac{1 - x_s^A}{1 - x_l^A} = \frac{\Delta H_m^B}{R} \left(\frac{1}{T_m^B} - \frac{1}{T} \right) \quad (2)$$

Here R is the ideal gas constant, T_m^i is the melting temperatures of the end-member i (A or B), ΔH_m^i is its enthalpy of fusion and x_s^A and x_l^A are the mole fractions in the solidus and liquidus for end-member A at temperature T .

The proposed CMI method, while computationally similar to the conventional moving interface method, is different because the liquid and solid regions have different compositions. For each CMI calculation two $12 \times 12 \times 24$ supercells of different compositions were joined to create a $12 \times 12 \times 48$ supercell. Firstly, the whole system was equilibrated to the target temperature at 0 GPa, then the CMI method was implemented, as described below, for a duration of 1 ns. A calculation of a liquidus point using the CMI method is summarised below with

respect to the schematic Cu–Ni binary phase diagram in Fig. 1.

1. An initial test temperature T_i is chosen (black dashed line in Fig. 1), typically between the melting point of the end members; in this range, the end member A is known to be in the liquid state while the end member B is known to be solid.
2. The liquid phase is created with composition of the end-member A and equilibrated at temperature T_i (the black point in Fig. 1).
3. A test composition x_i of the A–B mixture is chosen (pink dashed line in Fig. 1), and the solid phase is created with this composition and equilibrated at the test temperature T_i .
4. The two structures are joined to form a single simulation supercell with the two distinct compositions and two liquid/solid interfaces. A simulation cell for this case is shown in Fig. 1a at 0 ns (i.e. before equilibration of the whole system, $t = 0$).
5. Running an MD simulation at T_i in Fig. 1a, the liquid side of the system will consume the solid so that the whole system will melt at this system energy. This process is presented for the $\text{Cu}_{50}\text{Ni}_{50}$ system at 1610 K in Fig. 1a. This case is represented by an open pink square as it has been determined that the whole system melts, that is, it is above the liquidus.
6. The MD calculation procedure is repeated for lower temperatures. In Fig. 1b the next two lower temperatures are still above the liquidus so are therefore also represented by open pink squares.
7. The temperature is lowered until it is determined that the system has crossed the liquidus line. At this point the system energy is such that both the solid and liquid regimes coexist. This point is represented by a solid pink circle in Fig. 1b. Evidence that the system is now in the two phase regime is presented in Fig. 1b as a series of three simulation snapshots, starting at 0 ns and ending at 1 ns.

To calculate a point on the solidus the converse process is carried out. That is, a series of simulations are carried out with progressively increasing temperature for a system in which the composition of the solid phase is the end-member B and the composition of the liquid phase is the target A–B solution. The whole system will solidify until a temperature where both the solid and liquid regimes exist, that is, the system has crossed the solidus. It is important to understand that the melting process, at the atomic scale, is not an equilibrium process. The liquid is to be a medium into which the solid melts and therefore it is not crucial that the liquid has the equilibrium composition. Of course, the liquid can not deviate too far from the equilibrium composition, but as long as it is close, a concentration gradient will form in the liquid near the interface during the first few timesteps of the simulation. This local change in composition at the interface is what enables our simplified approach to calculate the liquidus and solidus.

Fig. 2 shows the compendium of CMI predictions for the Cu–Ni phase diagram and its comparison with the ideal model. The pink and blue dashed lines are the ideal liquidus and solidus lines determined via Eqs. 1 and 2 using the calculated melting points and enthalpies of fusion. Using the CMI method, the open pink squares and open blue circles indicate when the MD supercell completely melts or solidifies, indicating the system is in the liquid or solid region of the phase diagram. The solid pink circles represent when the system melts but there is some solid left. The solid blue circles represent when some of the liquid solidifies but there is some liquid left. Using the MD results, a 2nd order polynomial was fit to the temperature identifying the limiting two-phase temperatures at specific concentrations that therefore outline the liquidus and solidus; represented by the solid pink and blue curves respectively. This fit was chosen as a visual aid to observe the liquidus and solidus on the binary phase diagram. The grey shaded region is a 75% confidence level (confidence interval of liquidus is narrower than line thickness and therefore not visible).

It is found that the MD simulations are able to generate data of sufficient temperature resolution to be used to generate liquidus and solidus boundaries that correspond closely with the ideal predictions

² A 32,000 atom supercell was heated and cooled with $\Delta T = 25$ K. The system was equilibrated for 100 ps and average values obtained from the final 20 ps.

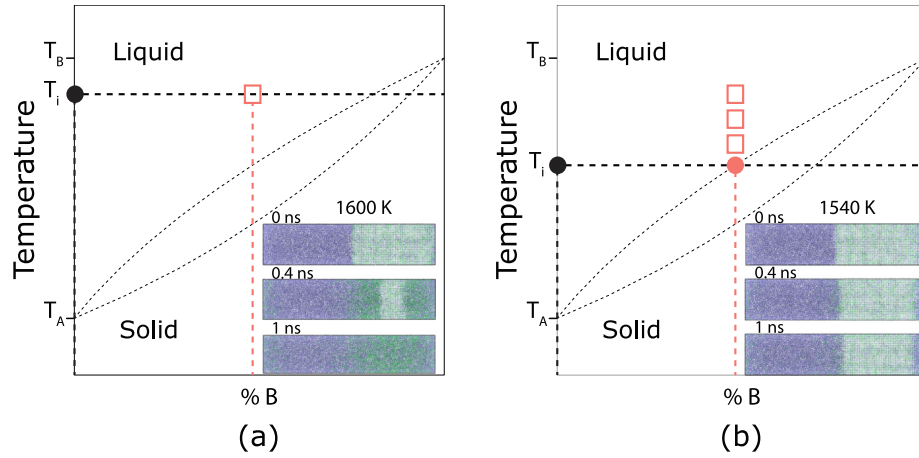


Fig. 1. Schematic of the Cu-Ni binary phase diagram where T_A is the melting point of A and T_B is the melting point of B. The CMI method is outlined for two simulations. The filled black circle indicates the liquid composition at temperature T_i , shown in blue in the three blocks on the right-hand side. The open pink square identifies the composition of the (initially) solid, shown in green in the three blocks. (a) represents a temperature above the liquidus such that the solid region melts at the chosen composition. (b) shows a temperature/composition where both the liquid and solid phase can coexist and is marked by a filled pink circle signifying the liquidus has been reached. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

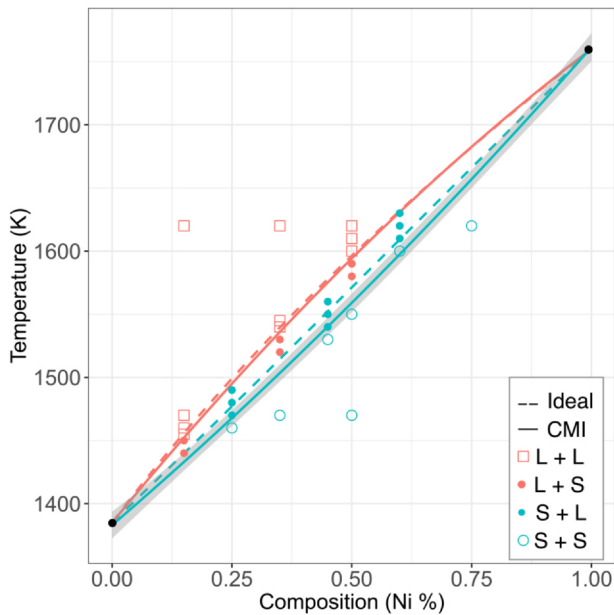


Fig. 2. Binary phase diagram predictions from the ideal model (dashed lines) and from CMI MD calculations (solid lines). The grey shaded region represents the 75% confidence interval of the quadratic fit. Pink and blue symbols represent liquidus and solidus calculations, respectively. Open and filled symbols represent simulations that ended in a single phase and two-phase equilibrium respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for the Cu-Ni system [25]. The calculated liquidus from the CMI method is almost identical to the ideal case whereas the solidus is slightly lower than the ideal case. Since these boundaries are predicted from dynamics it is possible that they are closer to “reality” than assuming the ideal case. The discrepancy between CMI predictions and those using ideal mixing laws are too small to be corroborated by the experimental data [25]. Direct correspondence to the phase diagram is also made difficult because the melting points of the end-members are different to those predicted by the potentials used here. Therefore, the two sets of the liquidus and solidus lines are displaced from each other. Nevertheless, the predicted and experimental temperature separations between liquidus and solidus lines are close, as shown in Fig. 3.

Interestingly, for the liquidus simulations, a small amount of loss of

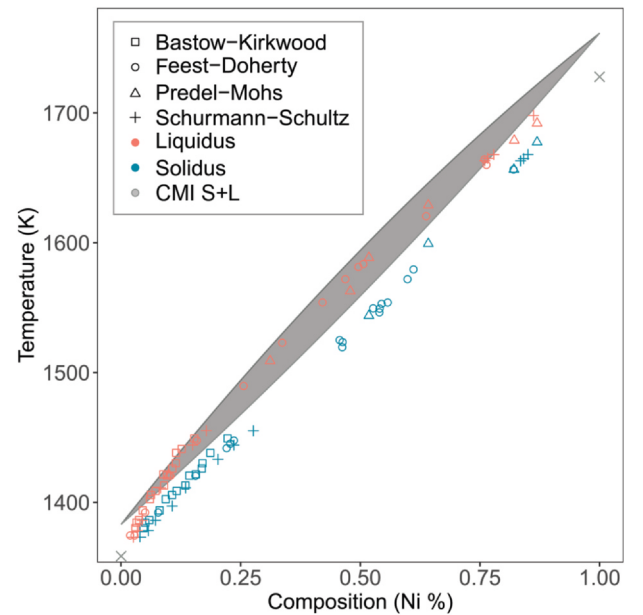


Fig. 3. Blue and pink points represent experimental values [28–31] for the Cu-Ni binary phase diagram solidus and liquidus, respectively. The grey shaded region represents the solid-liquid region predicted by the CMI method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

solid phase is always observed, even when the temperature is below the liquidus boundary. This is explained by heterogeneous melting at the interface; a process that may occur at temperatures much lower than the melting point, but over significantly longer time-scales. Interface heterogeneous melting is driven by the concentration gradient of B atoms (Ni in this case) into the liquid phase (nominally pure A, or Cu). In a dynamic equilibrium, atoms at the interface continually melt and solidify. However, as the B atoms (Ni) melt into the liquid A phase (Cu), they will form a concentration gradient that drives diffusion of B atoms towards the bulk of the liquid phase. As a consequence, the interface will recede into the solid phase.

To test the sensitivity of this process, and more generally to ascertain the effect of approximating the composition of the liquid as end-member A, a number of simulations were repeated where the solid had a composition of $\text{Cu}_{50}\text{Ni}_{50}$ and the pure Cu liquid side was replaced by

increasing amounts of Ni, from 5% to 50% with steps of 5%. Two temperatures were chosen for these simulation runs, 1560 K (in the solid region) and 1580 K (in the 2-phase region). At 1580 K, all the simulation runs yield the same result: a system that contains a liquid phase with some solid, consistent with being in the 2-phase region. A general trend was observed whereby as the Ni concentration increases, the rate at which the solid melts decreases. This suggests that, on the time-scale of these calculations, the liquid region provides a low Ni concentration medium that facilitates the formation of an appropriate liquid structure with which the solid can form a stable interface. At 1560 K, from Ni 0% to 40% there is slight melting and the system consists of liquid and solid. When the Ni concentration is increased to 45% at this temperature, the system begins to solidify, however over the time-scale of our simulation there is still liquid in the system. Finally, when the Ni content is at 50% the system fully solidifies. This strong sensitivity to the liquid concentration past 40% Ni, when the solid contains 50% Ni, is a further indication that at 1560 K we are close to the solidus.

This may be a consequence of the melting being liquid diffusion rate limited, rather than heat transfer limited. Thus, the liquid region does not have to be pure A, its purpose is to provide a low B concentration medium into which the solid can melt. Equally, for the solidus calculation; for this system on these time-scales, the solid does not have to be pure B, its purpose is to provide an appropriate surface onto which solid can precipitate.

The results obtained from the Cu–Ni test case are encouraging, and it is proposed that this CMI model may be used more generally to predict the behaviour of more complex types of solid solutions that deviate strongly from ideal mixing behaviour.

Data availability

The data that support the findings of this study are available from doi: 10.17632/xydncc3cy7.1.

CRediT authorship contribution statement

C.O.T. Galvin: Investigation, Writing - original draft. **R.W. Grimes:** Conceptualization, Writing - review & editing. **P.A. Burr:** Methodology, Resources, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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