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# Molecular dynamics simulation of liquid lithium

M Canales†, J A Padró†, L E González§ and A Giró†

† Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Pau Gargallo 5, 08028 Barcelona, Spain

‡ Departament de Física Fonamental, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

§ Departamento de Física Teórica y Física Atómica y Nuclear, Universidad de Valladolid, 47011 Valladolid, Spain

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**Abstract.** Liquid  ${}^7\text{Li}$  at 470 K is studied by molecular dynamics simulation. A recently proposed interionic effective potential with no adjustable parameters is assumed. Both structural and dynamical properties show very good agreement with the available experimental information.

## 1. Introduction

The microscopic behaviour of liquid metals is ordinarily investigated by both neutron (or x-ray) scattering and molecular dynamics (MD) simulation. Because of practical difficulties the information from experiments is only partial and the MD method is a very helpful tool to complement the experimental data. When suitable interaction potentials are assumed, MD simulation provides realistic and detailed information on the atomic trajectories which is also very useful for checking the theoretical approximations [1, 2]. Several MD simulations of liquid alkali metals have been carried out. Space-time-dependent properties of liquid Rb [3, 4] and Cs [5] have been fully investigated. However, MD studies of the other liquid alkali metals are still incomplete [6–12].

Computer simulations of liquid Li by both ordinary [7] and first-principles [11] MD methods have been performed. Nevertheless these studies are devoted to the analysis of the structure- and time-dependent properties of single particles and, to our knowledge, MD studies of collective time-dependent properties have not been carried out. In this paper we show the results obtained from MD simulations of liquid Li using a recently proposed effective interionic potential which does not require the use of adjustable parameters [13, 14]. Recent x-ray [15] and neutron [16–18] scattering measurements of the dynamic structure factor allow us to perform a rigorous test of the assumed potential.

## 2. Computation details

Liquid  ${}^7\text{Li}$  at  $T = 470$  K and  $\rho = 4.45 \times 10^{-2}$  atoms  $\text{\AA}^{-3}$  was simulated by the MD method. A set of 668 particles in a cubic box with periodic boundary conditions was considered. The Beeman algorithm with a time step of 3 fs was used for the numerical integration of the classical equations of motion. The properties were calculated from the configurations

generated during a run of  $10^5$  equilibrium time steps after an equilibration period of  $10^4$  time steps.

The interaction potential  $V(r)$  used in the MD simulations is shown in figure 1. The interactions were truncated at 9.25 Å.  $V(r)$  was constructed within the standard second-order perturbation theory, using a local pseudopotential derived from the neutral pseudo-atom method (NPA). The procedure for the calculation of  $V(r)$  is, briefly, as follows. The electron density displaced when an ion is embedded in an electron gas is computed through the NPA [19, 20] using as input the atomic number, the valence and the mean electronic density. Then, a local pseudopotential, which in the standard linear response theory reproduces this electronic density, is constructed. More details about  $V(r)$  have been given elsewhere [13, 14].

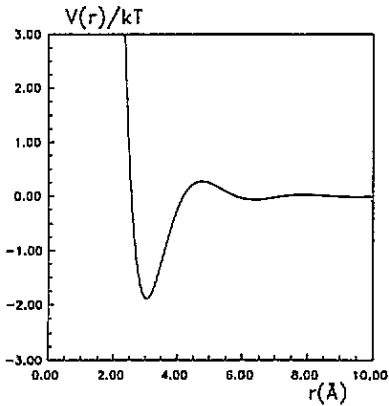


Figure 1. Interaction potential used in the MD simulations.

### 3. Results and discussion

#### 3.1. Structure and thermodynamic properties

The radial distribution function  $g(r)$  was calculated from the relative positions of particles, and the structure factor  $S(k)$  was computed by Fourier transforming the  $g(r)$ -function. Unfortunately the  $S(k)$ -factors of lithium found by different workers show noticeable discrepancies [21]. It may be observed in figure 2 that our MD results are in very good agreement with the neutron measurements of Ruppertsberg and co-workers [21]. The x-ray measurements of Waseda and Olbrich [21] show a lower  $S(k)$ -maximum and their discrepancies with our results are larger.

$S(k)$  was also calculated using the VMHC integral equation method and assuming the same interaction potential as in this work [13, 14]. These theoretical results are in good agreement with the MD findings and only small discrepancies can be observed around the second  $S(k)$ -maximum (figure 2). It should be noted that the MD results are in better accordance with the experimental data.

The internal energy of a liquid metal can be written as [22]

$$E = \frac{3}{2}k_B T + v_0(n) + 2\pi\rho \int_0^\infty r^2 V(r)g(r) dr \quad (1)$$

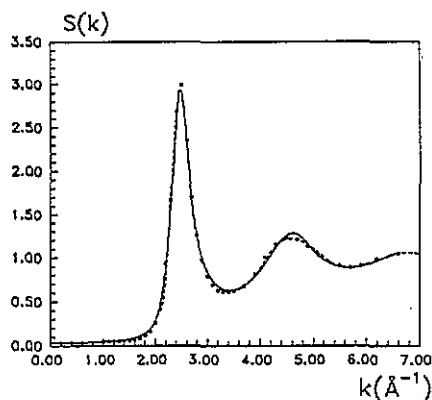


Figure 2. Structure factor from MD simulation (---), neutron scattering experiments [21] (\*) and using the VMHC approximation [13, 14] (—).

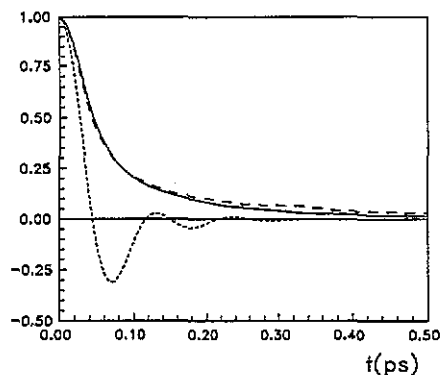


Figure 3. Normalized time correlation functions of velocities (---) and non-diagonal (—) and diagonal (— · —) stress tensor elements.

where  $v_0(n)$  is a volume term which may be theoretically calculated [13, 14] and the last term is a structural ( $E_{\text{str}}$ ) term which may be determined from the MD simulations. The resulting energy is in quite good agreement with the experimental value [23] (table 1). The structural contribution to the energy ( $E_{\text{str}}/Nk_{\text{B}}T = -7.15$ ) is close to the value obtained through the VMHC approximation ( $E_{\text{str}}/Nk_{\text{B}}T = -7.23$ ) [13, 14].

Table 1. Comparison of the properties calculated from the MD simulation with the experimental values.

Property (units)	MD simulation value	Experimental value
$E_{\text{str}} (Nk_{\text{B}}T)$	-7.15	—
$E (Nk_{\text{B}}T)$	-184	-177 [23]
$C_v (\text{kJ kg}^{-1} \text{K}^{-1})$	4.2	4.1 [25]
$D (10^{-5} \text{cm}^2 \text{s}^{-1})$	6.3	6.4 [26]
$\eta_s (10^{-4} \text{Pa s})$	5.5	5.75 [30]
$\eta_v (10^{-4} \text{Pa s})$	2.3	—

The constant-volume specific heat capacity  $C_v$  may be calculated from the fluctuations in the kinetic energy  $E_k$  during the MD simulations according to the expression [24] (it should be noted that the volume term of the energy plays no role in the calculation of  $C_v$ )

$$C_v = \{1 - \langle E_k \rangle \langle 1/E_k \rangle + (2/3N) \langle E_k \rangle \langle 1/E_k \rangle\}^{-1}. \quad (2)$$

$C_v$  was determined from a MD simulation of a mixture made up of 92.6% of  $^7\text{Li}$  and 7.4% of  $^6\text{Li}$ . The resulting  $C_v$ -value ( $C_v = 4.2 \pm 0.1 \text{ kJ kg}^{-1} \text{K}^{-1}$ ) is very close to that from the experiments with natural Li ( $C_v = 4.1 \text{ kJ kg}^{-1} \text{K}^{-1}$ ) [25].

### 3.2. Time correlation functions and transport coefficients

Individual atomic motions were analysed through the velocity autocorrelation function  $C(t)$  and mean square displacement  $r^2(t)$ . The  $C(t)$ -function (figure 3) goes to zero very rapidly

and it becomes negligible at very short times. Moreover,  $C(t)$  shows an important back-scattering around  $t = 0.07$  ps which reflects the high density of the simulated system. The self-diffusion coefficient was determined by two methods, i.e. as the time integral of  $C(t)$  and from the long-time slope of  $r^2(t)$ . The result in both cases is  $D = (6.3 \pm 0.1) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . This value is very close to the self-diffusion coefficient of  ${}^7\text{Li}$  measured by Murday and Cotts [26] using NMR techniques ( $D = (6.4 \pm 0.5) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ). The possible influence of quantum mechanical effects on the  $D$ -value for Li [27] cannot be analysed from our classical simulations.

The time-dependent elements of the microscopic stress tensor  $J_p^{xy}(t)$  [28] were calculated from the MD positions and velocities. Then, the corresponding time autocorrelation functions were computed. According to the Green-Kubo relation the time integral of the non-diagonal ( $x \neq y$ ) elements can be used for the calculation of the shear viscosity [1, 28]

$$\eta_s (V k_B T)^{-1} \int_0^\infty \langle J_p^{xy}(t) J_p^{xy}(0) \rangle dt. \quad (3)$$

$\eta_s$  may also be calculated by an Einstein-like expression from the slope of a generalized 'mean square displacement' [28, 29]. The result obtained from these procedures ( $\eta_s = (5.5 \pm 0.1) \times 10^{-4} \text{ Pa s}$ ) is in acceptable agreement with the experimental value ( $\eta_s = (5.7 \pm 0.05) \times 10^{-4} \text{ Pa s}$  [30]).

The longitudinal viscosity coefficient  $\eta_L$  may be calculated from the diagonal elements ( $x = y$ ) of the stress tensor by the Green-Kubo expression [1, 28]

$$\eta_L = (V k_B T)^{-1} \int_0^\infty \langle [J_p^{xx}(t) - pV][J_p^{xx}(0) - pV] \rangle dt. \quad (4)$$

The  $\eta_L$ -values calculated from this expression and from the corresponding 'mean square displacement' are very close ( $\eta_L = (9.6 \pm 0.1) \times 10^{-4} \text{ Pa s}$ ). The bulk viscosity coefficient  $\eta_v$  given in table 1 was determined by the relation

$$\eta_v = \eta_L - \frac{4}{3} \eta_s. \quad (5)$$

The normalized time autocorrelation functions of both non-diagonal and diagonal stress tensor elements are represented in figure 3. As for the Lennard-Jones systems [28, 29] the shapes of the two functions are very similar and do not show negative values. Moreover the decay of the time correlations of these collective properties is markedly slower than that of the  $C(t)$  function.

### 3.3. Dynamic structure factors

Both the self intermediate scattering function  $F_s(k, t)$  and the intermediate scattering function  $F(k, t)$  [1, 5] were determined from the trajectories generated during the MD simulations of  ${}^7\text{Li}$ . These functions were obtained from  $t = 0$  to  $t = 3$  ps for ten different  $k$ -values (between  $k = 0.36$  and  $k = 5.0 \text{ \AA}^{-1}$ ).

The self dynamic structure factors  $S_s(k, \omega)$  and the dynamic structure factor  $S(k, \omega)$  were obtained as the Fourier transforms of the corresponding scattering functions. Because of the slow decay of  $F_s(k, t)$  for the three smallest  $k$ -values, the Fourier transforms of these functions were calculated by assuming an exponential behaviour, which is theoretically predicted in the hydrodynamic limit [1, 2]. A window function was employed to remove

the cut-off noise in the Fourier transform of  $F(k, t)$ . In order to preserve the moments of  $S(k, \omega)$  (which are also derivatives of  $F(k, t)$  at  $t = 0$ ) the window was chosen constant for small times and slowly decaying up to zero at the last considered point of  $F(k, t)$ . This procedure renders well behaved structure factors, although it introduces the well known effects of broadening and somewhat lowering the peaks.

The  $S(k, \omega)$  results from MD are shown in figure 4. For small  $k$ -values ( $k \leq 1.76 \text{ \AA}^{-1}$ ),  $S(k, \omega)$  shows well defined peaks which indicate the existence of collective excitations. For larger  $k$ -values we cannot directly observe the existence of maxima and the values of  $S(k, \omega)$  increase to  $k = 2.5 \text{ \AA}^{-1}$  which corresponds to the maximum of  $S(k)$  (the different vertical scales used in figure 4 should be noted). These results show the same qualitative trends as those for other liquid metals [1, 5].

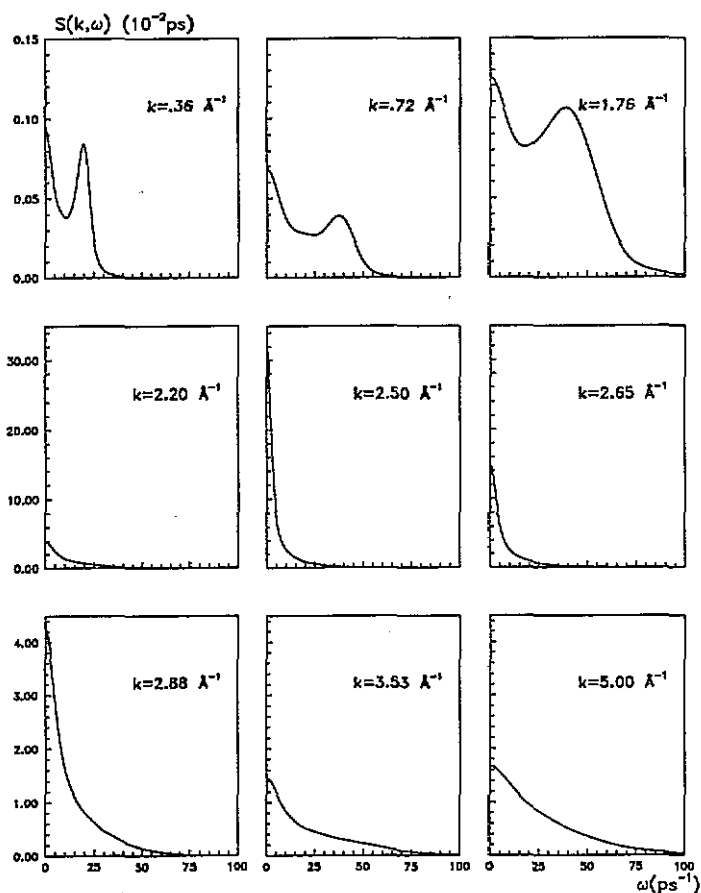


Figure 4. Dynamic structure factors for different  $k$ -values.

We also calculated the longitudinal current correlation function  $C_1(k, \omega) = \omega^2 S(k, \omega)$ . The frequencies  $\omega_1^m(k)$  of the peaks for the curves of different  $K$  are represented in figure 5. These results are consistent with the dispersion curves deduced from the  $S(k, \omega)$  peaks obtained from x-rays and neutron scattering experiments [15, 18]. As for other liquid metals [1, 5] we observe shear relaxation effects, i.e. the  $\omega_1^m(k)$ -values for small  $k$  are

slightly higher than the straight line corresponding to the adiabatic sound velocity for Li ( $c_s = 4550 \text{ m s}^{-1}$ ). As expected, our  $\omega_1^m(k)$  results are located between the low-frequency ( $\omega_0(k) = k[k_B T \gamma / m S(k)]^{1/2}$ ) and the high-frequency ( $\omega_\infty(k) = [\omega_{11}^2(k)]^{1/2}$ ) limits (see ch. 6 in [2]), where  $\omega_{11}^2(k)$  is related to the second moment of  $C_1(k, \omega)$  [1]. In the calculation of  $\omega_0(k)$  we used the experimental value of  $\gamma = 1.06$  [25] and the theoretical  $S(k)$  [13, 14] because of the uncertainties in both the experimental and the MD structure factors for small  $k$ .

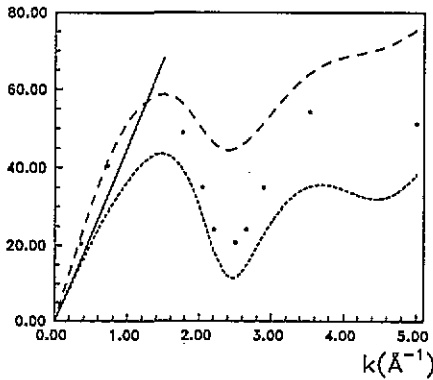


Figure 5. Dispersion curves: \*,  $\omega_1^m(k)$  from the MD simulation; —, adiabatic sound velocity; ---, low-frequency  $\omega_0(k)$  limit; - · - ·, high-frequency  $\omega_\infty(k)$  limit.

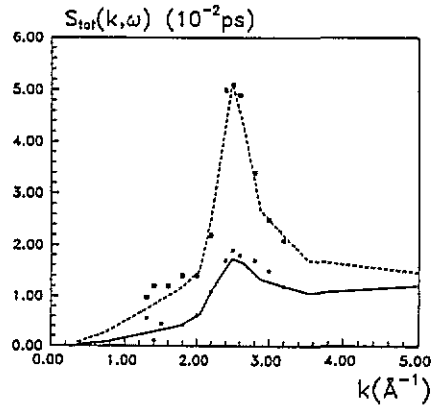


Figure 6.  $S_{\text{tot}}(k, \omega)$  from MD simulation —,  $\omega = 11 \text{ ps}^{-1}$ ; ---,  $\omega = 5 \text{ ps}^{-1}$  and from neutron experiments [17] (\*,  $\omega = 11 \text{ ps}^{-1}$ ; ■,  $\omega = 5 \text{ ps}^{-1}$ ).

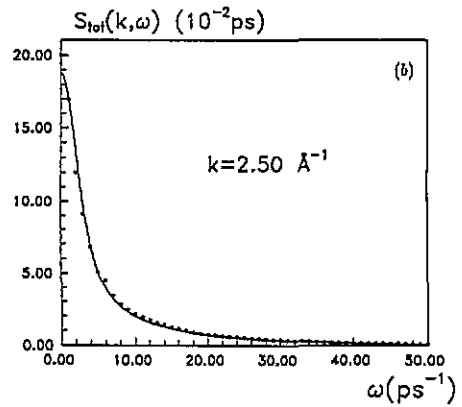
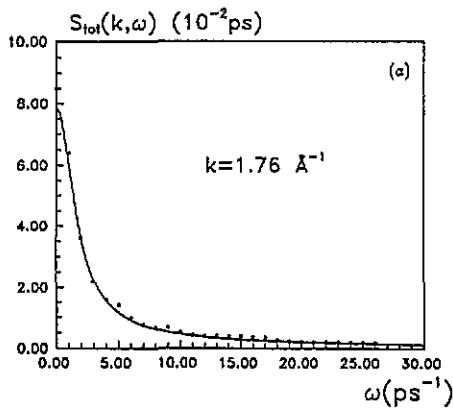


Figure 7.  $S_{\text{tot}}(k, \omega)$  for (a)  $k = 1.76 \text{ \AA}^{-1}$  and (b)  $k = 2.5 \text{ \AA}^{-1}$  from MD simulation (—) and from neutron experiments [18] (\*).

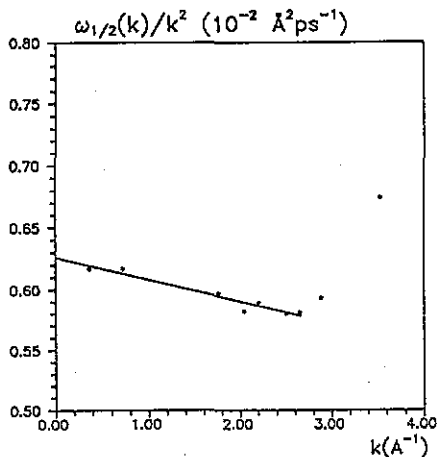


Figure 8.  $\omega_{1/2}(k)/k^2$  from MD simulation (\*); —, linear fit of the first seven points.

Neutron scattering [17, 18] and MD results for the total dynamic structure factor  $S_{\text{tot}}(k, \omega)$  are compared in figures 6 and 7.  $S_{\text{tot}}(k, \omega)$  is defined by

$$S_{\text{tot}}(k, \omega) = (\sigma^i + \sigma^c)^{-1} [\sigma^i S_s(k, \omega) + \sigma^c S(k, \omega)] \quad (6)$$

where  $\sigma^i = 0.68$  b and  $\sigma^c = 0.619$  b are the incoherent and coherent cross sections, respectively, for  ${}^7\text{Li}$ . The  $S_{\text{tot}}(k, \omega)$ -functions for  $\omega = 5$  and  $\omega = 11$   $\text{ps}^{-1}$ , represented in figure 6 as functions of  $k$ , show that the simulation and experimental findings are in very good agreement. In figure 7, we show  $S_{\text{tot}}(k, \omega)$  as a function of  $\omega$  for constant  $k = 1.76$  and  $2.5$   $\text{\AA}^{-1}$ . The agreement between simulation and experiment is also remarkable and the only noticeable differences appear for  $\omega = 0$ . However, it should be noted that the experimental uncertainties for  $\omega = 0$  are rather important because of the resolution limitations.

The half-width  $\omega_{1/2}(k)$  at half-maximum of the  $S_s(k, \omega)$ -functions were also calculated. The resulting  $\omega_{1/2}(k)/k^2$ -values are plotted as a function of  $k$  in figure 8. We can observe that  $\omega_{1/2}(k)/k^2$  for  $k < 2.65$   $\text{\AA}^{-1}$  diminishes when  $k$  increases. We fitted these points to the equation [17, 31]

$$\omega_{1/2}(k)/k^2 = D(1 - bk). \quad (7)$$

The results of the fit are  $D = 6.3 \times 10^{-1}$   $\text{\AA}^2 \text{ ps}^{-1}$  and  $b = 2.87 \times 10^{-2}$   $\text{\AA}$ . The value of  $D$  is in satisfactory agreement with the results obtained from the time correlations of single particles (section 3.2). The value of  $b$  is larger than that deduced from the neutron scattering measurements of de Jong *et al* [17] but smaller than the theoretical mode-coupling prediction ( $b = 3.84 \times 10^{-2}$   $\text{\AA}$ ).

#### 4. Concluding remarks

The results obtained in this work show that the properties of both the simulated fluid and the real  ${}^7\text{Li}$  liquid are very similar. This agreement indicates that the assumed interionic effective potential is valid not only for the study of the equilibrium properties but also for the time-dependent properties. Moreover, it should be emphasized that, although our results have been obtained from a classical simulation, they appear to be sufficiently reliable. This suggests that quantum effects will not introduce significant qualitative changes in the microscopic properties of liquid lithium.



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