

Viscosity of liquid Na–K alloys from molecular dynamics simulations

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Abstract

The shear viscosity of liquid Na–K alloys is computed from molecular dynamics simulations using the Green–Kubo formalism. Interatomic interactions are described using effective pair potentials obtained from Fiolhais pseudo-potential and self-consistent screening. The composition dependence of the viscosity is first investigated at 373 K, then its temperature dependence at three different compositions, namely Na₁₀–K₉₀, Na₅₀–K₅₀, and Na₉₀–K₁₀. Simulation results are first compared with available experimental data. The evolution of the viscosity of the alloys versus temperature is similar to that of a pure one component fluid. This is discussed in connection with the chemical order of the mixtures.

Keywords: liquid alloy, viscosity, molecular dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

The viscosity of liquid metals and alloys is known to be very low (lower than water). Moreover, their remarkably high thermal and electrical conductivities make them potential candidates for many technological purposes like flexible devices [1], high capacity batteries [2–4], or cooling of industrial plants [5].

In a series of articles [6–8], we investigated the behaviour of the viscosity of liquid alkali metals over a wide pressure and temperature range of their phase diagram. We have been able to show that the viscosity of liquid alkali metals has a universal dependence on temperature and density. Considering the extreme thermodynamic conditions, these studies were performed using molecular dynamics simulations.

As their composition allows them to be tailored more easily than pure metals, liquid alloys can be more conveniently fitted for specific purposes. Therefore, we extended our study to alloys [9], a first one (K–Cs) with random chemical order and a second one (Li–Bi) exhibiting strong hetero-coordination tendencies.

In this study, we investigate the viscosity of Na–K liquid alloys. Our motivations are triple. First, on a fundamental point of view, this alloy is known to exhibit rather homo-coordination tendencies [10], which will add to our knowledge of

the influence of chemical order on viscosity. Second, on an application point of view, as this eutectic alloy is liquid down to 260.5 K (at 32 atomic percent of Na) [11], it would remain liquid over a wider working temperature range, which could be useful for practical purposes like as coolant for nuclear reactor [5]. And third, on a technical point of view, interactions between atoms in this alloy can be accurately described by effective pair potentials, which is essential in order to perform large scale simulations to investigate the composition and temperature dependence of its viscosity. As a matter of interest, some previous studies using effective pair potentials have been devoted to Na–K alloys. Static structure [12] and diffusion properties [13] have been studied with neutral pseudo atom model. They also have been already studied [10] using Fiolhais *et al* [14] model of interactions. As this model appears to be transferable to many different thermodynamic conditions of many alkali pure metals and alloys, and in the continuation of our previous studies of the viscosity, we have chosen to use it for the present study of the viscosity of Na–K alloys. Indeed, due to difficulties in measuring such low viscosity, and because these metals are highly reactive, there are no recent experimental data [15, 16] of the viscosity of this alloy.

After this introduction, we will present the technical details as well as some thermodynamic issues in section 2. Then, our

results will be presented in section 3, focusing more specifically on the composition and temperature dependence of viscosity.

2. Formalism

2.1. Molecular dynamics simulations

We performed classical molecular dynamics simulations in the microcanonical ensemble (N, V, E) where the number of particles N , the volume V , and the total energy E are kept constant. We used $N = 2048$ particles which were divided into Na and K kinds in due proportions. The volume of the cubic box was fitted to the desired density and periodic boundary conditions were applied. Using Verlet's algorithm in its velocity form, the equations of motion of these atoms were integrated using a time step $\Delta t \approx 0.1$ fs, depending slightly on the state point. The atoms were initially distributed over an FCC lattice with random chemical order. After a thermalisation stage of 60000 time steps long enough to allow melting and relaxation of initial order constraints, the production lasted 6000000 time steps.

From the simulations, we obtained the positions \mathbf{r} , velocities \mathbf{v} and forces \mathbf{f} of the atoms from which the stress tensor $\sigma(t)$ could be calculated. Its instantaneous elements read

$$\sigma_{\alpha\beta}(t) = -\frac{1}{V} \left(\sum_{i=1}^N m_i (\mathbf{v}_i)_\alpha (\mathbf{v}_i)_\beta + \sum_{i=1}^{N-1} \sum_{j>i}^N (\mathbf{r}_{ij})_\alpha (\mathbf{f}_{ij})_\beta \right) + \sigma_{\alpha\beta}^{(0)}(\rho, T), \quad (1)$$

where α and β stand for x , y , or z . $\sigma_{\alpha\beta}^{(0)}$ is a contribution specific to metallic liquids. As it does not depend on time, it does not contribute to the fluctuations of the stress-tensor elements $\delta\sigma_{\alpha\beta}(t) = \sigma_{\alpha\beta}(t) - \overline{\sigma_{\alpha\beta}}$, $\overline{\sigma_{\alpha\beta}}$ being its mean value over the whole simulation. From the off-diagonal elements (i.e. $\alpha \neq \beta$) stress auto-correlation function (SACF) $\langle \delta\sigma_{\alpha\beta}(0) \cdot \delta\sigma_{\alpha\beta}(t) \rangle$ where notation $\langle \dots \rangle$ refers to thermodynamic mean, the viscosity was calculated using Green-Kubo relation

$$\eta_{\alpha\beta} = \frac{V}{k_B T} \int_0^\infty \langle \delta\sigma_{\alpha\beta}(0) \cdot \delta\sigma_{\alpha\beta}(t) \rangle dt, \quad (2)$$

where V is the volume of the system, T , its temperature, and k_B , Boltzmann's constant.

As the SACF strongly fluctuates, three computational procedures were used to improve the viscosity computing accuracy (see [9] for more details). (i) At least 590000 time origins were considered in equation (2). (ii) We averaged over six equivalent off-diagonal elements of the stress tensor (σ_{xy} , σ_{yz} , σ_{xz} , $\frac{1}{2}(\sigma_{xx} - \sigma_{yy})$, $\frac{1}{2}(\sigma_{yy} - \sigma_{zz})$, and $\frac{1}{2}(\sigma_{xx} - \sigma_{zz})$). (3) We averaged over eight independent simulations corresponding to the same macroscopic state point. So, the statistical uncertainty of the computed viscosity was lower than 5%. An example of this improvement is illustrated in figure 1.

2.2. Model of interactions

In order to perform realistic simulations of Na-K liquid alloys, an accurate and transferable description of the interactions is required. Therefore, we used an effective ion-ion pair

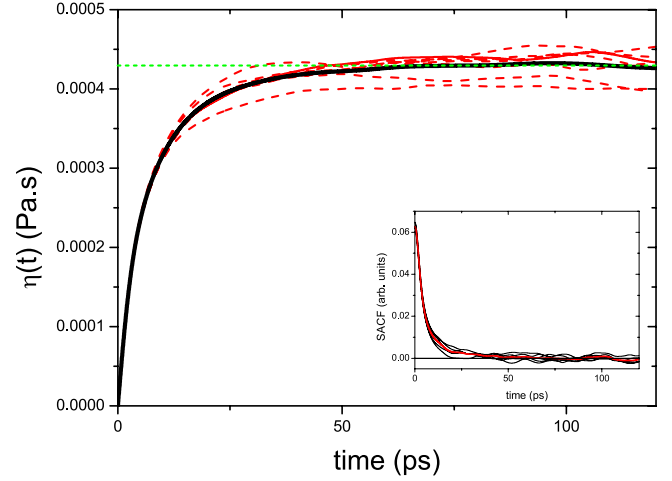


Figure 1. Illustration of the statistical improvement of the computation of the viscosity in the case of Na₅₀-K₅₀ at 373 K. SACF is computed starting with six different off-diagonal elements of the stress-tensor and considering 590000 time origins (thin black curves of the inset) from which a first mean is computed (thick red curve of the inset). Then, this mean curve is integrated over time to get the solid red curve of the main figure. This is done for eight independent runs (red curves) from which a final converged mean curve is obtained (thick solid black line). The asymptotic value (green dotted line) leads to the estimated viscosity.

potential deduced from Fiolhais *et al* [14] electron-ion model of interaction. This model of interaction was initially developed for the solid state and its transferability to the liquid state has been studied and ascertained in the case of pure alkali metals and their alloys (see [10] and references therein). When compared to available experimental data for these materials, it appears to predict accurately the static structure, as well as diffusion properties and dynamic structure. Especially in the case of Na-K alloys, interested readers are invited to refer to [10] to find a detailed analysis of static structure, self- and inter-diffusion, velocity auto-correlation functions and some thermodynamic properties.

This pair potential reads (in atomic units $e = \hbar = m_e = a_0 = 2$ Rydberg = 1)

$$u_{ij}(r) = \frac{Z_i Z_j}{r} \left\{ 1 - \frac{2}{\pi} \int_0^\infty F_{N_{ij}}(q) \frac{\sin qr}{q} dq \right\}, \quad (3)$$

where Z_i is the valency of atoms of species i and the so-called energy-wave number characteristic reads

$$F_{N_{ij}}(q) = \left(\frac{q^2}{4\pi} \right)^2 \frac{1}{Z_i Z_j} w_i(q) w_j(q) \left[1 - \frac{1}{\varepsilon(q)} \right] [1 - G(q)]. \quad (4)$$

In this equation, $w(q)$ is Fiolhais pseudopotential, $\varepsilon(q)$ and $G(q)$ are screening functions. This pair potential is density dependent and consequently depends on the composition of the alloy and the thermodynamic state point.

2.3. Thermodynamic considerations

2.3.1. Investigated state points. While pure Na and K melt at 371 and 336 K at ambient pressure, respectively, Na-K alloy phase diagram has an eutectic point at 260.5 K and 32 at.% Na

Table 1. Investigated state points from experimental densities of [16]. Top: density at 373 K as a function of composition. Bottom: density (in $\text{kg} \cdot \text{m}^{-3}$) as a function of temperature for three compositions.

K at. %	10	20	30	40	50	60	70	80	90
ρ ($\text{kg} \cdot \text{m}^{-3}$)	914.2	901.8	890.7	879.0	868.0	857.4	846.4	836.6	827.1
T (K)	280	300	400	500	600	700	800	900	1000
Na ₁₀ –K ₉₀	/	/	820.9	798.0	775.1	752.2	729.3	704.7	683.5
Na ₅₀ –K ₅₀	889.6	885.0	861.8	838.6	815.4	792.2	769.0	745.8	722.6
Na ₉₀ –K ₁₀	/	/	907.5	882.6	857.7	832.8	807.9	783.0	758.1

Table 2. Low- q limit of $S_{cc}(q)$ at 373 K from [10] where state points and potential were the same as in this work.

K at. %	10	20	30	40	50	60	70	80	90
$S_{cc}(0)$	0.12	0.24	0.30	0.325	0.335	0.32	0.27	0.195	0.11

[11]. In this study, we considered several state points. In order to investigate the composition dependence, we simulated nine regularly varied compositions at 373 K. We also studied three compositions, namely Na₁₀–K₉₀, Na₅₀–K₅₀, and Na₉₀–K₁₀, from 280 to 1000 K to examine the temperature influence. For each state point, the corresponding density at ambient pressure was determined from experimental data [16] (see table 1).

2.3.2. Chemical order. There exist many ways to evaluate the chemical order of a mixture, i.e. whether it is random, homocoordinated or heterocoordinated. In this study, we consider the low- q limit of the Bathia–Thornton partial structure factor $S_{cc}(q)$ related to concentration fluctuations. In a random mixture, $S_{cc}(0) = c_1 \cdot c_2$, the product of the concentrations of both component of the mixture. If it is larger, then the mixture has homocoordination trends, otherwise it tends to be heterocoordinated. As can be seen from table 2, Na–K alloys have homocoordination tendencies.

3. Results

3.1. Composition dependence

We first consider the influence of the composition on the viscosity of the alloy.

Our results at 373 K for nine concentrations are plotted in figure 2, as well as experimental data from [11, 15] and pure metal results from [8]. A shift exist between experimental and simulation data. It has already been observed for pure alkali metals, as well as liquid K–Cs alloy. Two reasons can be put forward. The first one is an inaccuracy in the description of the interactions which cannot be ruled out. The second one is the uncertainty in the experimental determination of the viscosity. Differences between both experimental references, even for pure sodium are worth being noticed. As we already mentioned in our previous studies, the measurement of the very low viscosity of these liquids is extremely sensitive to impurities in the sample, among which oxygen. (According to [17] 0.15 wt.% oxygen in Rb leads to an increase of 20% of

the viscosity.) The scarce experimental data date back to 1980 [11] or before. So, this demonstrates the need for an experimental clarification of this point. Nevertheless, the tendency of the composition dependence is well reproduced. Viscosity increases slightly and monotonously with Na concentration.

This evolution can be qualitatively related to the interactions in the alloy. As can be seen from [10] where the model of interactions was the same, interactions between Na–Na, Na–K and K–K pairs of atoms are quasi-additive, with a size asymmetry (K atoms being bigger than Na ones) and an interaction asymmetry (Na–Na attraction being stronger than K–K). These features are responsible for the observed homocoordination tendencies. Referring to the study of Lennard-Jones (LJ) mixtures [18], the observed slight increase of viscosity as x_{Na} increases is the result of the balancing of two effects, mass and attraction asymmetries which lead to a decrease and an increase of the viscosity, respectively. As for size asymmetry, viscosity is nearly insensitive to it.

3.2. Temperature dependence

Looking at the temperature dependence of the viscosity, our results are displayed in figure 3 together with available experimental results. The shift between experimental and simulation data is recovered, but it is less important when compared with data from Kitajima *et al* [15]. Whatever the composition, the tendency is the same and well reproduced by the simulation results. Interestingly, at low temperature where experimental data are lacking, this tendency seems to go on, and the viscosity increases strongly as temperature decreases (it nearly doubles between 400 and 300 K). This would have to be kept in mind when designing a device working at such temperatures.

This behaviour is well reproduced by an expression proposed for pure metals [6, 8]:

$$\eta(T) = (AT^2 + C)e^{B/T} \quad (5)$$

where A , B and C are density dependent parameters. The values of these parameters corresponding to the fitting curves

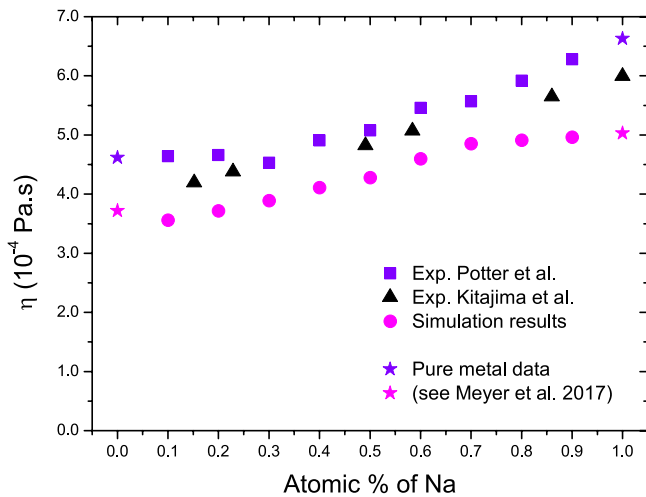


Figure 2. Viscosity of Na–K alloy versus concentration at 373 K. Experimental data are extracted from [11, 15]. Pure metal data, both experimental or from simulation, are obtained from [8].

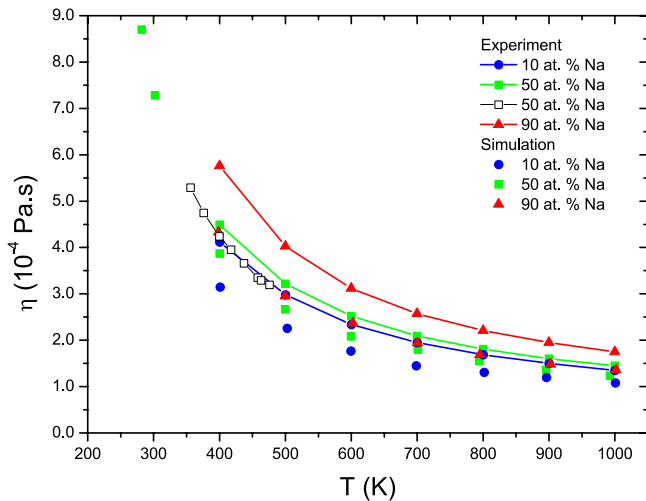


Figure 3. Viscosity of Na–K alloy versus temperature for three studied compositions. Experimental data are extracted from [11], except empty squares at 50 at.% which were obtained by [15].

in figure 4 are gathered in table 3. They are kept constant at a given composition, although density is slightly varying with temperature. The fitting range is responsible for the differences in the fitting parameters, especially the negative values of A at 10 and 90 at.% Na. In fact, as soon as the temperature range is large enough, parameters are of the same order as in pure Na and K, as is observed for the equiatomic alloy. It can also be noticed that A , B , and C values for alloys do not correspond to a simple linear interpolation between pure metals values. Anyway, equation (5) confirms its ability to describe the temperature dependence of metallic liquids.

Noticeably, the three alloys considered here behave like a pure metal. This has to be related to the additive interactions and the induced chemical order which do not change with temperature. In this kind of mixtures with weak homocoordination tendencies, but additive interactions, the viscosity keeps a temperature and composition dependence in accordance with what could be expected from studies like LJ.

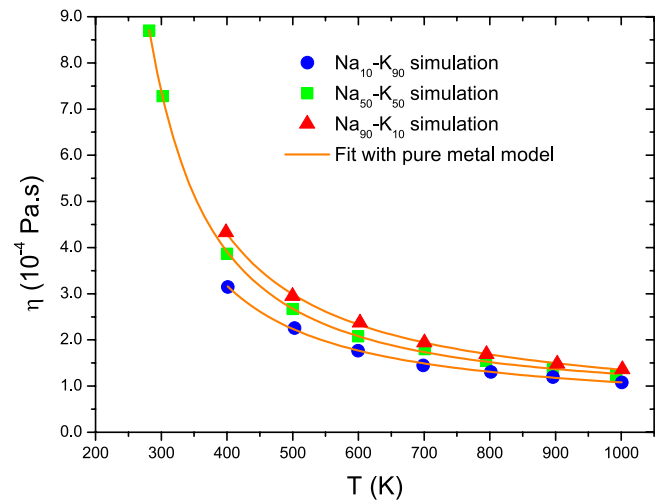


Figure 4. Simulation data fitted by pure metal empirical law.

Table 3. Fitting parameters of equation (5) corresponding to the functions drawn in figure 4.

Alloy	A ($\text{Pa} \cdot \text{s} \cdot \text{K}^{-2}$)	B (K)	C ($\text{Pa} \cdot \text{s}$)
pure K	$+1.70 \times 10^{-12}$	867.4	8.51×10^{-5}
Na ₁₀ –K ₉₀	-7.94×10^{-12}	706.11	7.00×10^{-5}
Na ₅₀ –K ₅₀	$+9.03 \times 10^{-13}$	762.75	6.00×10^{-5}
Na ₉₀ –K ₁₀	-2.94×10^{-12}	688.75	6.00×10^{-5}
pure Na	$+1.80 \times 10^{-12}$	954.9	10.9×10^{-5}

4. Summary

In this study, we have investigated the temperature and composition dependence of the viscosity of Na–K liquid alloys. The agreement with available experimental data is good, considering the experimental uncertainty and emphasizes the need for new experimental data. Simulation and experimental data follow the same trends, our simulation data extending on a wider temperature range. In qualitative terms, Fiolhais potential seems to be successful in computing the shear viscosity of Na–K.

As a consequence of the additivity of the pair interactions and the induced homocoordination tendencies in the alloy, the evolution of the viscosity of Na–K versus concentration is rather smooth. Its evolution versus temperature is similar to that of a pure one component fluid. The shear viscosity of Na–K alloys can be well represented by the relation proposed by Meyer *et al* for liquid Na [6].

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