Molecular Dynamics Simulation of Liquid-Vapor Coexistence Curves of Metals

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Abstract. A Molecular dynamics implementation of Gibbs ensemble method is applied to determine liquid-vapor coexistence curves of metals using embedded atom model potentials. As an application of the code we developed, the liquid-vapor coexistence curves of Aluminum and Copper are simulated using Cai and Ye potential. The critical constants obtained were found to be slightly lower than the range of experimental results. The results show that the potentials parameters obtained by fitting to low temperature solid properties are not adequate to accurately determine the liquid-vapor phase diagram.

1. Introduction
The liquid-vapor phase diagram (LVPD) of metals finds important applications in a number of areas of physics and engineering. However, experiments to obtain LVPD of metals are difficult because of high pressures and temperatures involved. In such situations, computer simulations work as a reliable tool to complement the experiments. An elegant Monte-Carlo method for simulating the liquid vapor coexistence has been developed by Panagiotopoulos[1] and is called as Gibbs ensemble method. It has the advantage of direct calculation of phase coexistence properties of fluids from a single simulation. The method has been extensively used to obtain the LVPD of organic liquids using pair potentials. Later, many molecular dynamics versions of Gibbs ensemble have been proposed[2, 3, 4, 5, 6]. In this paper we use the Gibbs ensemble molecular dynamics (GEMD) method to obtain the LVPD of simple metals using Embedded Atom Model[7] Potentials. The method we use in the code we developed is close to that of Wen-ze et.al.[6].

The EAM potential is introduced by Daw and Baskes for metals. It, in addition to the pair potential term contains an embedding term which takes into account the effect of de-localized electrons on the atoms or molecules in the system. The standard pair potentials which do not take this effect (metallic bonding) into account could not explain some characteristic properties of metals like the ratio of elastic constants $c_{12} : c_{44}$, the vacancy formation energy etc. The EAM potentials have been used in a wide variety of problems of materials science and excellent results have been obtained[8]. Many forms of EAM potentials have been formulated by fitting to data from experiments or ab-initio calculations for solids[8]. Of these, the one developed by Cai and Ye[9] is interesting as it has a smaller number of fitted parameters when compared to many other potentials. The Cai and Ye potential has been recently applied to study the properties of liquid nickel and good agreement has been found with experiments for zero pressure melting[10].
We choose this potential to study the liquid vapor phase diagram of aluminum and copper using molecular dynamics.

2. The Embedded Atom Model potential
The total energy $E$ of an $N$-particle interacting system in the EAM formalism can be written as

$$E[\rho] = \sum_{i=1}^{N} F(\rho_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j(i\neq i)=1}^{N} \phi(\vec{r}_{ij}) \quad (1)$$

where $F(\rho_i)$ is the embedding term which is equal to the energy required to place an impurity atom at the site $i$ and $\phi(\vec{r}_{ij})$ is the pair potential. In the Cai and Ye potential the embedding term is given by

$$F(\rho) = -F_0 \left( 1 - \ln \left( \frac{\rho}{\rho_e} \right)^n \right) \left( \frac{\rho}{\rho_e} \right)^n + F_1 \left( \frac{\rho}{\rho_e} \right) \quad (2)$$

where $\rho_e$ is the equilibrium host electron density. $F_0 = E_c - E^f_v$ is the difference between cohesive energy $E_c$ and the vacancy formation energy $E^f_v$ and $n = 0.5$ is a dimensionless constant. The host electron density at $i^{th}$ site is given by

$$\rho_i = \sum_{i(\neq j)=1}^{N} f(\vec{r}_{ij}) \quad (3)$$

where

$$f(r) = f_e \exp(-\chi(r - r_e)) \quad (4)$$

$f_e$ is a scaling constant taken to be 1 for pure metals. $r_e$ is the equilibrium nearest neighbor distance.

The pair potential is given by

$$\phi(r) = -\alpha \left( 1 + \beta \left( \frac{r}{r_a} - 1 \right) \right) \exp \left( -\beta \left( \frac{r}{r_a} - 1 \right) \right) \quad (5)$$

where $F_1, \alpha, \beta, \chi, r_a$ are fitted parameters. During the fitting, the cutoff distance for the interaction is taken as $r_{cut} = 1.65a_0$ where $a_0$ is the lattice parameter. The detailed simulation procedure is as follows.

3. The Gibbs Ensemble Molecular Dynamics Method
The basic idea of GEMD is to simulate the conditions of liquid-vapor coexistence. The system will contain two simulation boxes. Total number of particles in the system is kept constant. However the number of particles in individual boxes can vary. One box is assumed to be situated in an infinite medium of homogeneous liquid at a (given) constant temperature and the other is assumed to be situated in an infinite medium of homogeneous vapor at the same temperature. Since the idea is to get the thermodynamic properties of a macroscopic system, the interface effects are neglected. The coexistence conditions are simulated by evolving the boxes in such a way that they have same temperature, pressure and chemical potential after equilibration as required by the Gibbs phase rule. Initially, each box is given a guess density (i.e., no. of particles and volume). The equilibration would be faster if the guess densities are closer to the coexisting liquid and vapor densities. Periodic boundary conditions are applied to each box to ensure that they represent the bulk coexisting phases. Temperature fluctuations in each box are controlled by a Berendsen thermostat [11] so that they reach the given temperature. Pressures in both
the boxes are equalized by controlling the volume fluctuations using a Berendsen barostat. This is done by adjusting the volume of each box such that the instantaneous pressure in one box becomes equal to the instantaneous pressure in the other. However the total volume of the two boxes is not restricted to be constant. The particle transfer step to equilibrate the chemical potential in both boxes is carried out after each five hundred time steps by comparing their chemical potentials. It is done as follows: A particle is chosen randomly from the box where chemical potential is more and is removed from it. Correspondingly a particle is introduced into the other with its potential energy calculated and the velocity taken from the Boltzmann distribution of corresponding temperature. However it is taken care that the introduced particle is not too close to any other particle in the box. With the above three procedures being done during the simulation, the two boxes evolve in time in such away that they have same temperature, pressure and the chemical potential after equilibration. For a given temperature, the system may phase separate into liquid in one box and gas in the other with proper choices of initial densities.

The method described above has been tested for the Lennard-Jones fluid initially. The phase diagram obtained exactly matched with that of the earlier simulations[1] validating the code we developed. Later the code has been used to simulate the liquid-vapor phase diagram of Aluminum and Copper using the Cai and Ye potential. Time step used for the simulations is 1 femto second and each simulation run has typically $5 \times 10^5$ equilibration and production steps. The chemical potential has been evaluated using Widom’s test particle insertion method[12]. In each step 200 test particles are inserted and the chemical potential is calculated after each five hundred steps. Total number of particles used in the simulation are 1000. The initial densities have been chosen so that after equilibration, both the boxes contain a good number of particles (few hundreds) so that the averages are reliable and deviations are small. The parameters for Berendsen thermostat and barostat are taken from an earlier work[13].

4. Results and Discussion

![Figure 1. Temperature Vs Density for Aluminum.](image1)

![Figure 2. Temperature Vs Density for Copper.](image2)

The Temperature($T$) Versus Density($\rho$) diagrams for Aluminum and Copper are shown in figures 1 and 2. The critical temperature($T_c$) and critical density ($\rho_c$) are obtained by fitting the simulation data using the law of rectilinear diameters

$$\frac{\rho_l + \rho_v}{2} = \rho_c + A(T - T_c)$$

(6)
and the power law

$$\rho_l - \rho_v = B(T - T_c)^\beta$$  \hspace{1cm} (7)$$

where $\rho_l$ and $\rho_v$ are liquid and vapor densities. $A$ and $B$ are fitting constants and $\beta = 0.33$.

$T_c$ and $\rho_c$ for Aluminum are $3140 \pm 11$ K and $0.53 \pm 0.03$ gm/cc respectively. For Copper $T_c$ and $\rho_c$ are respectively $4651 \pm 70$ K and $2.05 \pm 0.022$ gm/cc. A view at the earlier literature data available for liquid-vapor phase diagram of Aluminum [14, 15, 16, 17] shows that there is a huge scatter in the value predicted for $T_c$ from around 5500 K to 9000 K. Whereas the predicted value for $\rho_c$ is in between 0.3 gm/cc and 0.7 gm/cc. Similarly, the literature data for Copper [14, 16, 18] for $T_c$ varied from 5100 and 8600 and $\rho_c$ has the range 1.7 to 3.6 gm/cc. The results show that for both Aluminum and Copper, the $T_c$ predicted by Cai and Ye potential is lesser than the minimum of the predicted value. However the $\rho_c$ predicted by it is within the range of predicted values from literature. To check the dependence of the results on particle number we have carried out simulations for few temperatures with 1728 particles. The results are seen to change negligibly.

The low $T_c$ predicted by the Cai and Ye potential may be attributed to low well depth of the pair potential and the embedding function. Also, the potential parameters are obtained by fitting to the solid data like vacancy formation energy, cohesive energy, elastic constants etc. Thus current simulation results show that the EAM potentials parametrized for solid state are not adequate to describe the fluid state far from melting. The potentials have to be reparametrized using liquid state data like vapor pressure etc. Alternatively, ab-initio simulations may be done to obtain the liquid vapor phase diagrams. However, the enormous computational time required limits the total number of particles to a small number in order to obtain results in a reasonable period of time. But in the two phase coexistence regime, simulations with a small number of particles may not be reliable. Instead, the ab-initio simulations may be used to obtain the potential parameters and then the potential could be used in classical molecular dynamics simulations. Thus, with a good potential to describe the liquid metals, the gibbs ensemble method can be considered as a reliable tool to obtain the liquid-vapor phase diagram without going for experiments.

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