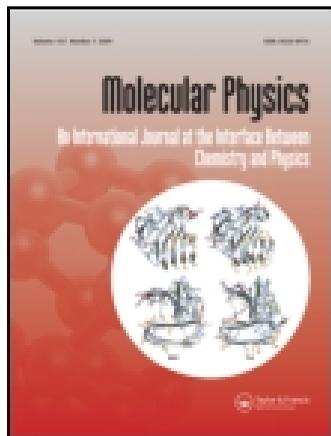


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# Interfacial properties of Morse fluids

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The interfacial properties as reflected in the interfacial tension values and the density profile of Morse fluids has been studied. The parameter range is chosen to coincide with that describing the behaviour of solid metals. The interfacial tension has been found to follow Guggenheim's and MacLeod's relations. However, the constants, while independent of temperature for each metal, are not the universal values predicted; with the exception of Macleod's exponent  $p$ . The density profile illustrates the change in densities across the interface dividing the coexisting vapour and liquid phases. The correlation length is also found to follow the universal relation with temperature, but again the constants, while independent of temperature, are dependent on the type of metal. The value of constant  $\nu$  is found to be different for all five metals considered and is found to differ from the three-dimensional Ising model value of  $\nu=0.630$ , which is also predicted by applying the Lennard–Jones model.

## 1. Introduction

Surface tension is a property which can explain many natural phenomena and has also been exploited in various industrial applications. Experimental studies at high temperatures and pressures, such as the conditions where metal vapours coexist with their respective melts, are difficult to perform. Computer simulations provide us the means to study the interfacial properties at these harsh conditions.

The surface tension of model systems such as the Lennard–Jones potential energy function (PEF), has been determined by various authors using different molecular simulation techniques. Surface tension has been determined conventionally by the slab-based molecular simulation techniques where a liquid phase is bounded on both sides by a coexisting vapour phase in a simulation box of constant volume and the pressure components at the interface are determined either by using molecular dynamics and the virial equation, or the Monte Carlo free energy perturbation method where the perturbation move involves changing the volume of the system. One of the drawbacks of this method is that for conditions close to the critical point, achieving equilibrium itself requires a long time computationally.

In recent years, the grand-canonical transition matrix Monte Carlo (GC-TMMC) method has been used successfully to predict the vapour–liquid interfacial tension of fluids including Lennard–Jones potential [1], square-well model [2], chain molecules [3], mixtures [4] as well as in the presence of external surfaces [5, 6]. This method in particular is attractive in the neighbourhood of the critical point. We utilize this GC-TMMC method, which we have used previously to determine the vapour–liquid equilibrium (VLE) curves [7], to determine the surface tension of Morse fluids. The Morse PEF [8] has been used to study the solid phase metals by various authors. Girifalco and Weizer [9] and Lincoln *et al.* [10] determined the parameters for this PEF for solid metals and calculated theoretically the elastic constants for certain metals and showed that their results were in good agreement with experimental data. Ruffa determined the dependence of elastic shear moduli on the thermal expansion properties and conjectured the association of melting in cubic metals with the maximum allowable thermal expansion in the solid metal using the Morse PEF [11, 12]. Chakraborty *et al.* [13] studied the general behaviour of the melting transition of Morse solids, including parameter ranges describing metals.

The metals considered in this study are sodium (Na), potassium (K), aluminium (Al), copper (Cu) and gold (Au). At normal temperatures and pressures, these metals exist in the solid phase with Na and K

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assuming a body centred cubic structure (bcc) while Al, Cu and Au have face centred cubic (fcc) structures. However, vapours and melts of metals are known to exist in extreme conditions and have distinctly different constituent species as compared to solid metals [14].

The mathematical expression for the Morse PEF is as shown below:

$$U(r_{ij}) = D[e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)}] \quad (1)$$

where  $D$  is the well-depth,  $\alpha$  is a constant with dimensions of reciprocal length, and  $r_0$  is the equilibrium distance of approach for the two particles separated by a distance  $r$ . The values of the Morse parameters (shown in table 1) studied are chosen to coincide with those of the metals. The parameters  $D$ ,  $\alpha$ , and  $r_0$  used here, have been determined by Lincoln *et al.* [10] through a fitting procedure to experimental data for the lattice constants, bulk moduli, and cohesive energies of the respective metals in their solid states at room temperature. The fcc metals display higher steepness and shorter range as compared to bcc metals on account of the differences in their parameters, which is reflected in figure 1. Studies for the VLE curves have been shown that the parameters need refinement to predict accurate results for the fluid phases. An accurate and realistic description of metals in any of the states of matter should involve many-body potentials. However, conducting simulations using a simple pair PEF is computationally less expensive as compared to a many-body PEF without much loss of generality and we have considered that the complex interactions between the constituent species can be approximated to the Morse PEF. Further, our aim in this study is to investigate the surface tension characteristics of the Morse fluids assuming the accuracy and transferability of the solid phase parameters when applied to fluid phases. We determine the effect of temperature on the surface tension of these Morse fluids.

The two coexisting vapour and liquid phases are separated by an interface, across which there is a change in density, while the temperature, pressure, and chemical potential of the two bulk phases remain identical.

Table 1. Values of the parameters for the Morse PEF.

Metal	$D \cdot 10^{-13}$ (ergs)	$\alpha$ ( $\text{\AA}^{-1}$ )	$r_0$ ( $\text{\AA}$ )	$\alpha r_0$
Al	4.3264	1.0341	3.4068	3.5230
Cu	5.2587	1.3123	2.8985	3.8037
Au	7.6148	1.5830	3.0242	4.7873
Na	0.9241	0.5504	5.3678	2.9544
K	0.8530	0.4766	6.4130	3.0564

The density profile gives a measure of the abrupt change in density from the vapour phase to the liquid phase, and the length of the simulation box across which this change occurs is defined as the interface width. The structure of the interface as predicted by the density profile has also been studied here. The density profile has been determined by using the slab-based molecular simulation technique.

The following section describes the simulation methods followed to determine the surface tension for the Morse fluids. Section 3 describes the results of our study. The conclusions of this study are given in section 4.

## 2. Simulation method

The grand canonical transition matrix Monte Carlo method (details described in [1, 15]) is used to determine the free energy as a function of particle number. The simulations are carried out in the grand canonical ensemble where the chemical potential,  $\beta\mu$ , volume,  $V$ , and temperature,  $T$ , of the system are held constant while varying the particle number,  $N$ . Multicanonical sampling [16] is used to speed up the simulations. To evaluate the chemical potential, at which two phases coexist, histogram reweighting technique [17] is utilized. The trial moves include displacement of the particles,

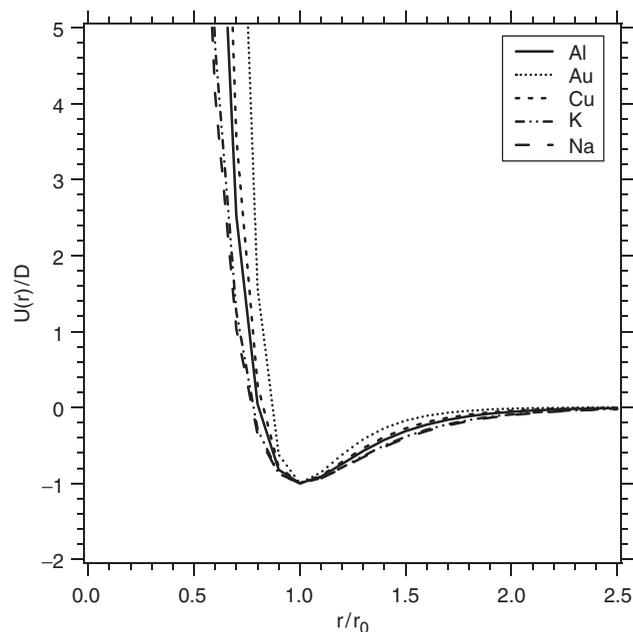


Figure 1. Morse potential scaled by energetic parameter,  $D$ , against reduced distance (scaled by equilibrium distance) for different metals.

and insertion and deletion of the particles performed with frequency 10:45:45 respectively.

The interfacial free energy,  $\beta F_L$ , for a simulation box length,  $L$ , is determined as shown below,

$$\beta F_L = \frac{1}{2} [\ln \Pi_{\max}^V + \ln \Pi_{\max}^L] - \ln \Pi_{\min}^{\text{interface}} \quad (2)$$

where  $\ln \Pi_{\max}^V$ ,  $\ln \Pi_{\max}^L$  corresponds to the maximum probabilities in the vapour and liquid regions respectively and  $\ln \Pi_{\min}^V$  corresponds to the minimum probability in the interface region.

To determine the statistical error in  $\beta F_L$ , at least two independent simulation runs are performed for a given box length at a given temperature for each metal.

Binder's formalism [18], equation (3), is used to determine the interfacial tension in the infinite limit, i.e.  $L \rightarrow \infty$ :

$$\beta \gamma_L = \frac{\beta F_L}{2L^2} = C_1 \frac{1}{L^2} + C_2 \frac{1}{L} + \beta \gamma \quad (3)$$

where  $\gamma_L$  and  $\gamma$  are the finite size and infinite size interfacial tension respectively

Thus, simulations at any given temperature are repeated for at least three different box lengths,  $L$  and  $\beta F_L/2L^2$  are determined for each  $L$ . Equation (3) is then used to determine  $\gamma$  at that temperature  $T$ . All temperatures considered are less than the critical temperature, i.e.  $T < T_C$  for each of the five metals studied here. The temperature range and simulation box lengths studied for each metal is given in table 2.

The slab-based molecular simulation technique [2, 19, 20] was used to determine the density profile at the interface of the coexisting vapour and liquid phases. Monte Carlo simulations are conducted in the canonical ensemble with  $N=2000$  particles where the liquid phase is present as a slab of the simulation box in coexistence with the vapour phase filling up the rest of the simulation cell. Simulation box size was set based on the liquid and vapour densities calculated in our previous work [7]. There are two interfaces in the simulation box as periodic boundary conditions are used. Simulations were done in NVT ensemble.

Table 2. Finite size scaling of surface tension,  $\beta \gamma_L$  in N/m.  $L_1$ ,  $L_2$  and  $L_3$  are the three box lengths considered, measured in Angstrom at temperature  $T$ , measured in Kelvin.

Metal	$T$ (K)	$L_1$	$\beta \gamma_L$	$L_2$	$\beta \gamma_L$	$L_3$	$\beta \gamma_L$
Na	2600	25	0.048133(21)	30	0.071251(20)	35	0.088041(31)
	2800	30	0.061917(17)	35	0.076743(35)	40	0.088872(57)
	3200	30	0.026162(64)	35	0.033267(56)	40	0.038813(56)
	3400	25	0.009514(21)	30	0.017170(32)	35	0.022210(57)
	3600	30	0.010438(14)	35	0.013841(28)	40	0.016291(46)
	K	2000	40	0.036712(17)	45	0.041549(48)	50
2200		40	0.023972(11)	45	0.027232(33)	50	0.030175(25)
2400		40	0.014754(17)	45	0.016818(19)	50	0.018647(17)
2600		40	0.008254(07)	45	0.009447(19)	50	0.010482(07)
2800		45	0.004482(08)	50	0.004993(20)	55	0.005455(11)
3000		45	0.001520(09)	50	0.001682(22)	55	0.001825(11)
Al	6200	25	0.3074(25)	30	0.3439(100)	35	0.3481(11)
	6600	25	0.2202(01)	30	0.2453(01)	35	0.2604(01)
	7000	25	0.1495(02)	30	0.1686(01)	35	0.1829(02)
	7400	25	0.09434(02)	30	0.1067(01)	35	0.1175(02)
	8000	25	0.03771(01)	30	0.04213(27)	35	0.04621(43)
	Au	5600	25	0.4851(06)	30	0.4919(14)	35
6000		25	0.3281(07)	30	0.3413(10)	35	0.3478(11)
6400		25	0.2003(08)	30	0.2135(03)	35	0.2222(02)
6800		25	0.1014(02)	30	0.1090(04)	35	0.1148(05)
7200		25	0.03590(05)	30	0.03697(12)	35	0.03825(37)
Cu		6400	25	0.3706(04)	30	0.3828(05)	35
	6800	25	0.2538(02)	30	0.2739(05)	35	0.2829(05)
	7200	25	0.1591(02)	30	0.1752(01)	35	0.1861(05)
	7800	25	0.05942(14)	30	0.06505(19)	35	0.07079(24)
	8200	20	0.02019(02)	25	0.02059(143)	35	0.02286(29)

Equilibration period consisted of  $2 \times 10^8$  MC steps and averages were taken for  $2 \times 10^8$  MC steps.

### 3. Results and discussion

The GC-TMMC simulations give the grand canonical probability distribution,  $\Pi(N)$  as a function of number of Morse atoms,  $N$ , for each of the five metals studied here. Figure 2(a) is a representative illustration of the results of GC-TMMC simulations, showing  $\ln \Pi(N)$  versus  $N$  plots, at coexistence, for Al at temperature,

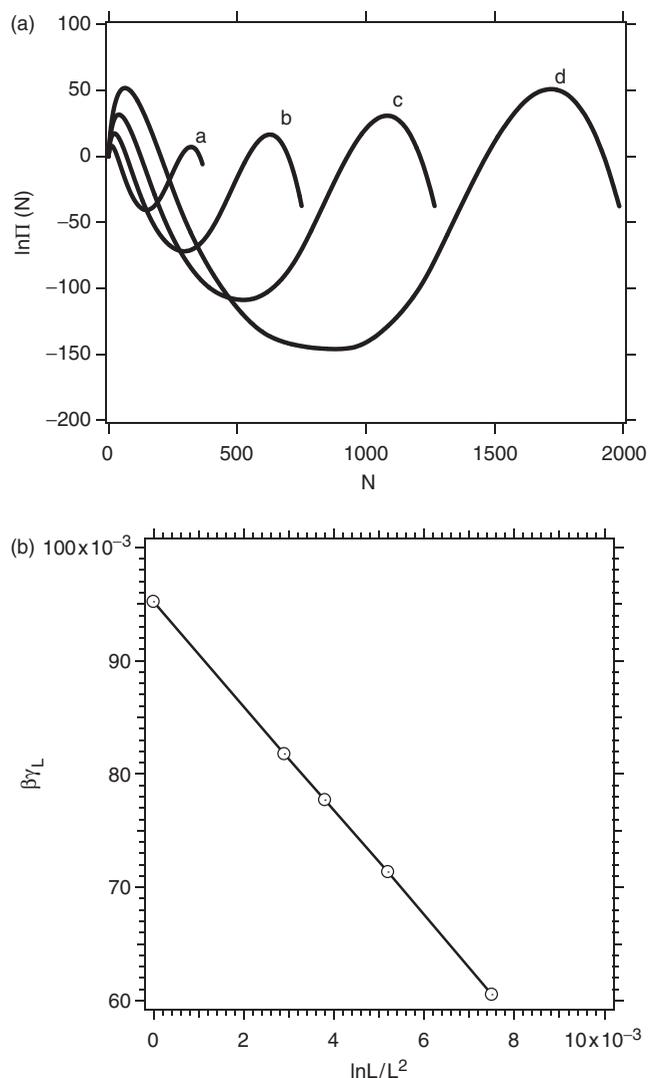


Figure 2. (a) Particle number probability distribution,  $\Pi(N)$ , for Al against number of particles in the box for varying box sizes at  $T=6200$  K and at coexistence chemical potential. Curves a, b, c and d are for simulation box lengths  $20 \text{ \AA}$ ,  $25 \text{ \AA}$ ,  $30 \text{ \AA}$  and  $35 \text{ \AA}$  respectively. (b) Finite size scaling of surface tension of Al at  $T=6200$  K.

$T=6200$  K and four different simulation box lengths,  $L=20 \text{ \AA}$ ,  $25 \text{ \AA}$ ,  $30 \text{ \AA}$  and  $35 \text{ \AA}$ . For each simulation box length,  $L$ , the free energy of the interface,  $\beta F_L$ , is determined using equation (2). Binder's formalism, given in equation (3) is used to determine the surface tension of the coexisting bulk phases as also reflected in figure 2(b), which shows a plot of  $\beta \gamma_L$  as a function of  $\ln L/L^2$  for Al at  $T=6200$  K. To determine the statistical error, for each  $L$ , at least two independent simulation runs were conducted.

The surface tension for each of the metals is plotted as a function of temperature in figure 3.

According to Guggenheim [21] the temperature dependence of surface tension,  $\gamma$ , is given by the empirical relation:

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_C}\right)^{1+r} \quad (4)$$

where  $\gamma_0$  and  $r$  are constants independent of temperature. Guggenheim determined  $r$  to be  $2/9$  from experimental data for neon, argon, nitrogen, and oxygen. The values for  $r$  and  $\gamma_0$  for the five metals under consideration in this study are given in table 3. The values for  $r$  range from  $0.0644$  for K to  $0.6038$  for Cu, with the  $r$  value of Na ( $r=0.2082$ ) being the closest to the value reported to be a constant by Guggenheim.

Macleod's equation, [22] equation (5), relates the surface tension,  $\gamma$ , to the densities of the coexisting

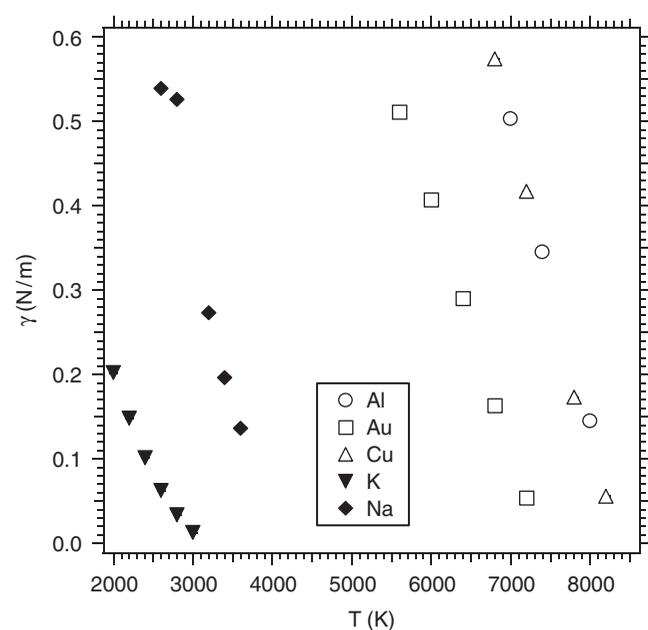


Figure 3. Surface tension, in N/m, of metals as a function of temperature.

vapour and liquid phases,  $\rho_v$  and  $\rho_l$ , respectively, at a given temperature,  $T$ :

$$\frac{\gamma}{(\rho_l - \rho_v)^p} = C \quad (5)$$

Macleod showed that the constant  $C$  is independent of temperature for a given substance and the approximate value of  $p$  is 4.0 based on the behaviour of organic compounds such as benzene, chloro-benzene, ether, methyl formate and ethyl acetate. Guggenheim calculated the value of  $p$  to be 11/3 on the basis of  $r=2/9$ . Table 4 presents the values of  $p$  and  $\ln C$  for metals studied here. The value of  $p$  ranges from 3.855 for Na to 4.2393 for Au, and shows that Macleod's approximate estimate of  $p$  value as 4.0 holds for the metals described as Morse fluids too. The value of  $p$  for each of the five metals is higher than Guggenheim's value. The constant  $C$  is found to be independent of temperature for each of the metals considered here, as can be observed by the straight line behaviour of  $\ln \gamma$  versus  $\ln(\rho_l - \rho_v)$  plots shown in figure 4.

The results obtained from the GC-TMMC simulations for determination of surface tension for Al are collectively presented in table 5. Finite size effects on the chemical potentials, pressures, and coexistence densities of the vapour and liquid phases are observed to be insignificant. This is observed for all the five metals considered in this study though only simulation data for Al is shown in table 5.

Figure 5(a) to (e) show the interface profile for the five metals considered here at the temperatures indicated in the respective figure legends. All temperatures

considered are below the critical temperature of the metal studied. The correlation length,  $\xi$ , is determined using the square gradient theory [23] and is expressed as a function of temperature as given in the equation

$$\xi = \xi_0 \left(1 - \frac{T}{T_C}\right)^{-\nu} \quad (6)$$

where  $\xi_0$  and  $\nu$  are constants. The values of  $\xi_0$  and  $\nu$  are given in table 6 for each of the five metals. Figure 6 illustrates that the correlation length varies with temperature as in equation (6). The value of  $\nu$  in case of all five metals is very different from the three dimensional Ising model [24] predicted value of 0.630, which has also been found to be true for Lennard-Jones fluids [24]. The Morse potential is therefore able to demonstrate the deviation in the behaviour of fluid metals from simple fluids.

#### 4. Conclusions

The interfacial tension and density profiles of the coexisting vapour and liquid phases are determined for Morse fluids. The parameters of the model considered are taken to be in the range coinciding with those describing metals. The interfacial tension values for all five metals follow the Guggenheim relation and Macleod's equation. However, the values

Table 3. Values for  $r$  and  $\gamma_0$  in the Guggenheim equation.

Metal	$r$	$\gamma_0$
Al	0.0972	3.409276
Cu	0.6038	6.744315
Au	0.3543	3.416443
K	0.2082	0.621388
Na	0.0644	1.763852

Table 4. Values for  $p$  and  $\ln C$  in Macleod's equation (5).

Metal	$p$	$\ln C$
Al	3.9988	-29.989
Cu	4.0296	-34.919
Au	4.2393	-40.624
K	3.8550	-27.063
Na	3.8567	-27.271

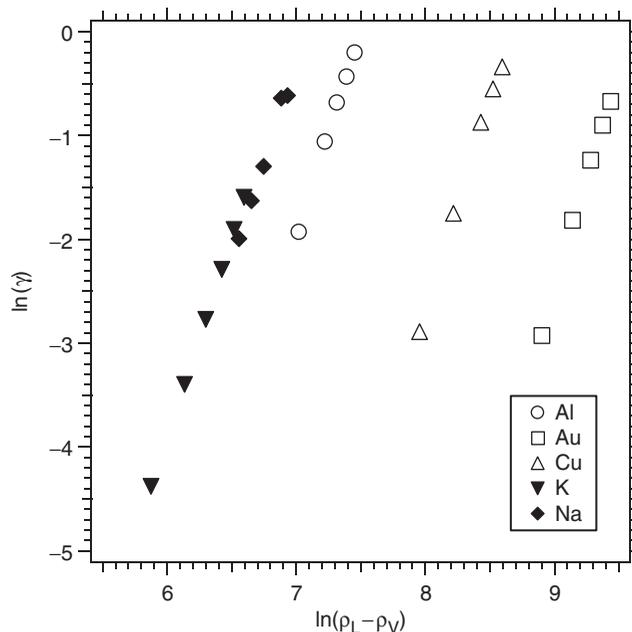


Figure 4. Surface tension plot as per MacLeod's relation. Units of  $\gamma$  and  $\rho$  are in N/m and  $\text{kg/m}^3$  respectively.

Table 5. Finite size effects on the chemical potentials (in units of  $D$ ), pressures (in units of  $D/(\text{\AA})^3$ ) and coexistence number densities (in units of molecules/ $(\text{\AA})^3$ ) of the vapour and liquid phases for Al. The numbers in the brackets are the errors in the last significant digits. The errors are not indicated where the error is an order of magnitude smaller than the last significant.

$L$	$T$ (K)	$\beta\mu$	$P$	$\rho_L$	$\rho_v$
25	6200	-6.79547(08)	0.00254	0.04006(1)	0.00151
	6600	-6.54242(21)	0.00359	0.03835(1)	0.00210
	7000	-6.32214(35)	0.00492	0.03646(1)	0.00286
	7400	-6.12984(35)	0.00653	0.03446(7)	0.00384
	8000	-5.88524(13)	0.00954	0.03096(7)	0.00594(1)
30	6200	-6.8009(65)	0.00252	0.044(6)	0.00150(1)
	6600	-6.54294(07)	0.00359	0.03831(2)	0.00210
	7000	-6.32265(01)	0.00491	0.03650(1)	0.00286
	7400	-6.13031(04)	0.00653	0.03449	0.00384
	8000	-5.88618(20)	0.00953	0.03096(4)	0.00592(1)
35	6200	-6.79569(24)	0.00254	0.04010(4)	0.00151
	6600	-6.54329(11)	0.00359	0.03837(1)	0.00210
	7000	-6.32258(39)	0.00491	0.03649(4)	0.00286
	7400	-6.13025(07)	0.00653	0.03448(2)	0.00384
	8000	-5.88586(39)	0.00953	0.03092(4)	0.00591

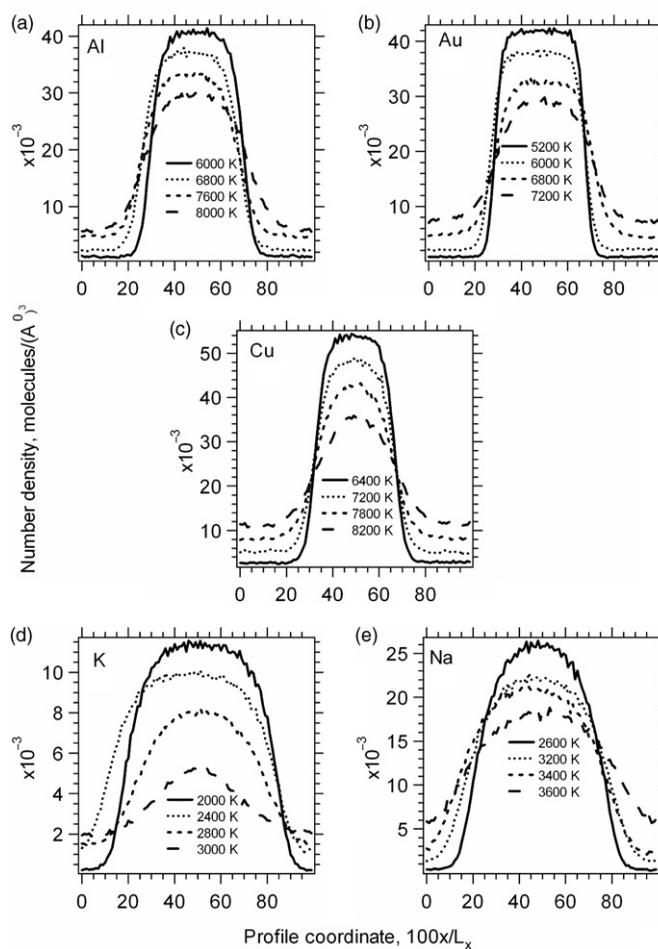
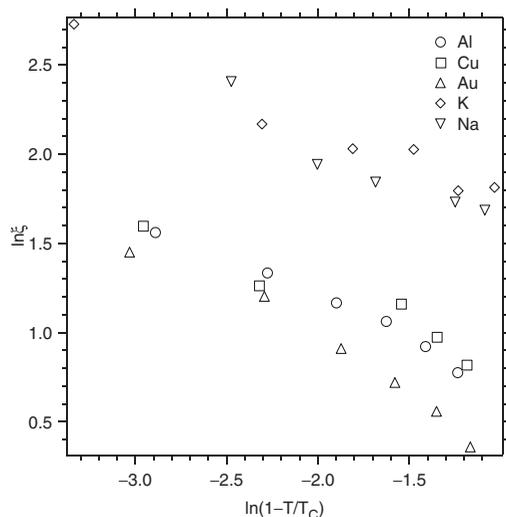


Figure 5. Vapour-liquid density profiles of different metals.

Table 6. Values for  $\xi_0$  and  $\nu$  in the Guggenheim equation.

Metal	$\xi_0$ (Å)	$\nu$
Al	1.31062	0.4579
Cu	1.566118	0.3816
Au	0.796602	0.5809
K	3.889964	0.3935
Na	3.008074	0.4823

Figure 6. Variation of correlation length,  $\xi$ , measured in Angstrom with temperature,  $T$ (Kelvin) for Al, Cu, Au, Na and K.

of the constants,  $\gamma_0$ ,  $r$ ,  $p$  and  $C$ , though found to be independent of temperature for each metal, vary with the metal studied. The value for  $p$  in Macleod's equation can be approximated to the value determined by Macleod, namely  $p=4$ . The density profiles demonstrate the transition of the vapour phase into the liquid phase in the simulation box. The correlation length as determined from the density profile is also found to follow the universal relation given by equation (6). The constants,  $\xi_0$  and  $\nu$ , are found to be independent of temperature for each metal. The value  $\nu$  is not a universal constant with Ising model value of 0.630, but again is different for each metal. Fluid metals are anticipated to behave differently from simple fluids. The Morse fluids describing the metals

are able to demonstrate differences in behaviour from simple fluids.

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