Molecular Dynamics Simulation of Potassium along the Liquid-Vapor Coexistence Curve

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The applicability of pair potential functions to liquid alkali metals is questionable. On the one hand, some recent reports in the literature suggest the validity of two-parameter pair-wise additive Lennard-Jones (LJ) potentials for liquid alkali metals. On the other hand, there are some reports suggesting the inaccuracy of pair potential functions for liquid metals. In this work, we have performed extensive molecular dynamics simulations of vapor-liquid phase equilibria in potassium to check the validity of the proposed LJ potentials and to improve their accuracy by changing the LJ exponents and taking into account the temperature-dependencies of the potential parameters. We have calculated the orthobaric liquid and vapor densities of potassium using LJ (12-6), LJ (8.5-4) and LJ (5-4), effective pair potential energy functions. The results show that using an LJ (8.5-4) potential energy function with temperature-independent parameters, ε and σ, is inadequate to account for the vapor-liquid coexistence properties of potassium. Taking into account the temperature-dependencies of the LJ parameters, $\varepsilon(T)$ and $\sigma(T)$, we obtained the densities of coexisting liquid and vapor potassium in a much better agreement with experimental data. Changing the magnitude of repulsive and attractive contributions to the potential energy function shows that a two-parameter LJ (5-4) potential can well reproduce the densities of liquid and vapor potassium. The results show that LJ (5-4) potential with temperature-dependent parameters produces the densities of liquid and vapor potassium more accurately, compared to the results obtained using LJ (12-6) and LJ (8.5-4) potential energy functions.

Keywords: Coexisting phases, Molecular dynamics simulation, Potential energy functions, Potassium

INTRODUCTION

There is an increasing demand for a reliable and consistent set of thermodynamic data for alkali metals. This demand is based on their growing technical importance, due mainly to their specific advantages for high temperature applications. Alkali metals act as working fluids for Rankine cycles, solar power plants and magnetohydrodynamic power generation [1,2]. The rapidly increasing fuel costs and the need for

improved thermal efficiency of power plants led to an increase in the peak temperature of the cycles. Due to the difficulties associated with experimental measurements, only few sources of experimental data are available on liquid metals, especially at very high temperatures and pressures. In these circumstances there is a growing need for an accurate theoretical model to supplement the available experimental data.

Of the most conventional methods of prediction one may address to the development of the equations of state and accurate correlation schemes to predict thermodynamic

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properties [3-8]. However, equations of state are not accurate enough to be applicable over a wide range of temperatures. Besides, they need some fitting parameters, which usually do not have a clear physical interpretation. Moreover, some input parameters, like the critical constants, in the equations of states require tedious experimental work to determine.

Molecular simulation methods, on the contrary, are useful and desirable tools to determine the bulk properties of fluids from molecular level properties. These methods do not invoke any approximations, give information about single molecules, which are not available experimentally, and can be applied to the study of models of variable complexity. However, the accuracy of predictions by molecular simulation methods strongly depends on the intermolecular potential energy function involved, but the determination of a suitable potential energy function has been proved to be a considerable challenge. This is even more complicated in the case of alkali metal vapors, as there are some contradictory reports in the literature. On the one hand, it is known that liquid metals do not obey pair-wise additive potentials [9-11]. On the other hand, some new reports on the development of equation of state for liquid alkali metals show the validity of a simple LJ-type potential with pair-wise additive interactions [12-14].

Although the LJ model is known to be inaccurate as a representation of the intermolecular potential for the inert gases [15], it is sufficiently close to reality in that the LJ fluid provides a convenient model for testing liquid theories and for investigating such phenomena as melting, the liquid-vapor interface, nucleation, *etc*. However, as stated above, there are some contradictory reports on the validity of such a potential model, with simple pair-wise additive interactions, to fluid metals. Therefore, the motivations of this work are: 1) check the validity of the proposed LJ pair-wise additive potentials to fluid potassium and 2) improve the accuracy of the LJ type potential by changing the LJ exponents and taking into account the temperature-dependencies of the LJ parameters. Three LJ potential energy functions are employed for this purpose; a) the conventional LJ (12-6) potential, proposed by Ghatee *et al*. [14] b) the LJ (8.5-4) potential energy function proposed by Kozhevnikov *et al*. [12] based on the volume-dependence of the internal pressure in liquid cesium and c) a modified LJ (5-4) potential energy function, which is proposed here based on the comparison of the results of the two former

potentials with experimental liquid and vapor densities and the freezing temperature of potassium. We have calculated the liquid-vapor equilibria as a sensitive test of the force field.

THEORY

Monte Carlo and molecular dynamics simulations on alkali metal melts have been performed employing the so-called density-dependent effective pair potentials [16,17]. The effective pair potential between metallic ions is given, in principle, by the self-consistent second-order perturbation calculation of the adiabatic potential energy of ions, and it is necessarily density dependent [16,17]. The density-dependent effective pair potential for alkali metals first proposed by Price *et al*. [18] and Price [19] and later developed by Shimoji [20], assuming the empty-core pseudo potential for the electron-ion interaction.

It is shown by Rahman [21,22] that this empty-core pair potential is useful in estimating the density fluctuations in liquid rubidium near the melting point. These density-dependent potentials have been employed to calculate mostly the structural properties of molten alkali metals using molecular simulation techniques [16,17]. However, calculations resulting in the density and other properties of alkali melts over a wide range of temperatures and pressures are scarce. May be the main difficulty in employing these potentials is that they are density-dependent; therefore, the potential energy parameters are state-dependent and they can not easily be implemented as a general potential energy function in Monte Carlo or molecular dynamics simulation codes. As a result, it is of great interest to develop theoretical expressions for the effective pair potential of fluid alkali metals, to calculate their thermodynamic properties using molecular simulation methods.

We assume that the potential energy interacting between a pair of potassium atoms is pair-wise additive. Therefore, the interaction energy among the atoms is written as:

$$U = \sum_{i}^{N} \sum_{j>i}^{N} u(r_{ij}) \qquad (1)$$

where r_{ij} is the distance between atoms i and j. This form of interaction between atoms neglects the simultaneous multi-

body interaction between atoms. In simulation methods a pair-wise additive potential is easier to perform, because the multi-body interactions will drastically increase the required time of simulation. One of the most useful pair potentials, which has widely been applied in simulation methods, is the proposed one in 1924 by Lennard-Jones [23,24], which reads as follows:

$$u(r) = k\varepsilon \left[\left(\frac{\sigma}{r} \right)^m - \left(\frac{\sigma}{r} \right)^n \right] \tag{2}$$

with

$$k = \frac{m}{m-n} \left(\frac{m}{n} \right)^{\frac{n}{m-n}} \tag{3}$$

where σ is the distance at which $u = 0$ and ε is the potential well depth. The common choice of m is $m = 6$, because the leading term in London's theory for dispersion forces varies ad r^{-6} [25]. It is also popular to choose $n = 12$, but this choice has no physical interpretation.

Thus, for almost all fluids, the dispersion forces are taken into account by an LJ (12-6) potential energy function. The effects of other kinds of interactions, like coulombic interactions, are then taken into account as separate terms in molecular simulation methods. However, if the dispersion forces are not a good estimate of the potential energy of interaction between atoms, the LJ (12-6) can not be considered as a proper potential model for this purpose. The potential energy of interaction in alkali metal atoms changes from a screened columbic potential in solid state to the LJ-type interaction in vapor state [26,27]. This means that a simple LJ (12-6) potential is not sufficient to account for the interaction energy over a whole fluid state, which is the subject of this study.

Based on the above-mentioned explanations, it seems that inclusion of multi-body interactions in the potential energy of interaction in fluid alkali metals may improve the validity of the force field. Recently, Raabe and Sadus [9] and Raabe et al. [10] have shown that three body interactions are important in calculating the vapor-liquid coexistence curve of mercury. In addition, the results reported by Koshevnikov et al. [12] show that liquid cesium obeys a simple LJ (8.5-4) potential energy function with pair-wise additive interactions. Similar findings are reported by Ghatee and Sanchooli [13], Ghatee et al. [14]

and Ghatee and Niroomand-Hosseini [28]. In this work, we first check the validity of LJ-type pair-wise additive forces, as the inclusion of multi-body interactions will considerably increase the simulation times.

In 2003, Ghatee and Sanchooli [13] adopted the conclusion by Kozhevnikov et al. [12] and reported the linearity of $(Z-1)V^{8.5/3}$ vs. $\rho^{-4.5/3}$, where Z is the compressibility factor and ρ is the density. They also applied this potential to calculate the transport properties of cesium vapor at high temperatures and concluded that LJ (8.5-4) potential energy function well describes the PVT properties of liquid cesium as well as the transport properties of low density gaseous cesium [13]. Ghatee and Niroomand-Hosseini [28] applied the same potential in the case of transport property calculations from the Chapman-Enskog solution of the Boltzmann equation for alkali vapors, including potassium, and concluded that LJ (8.5-4) potential is accurate enough for prediction of transport properties of low-density potassium vapor, over a temperature range of 700-1500 K. In this work, we will first check the validity of the conventional LJ, LJ (12-6) potential proposed by Ghateee et al. [14] and that of LJ (8.5-4) potential for fluid potassium with a set of parameters reported by Ghatee and Niroomand-Hosseini [28], by performing molecular dynamics simulation. Then, we will check the accuracy of other LJ-type potentials with different m and n in Eq. (2), and also take into account the temperature-dependencies of LJ parameters, σ and ε, with the intention of improving the results.

METHOD

Molecular dynamics simulations were performed in NPT ensemble for $N = 1000$ particles in liquid state and $N = 300$ particles in gaseous state. The volume of the simulation box was chosen in such a way that the resulting density corresponded to either the density of the liquid or the vapor phases of potassium and NPT ensemble simulations were performed. The coupling to a thermostat and a barostat was performed via a weak coupling method [29]. The coupling times were 0.2 ps for coupling to the barostat, and the time step was 2.5 ps. After equilibrating the initial configuration, for a period of 1 ns, a production run of 2 ns for liquid phase and 10 ns for the gas phase, was performed at specified temperatures and pressures to calculate the average density in

each phase.

First we tried the LJ (8.5-4) potential proposed by Kozhevnikov *et al.* [12] and checked by Ghatee and Niroomand-Hosseini [28] for the case of transport property calculation of low-density potassium, with the same set of parameters, ε and σ, reported by Ghatee and Niroomand-Hosseini [28]. The calculated results in Fig. 1 show that this potential is inadequate to predict the *PVT* properties of fluid potassium. Likewise, in the case of low-density gaseous potassium the results generated using this potential are not in a full agreement with experimental data [1], and the inaccuracies increase with increasing temperature. Although this potential produces more accurate results for gaseous potassium in the range of 500-1500 K as examined by Ghatee and Niroomand-Hosseini [28], nevertheless, in this temperature range the accuracies are not justifiable. For example, at T = 1500 K the vapor density obtained using this potential deviates more than 10% from the experimental

density [1]. Moreover, the LJ (8.5-4) potential leads to pronounced deviations in the case of liquid density calculations for potassium (see Fig. 1).

Comparing our results with those of Ghatee and Niroomand-Hosseini [28], as which regards transport property calculations, shows that the deviation in the vapor density within the same range of temperatures examined by these authors exceeds to more than 10%, while their results show that the deviation in the transport properties is about 3%. There is some possible sort of error cancellation in their method of obtaining transport properties. Additionally, the authors claim that they obtained the parameters of the potential energy function, LJ (8.5-4), from experimental *PVT* data. In a similar study Ghatee and Sanchooli [13] reported the parameters of LJ (8.5-4) potential based on the linearity of $(Z-1)V^{8.5/3}$ *vs.* $\rho^{-4.5/3}$ for liquid cesium. However, the results of this work show that the said potential can not generate accurate liquid densities.
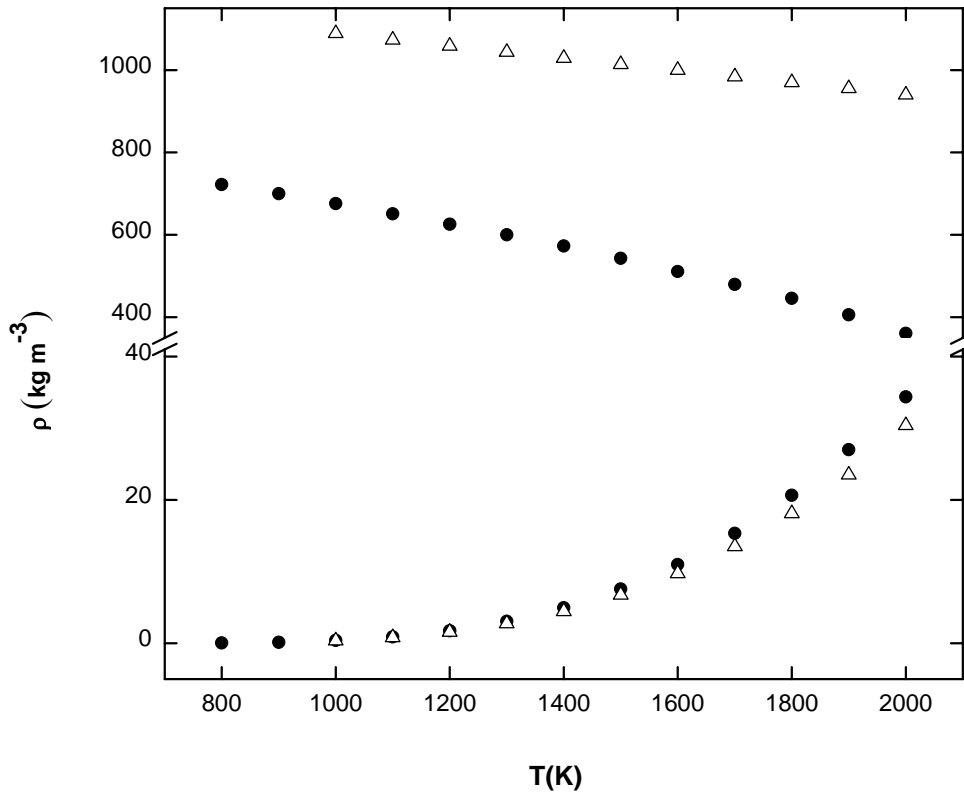
Fig. 1. The calculated densities of liquid and gaseous potassium using LJ (8.5-4) potential, with a set of parameters reported by Ghatee and Niroomand-Hosseini [26], compared with experiment [1].

We checked the linearity of $(Z-1)V^{-8.5/3}$ vs. $\rho^{-4.5/3}$ isotherms for liquid potassium, and concluded that there is nothing wrong with the linearity of these isotherms. But the conclusion obtained based on this linearity, i.e., obeying a simple LJ (8.5-4) potential energy function, is obviously not correct. It is worth mentioning that in the liquid-like density region, many other isotherms, like $(Z-1)V^2$ vs. ρ^2 [14], or PV^2 vs. ρ^2 [30] for liquid alkali metals, including liquid potassium, have already been reported to be linear. This means that the linearity of $(Z-1)V^{-8.5/3}$ vs. $\rho^{-4.5/3}$ isotherms does not prove the existence of a unique potential, like LJ (8.5-4) potential, for liquids. In fact because of the near pressure-independency of liquid density, isotherms of a function of Z vs. a function of density are linear. This is proved by the existence of the afore-cited linear isotherms [13,14,30], all observed for liquid metals, and also for ordinary fluids [31-33], but none of these regularities results in a specific potential energy function.

Because of the extended fluid range (melting point of 337 K and the critical point of 2280 K), probably an LJ potential with a single set of parameters, fitted at one temperature, can not predict the PVT properties over a range of temperatures as wide as 2000 K. It is worth mentioning that, for ordinary fluids, the vapor pressure curve extends just over a few hundred Kelvins. Therefore, one way to increase the accuracy of the predictions is to apply a temperature-dependent potential to the fluid potassium. This can be performed by introducing temperature-dependent parameters, ε (T) and σ (T), in the potential energy function. It is should be mentioned that the density-dependent potential energy function by Kozhevnikov *et al.* [12] obviously shows the temperature/density dependencies, which can be interpreted as a potential energy function with temperature-dependent parameters. Moreover, Raabe and Sadus [9] and Raabe *et al.* [10] also introduced temperature-dependency in their tree-body interactions for the sake of simulation of liquid mercury.

To this end we performed molecular dynamics simulation of liquid potassium at three temperatures and tried to fit the best values of ε and σ at each temperature and then fit the results for LJ parameters with a second-order polynomial as:

$$\varepsilon(T) = a + bT + cT^2 \qquad (4)$$

and

$$\sigma(T) = d + eT + fT^2 \qquad (5)$$

We have performed the same calculations for conventional LJ (12-6) potential and obtained the best set of coefficients to simulate fluid potassium. The coefficients are tabulated in Table 1. The calculated results for the density of liquid and vapor potassium are shown in Fig. 2, and are compared with experimental data [1]. Our results show that employing a conventional LJ (12-6) potential with temperature-dependent parameters leads to a considerable improvement in the predicted results. Nevertheless, the results pertaining to the fluid potassium density at high temperatures are not in good agreement with the experiment [1]. Furthermore, this potential leads to solidification of liquid potassium at around 900 K, a temperature quite higher than the experimental one, 337 K [1]. We tried to improve the prediction accuracy by fitting the potential energy parameters at lower temperatures, but it led to increasing inaccuracies at higher temperatures. The same calculations were performed with the LJ (8.5-4), using the set of coefficients shown in Table 1. The results are also shown in Fig. 2 and are compared with experimental data [1] and with the results of LJ (12-6) potential. The results show that this potential predicts the PVT properties of fluid potassium more accurately than that of LJ (12-6) potential, especially for liquid potassium.

Comparing the predicted results using LJ (12-6) and LJ (8.5-4) show that using a potential energy with longer ranger attraction and softer repulsion describes the fluid potassium

Table 1. The Coefficients of Eqs. (3) and (4) for LJ (12-6), LJ (8.5-4) and LJ (5-4) Potentials

Potential	a (kJ mol^{-1})	b (kJ mol^{-1} K^{-1})	c (kJ mol^{-1} K^{-2})	d (nm)	e (nm K^{-1})	f (nm K^{-2})
LJ (12-6)	14.35	0.0018	-4×10^{-7}	0.443	-3×10^{-5}	3×10^{-8}
LJ (8.5-4)	3.171	0.0002	8×10^{-8}	0.454	-3×10^{-7}	-1×10^{-10}
LJ (5-4)	12.75	-0.0032	-3×10^{-7}	0.613	-5×10^{-5}	3×10^{-8}
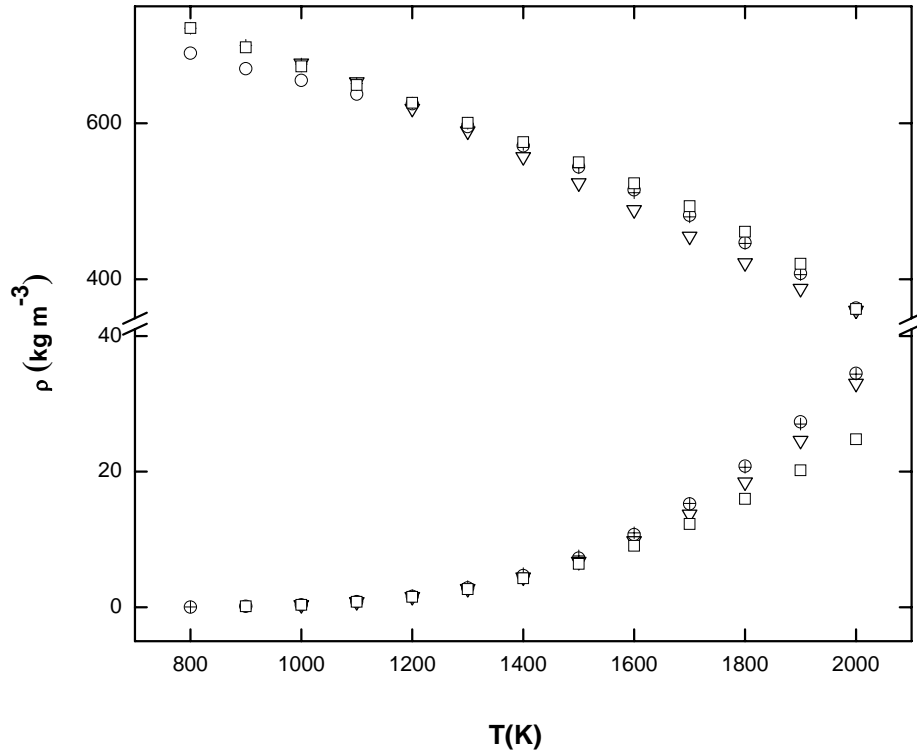
Fig. 2. Comparison of the calculated densities of liquid and gaseous potassium using temperature-dependent LJ (12-6), LJ (8.5-4) and LJ (5-4) potentials with experiment [1].

more appropriately. We employed varying values for *m* and *n* in Eq. (2), which means changing the magnitudes of attractive and repulsive contributions to the potential energy function. Our results showed that a further increase in the softness of the potential energy function improves the results. Therefore, the best potential energy function obtained in this work for this purpose is the LJ (5-4). Again the parameters of the potential, ε and σ, were fitted at three temperatures. The best values of coefficients are tabulated in Table 1.

The calculated densities of liquid and vapor phases, calculated by employing the LJ (5-4) potential with temperature-dependent parameters, are shown in Fig. 2 and are compared with the experimental data [1] and with the calculated results using LJ (12-6) and LJ (8.5-4) in the same figure. The results show that the new potential is superior to the LJ (12-6) and LJ (8.5-4) in predicting liquid-vapor line. Especially, for the vapor phase, the results of the new potential reveal better concordance with experiment [1]. Similarly, the

liquid and vapor densities at high temperatures (around 2000 K) show a better agreement with experiment compared to the LJ (12-6) and LJ (8.5-4) potentials. Additionally, this potential leads to freezing of liquid potassium at around 700 K. While there is a substantial error in predicting the freezing point of liquid potassium, the freezing point calculated using this potential is in a better agreement with experiment [1] compared to the predictions using LJ (12-6) potential, which predicts a freezing temperature of 900 K, and LJ (8.5-4) potential, which predicts a freezing temperature of 800 K. At this stage, our results show that taking into account the temperature-dependencies of LJ parameters and adjusting the magnitudes of attractive and repulsive forces play important roles in the accuracy of predictions. More accurate results can be obtained by introducing many-body interactions, like the method of Raabe and Sadus [9] and Raabe *et al.* [10]. This point needs more clarification.

In order to elucidate the structure of liquid and vapor

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potassium, we have also calculated the radial distribution functions, $g(r)$, of liquid potassium at $T = 800$, 1200 and 2000 K. The results are shown in Fig. 3. Although there is no report in the literature to compare with our calculated radial distributions functions at high temperatures, we can compare them with the results of Murphy [34], obtained by Monte Carlo simulation employing a realistic ion-ion potential, at 338 and 408 K. According to their calculations, the radial distribution function of liquid potassium at 338 and 408 K shows first peaks at 0.4455 and 0.449 nm, respectively. Our results show that the position of the first peak in $g(r)$ shifts from 0.497 nm at 800 K to 0.559 nm at 2000 K. The temperature-dependence of the position of the first peak compares finely with that of Murphy's [34], 5.17×10^{-5} K^{-1} *vs*. 5.0×10^{-5} K^{-1}. Moreover, the results of Murphy [34] show that the relative height of the first and second peaks to that of the third peak in $g(r)$ varies as: g(first peak)/g(second peak) = 2.16 and g(first peak)/g(third peak) = 1.15. Our results show that these ratios are: 2.50 and 1.13, and 2.15 and 1.14 at 800 K and 1200 K, respectively. Again our calculated relative heights in $g(r)$ are quite comparable to those of Murphy's [34]. The calculated radial distribution functions for potassium vapor at 1200 K and 2000 K are also shown in Fig. 4. The results yet

show that at this high-temperature regime the gaseous potassium shows some short-range order.

We have also checked the prediction ability of the present LJ (5-4) potential model by calculating the densities of compressed potassium over a wide range of pressures. The results are shown in Fig. 5, and show an acceptable accuracy over the pressure range for which experimental data exist in the literature [1]. Besides, the behavior of gaseous potassium at 2500 K and 3000 K is studied according to the present potential model. The results are shown in Fig. 6. It is worth mentioning that, even at this high temperature regime, the gaseous potassium shows considerable deviations from the ideality. Lack of experimental data at higher temperatures/ pressures prevents us from checking the prediction ability of the present potential model.

CONCLUSIONS

The results of the present molecular dynamics simulation study show that the LJ (8.5-4) potential energy function proposed by Kozhevnikov *et al*. [12] with the set of potential energy parameters reported by Ghatee and Niroomand-Hosseini [28] is inadequate to predict the liquid and vapor
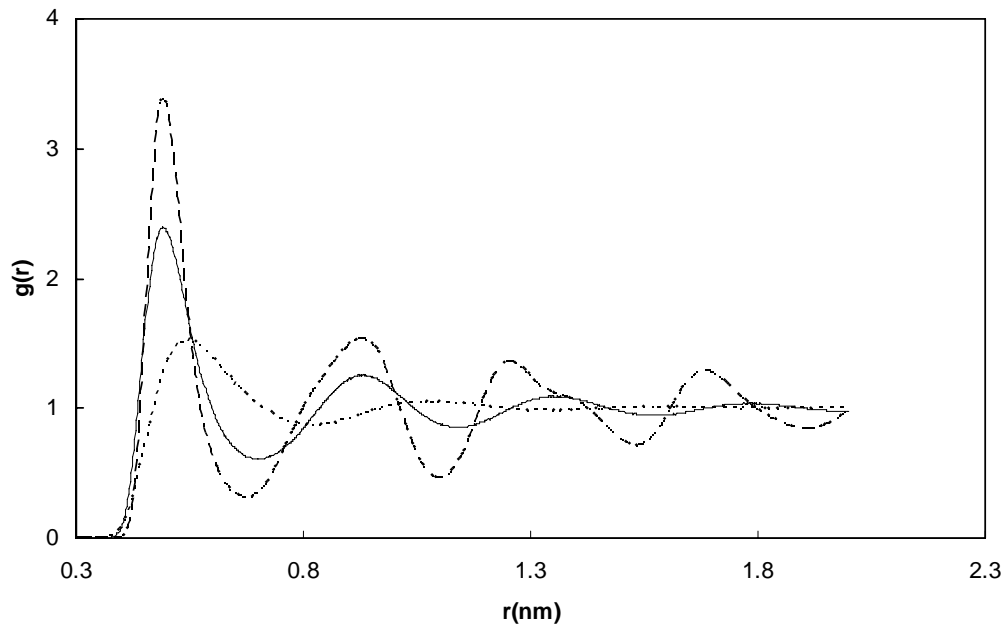
Fig. 3. The radial distribution function for liquid potassium at 800 K (dashed curve), 1200 K (full curve) and 2000 K (dotted curve).
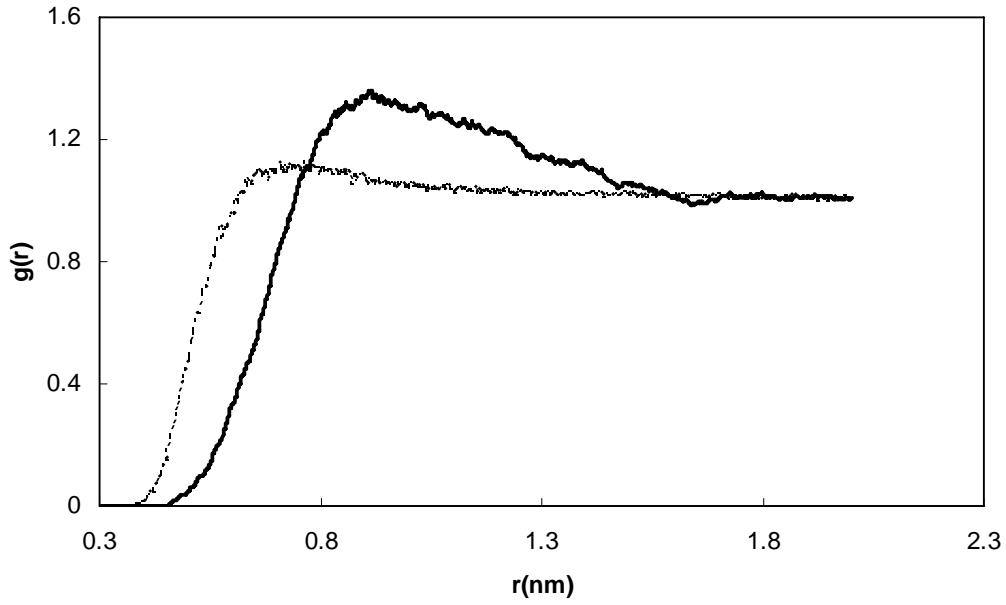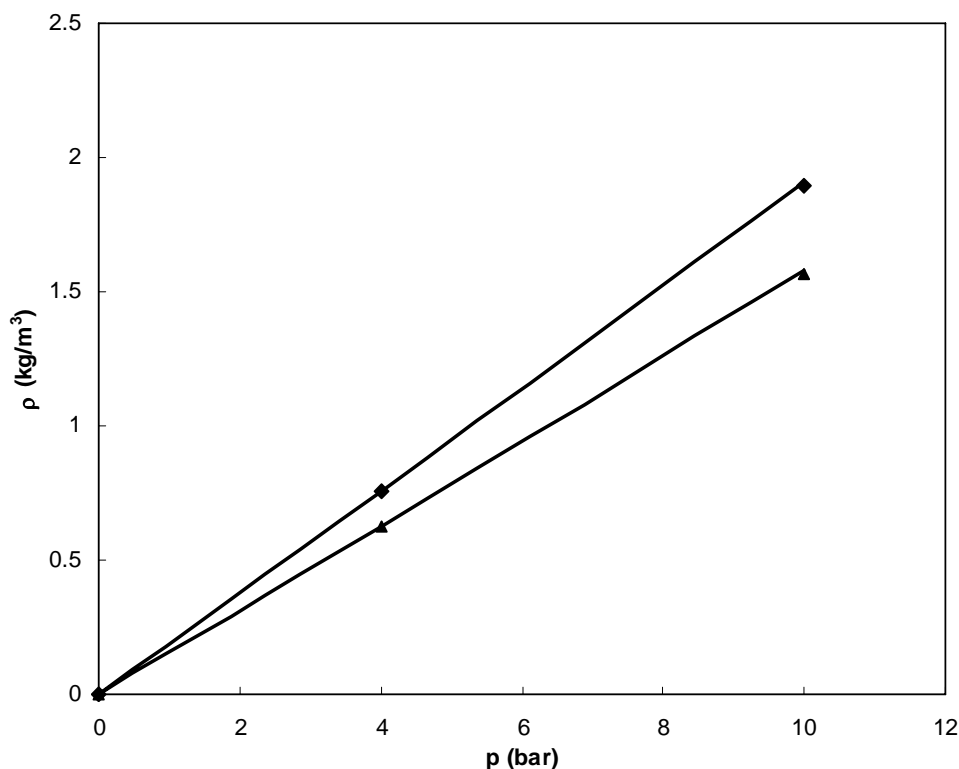
Fig. 4. The same as Fig. 3 for potassium vapor at 1200 K (full curve) and 2000 K (dotted curve).
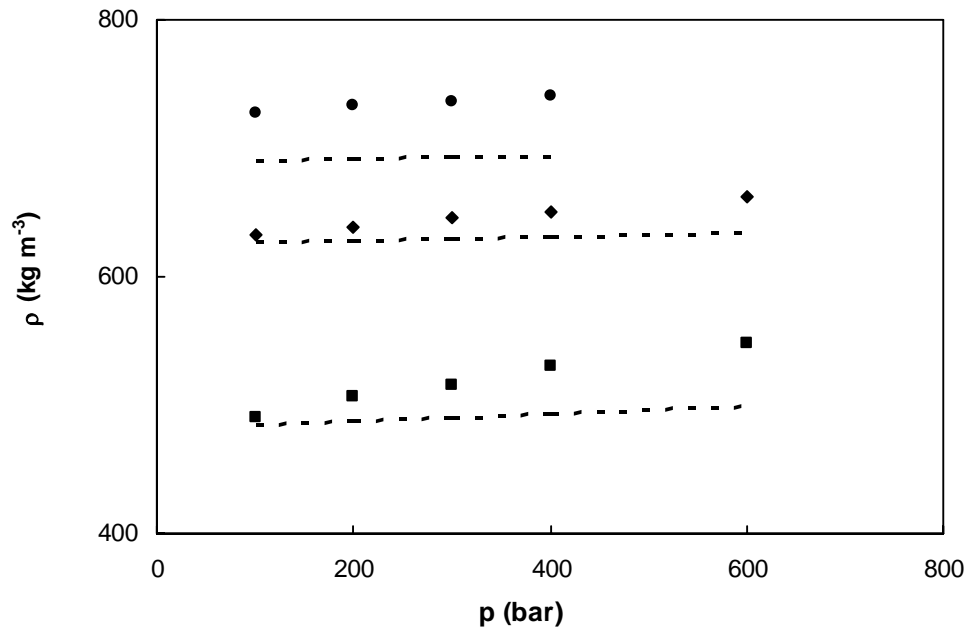
Fig. 5. Comparison of calculated and experimental densities of liquid potassium at 800 K (●), 1700 K (♦) and 2000 K (■). The points represent our calculations and the dashed lines indicate the experimental data [1].

Fig. 6. Comparison of calculated and experimental densities of gaseous potassium at 2500 K ($\blacklozenge$), and 3000 K ($\bullet$). The points represent our calculations and the lines indicate the experimental data [1].

densities of potassium with sufficient accuracy. Even though the potential energy parameters in this case are extracted by Ghatee and Niroomand-Hosseini [28] using linear isotherms of $(Z\text{-}1)V^{-8.5/3}$ *vs.* $\rho^{-4.5/3}$, the existence of such a regularity is no guarantee for potassium to obey an LJ (8.5-4) potential. In fact many similar linear isotherm regularities can exist in the liquid range for fluids, including alkali metal melts, because the liquid density in this range is insensitive to pressure change. Taking into account the temperature-dependencies of the parameters of LJ (8.5-4) and LJ (12-6) will result in a considerable improvement in the accuracy of the results. Our results also show that fluid potassium obeys a softer potential than LJ (8.5-4). Therefore, the best results in this work are produced by employing an LJ (5-4) potential, which well reproduces the experimental *PVT* data for liquid and vapor phases up to temperatures as high as 2000 K, for which the experimental data are available [1]. Taking into account the nature of many-body interactions, like the method of Raabe

and Sadus [9] and Raabe *et al*. [10], may increase the accuracy of the results. We are currently contemplating a hypothesis on the basis of this assumption which is important enough to warrant experimentation.

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