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The dynamic structure of liquid lithium: results for a new type of interaction

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Abstract

The static and dynamic structure of liquid lithium (470 K) in a computer experiment were investigated using a new type of interaction: the pair potential is constructed from an ab initio molecular dynamics method which makes the effective interionic potential self-consistent with the radial distribution functions on the basis of the quantal hypernetted-chain theory. Comparisons of the new calculations both with data obtained in ab initio simulations and with transport properties show very good agreement and thus justify the use of a more sophisticated interatomic pair potential.

1. Introduction

Systematic investigations of the atomic and dynamic structure of the liquid alkali metals performed during the past years [1,2] have shown that computer experiments have to be considered as complementary to neutron scattering experiments: together they offer a deeper insight into the dynamic properties of liquids. In a region sufficiently far from the critical point, both the structure and the thermodynamic properties obtained in computer experiments are in good agreement with experimental data. The only exception to this pattern among the alkalis is lithium, for which comparatively large discrepancies between theory and experiments are observed. Therefore, during the past few years an increased effort has been dedicated to study this element both in experiment [3,4] and theory [5,6]. The particular problem for lithium lies in its electronic structure: it does not have p-states in the ionic core, so the p-component of the valence orbitals cannot be 'pseudized'. Hence the pseudopotential is non-local, acting much more strongly on p- than on s-states. In particular, two attempts have been made with potentials based on theories more sophisticated than simple local pseudopotentials: the neutral pseudoatom method (NPA) [7] and an approach based on an optimized orthogonalized-plane-wave pseudopotentials [8]. In this contribution we propose a new interatomic pair potential which is calculated from a molecular dynamics (MD) method, making the effective interionic potential self-consistent with the radial distribution functions on the basis of the quantal hypernetted-chain theory. We present results obtained by this method for the dynamic structure factor at 470 K and compare those data with results from ab initio simulations [9]. Since the present study has to be considered as a test for the interatomic potential we have chosen a comparison with another computer experiment; furthermore

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the extraction of the dynamic structure factor from neutron scattering data requires the use of models [3], which might introduce some uncertainty in the data.

2. Theory

2.1. Construction of potential

In two-component model of a simple liquid metal (electrons, *e*, and ions, *I*) characterized by pair potentials $v_{ij}(r)$, pair distribution functions (PDFs), $g_{ij}(r)$, and direct correlations functions (DCFs), $c_{ij}(r)$. This model can be reduced by means of density functional theory to a one-component model of a liquid metal. One thus arrives at a set of two exact integral equations [10] (*i*) one equation for the DCF, $c(r)$, of a one-component fluid:

$$c(r) = \exp[-\beta v_{\text{eff}}(r) + \Gamma(r) + B_{II}(r)] - 1 - \Gamma(r) \qquad (1)$$

and a second equation for the effective interaction, $v_{\text{eff}}(r)$:

$$\beta v_{\text{eff}}(Q) = \beta v_{II}(Q) - \frac{|c_{eI}(Q)|^2 n_0^e \chi_Q^0}{1 - n_0^e c_{ee}(Q) \chi_Q^0}, \qquad (2)$$

with

$$\hat{B} c_{eI}(r) = n_e^0[r|(v_{eI} - \Gamma_{eI}/\beta - B_{eI}/\beta)] / n_0^e - 1 - \hat{B}\Gamma_{eI}(r). \qquad (3)$$

The term $n_e^0(r|U_e^{\text{eff}}$, is determined by solving the wave equation for an electron under the external potential $U_e^{\text{eff}}(r)$, χ_Q^0 is the density response function of the non-interacting electrons, n_0^e is the electron density, $\hat{B}$ is an operator representing some quantum effect and $\Gamma(r) = \int c(|\boldsymbol{r} - \boldsymbol{r}'|) n_0^I [g_{II}(r') - 1] \mathrm{d}\boldsymbol{r}'$. The effective interaction $v_{\text{eff}}(r)$ depends on the ion configuration through the term $\Gamma_{eI}(r) = \sum_{l=e,I} \int c_{el}(|\boldsymbol{r} - \boldsymbol{r}'|) n_0^l [g_{lI}(r) - 1] \mathrm{d}\boldsymbol{r}'$. The quantal hypernetted-chain (QHNC) $[B_{eI} \simeq 0]$ and some approximations are now introduced for Eqs. (1) and (2), which makes them tractable [10]. The effective potential $v_{\text{eff}}(r)$ is now obtained by an iterative procedure. We start with some reasonable initial guess and calculate $g_{II}(r)$ from a classical MD run, which helps us solve Eq. (1). We then obtain via Eq. (2) a new $v_{\text{eff}}(r)$ and iterate this cycle until self-consistency is obtained. Here, the integral equation for $c_{eI}(r)$, Eq. (2), is solved by the method described in Ref. [11]. This process yields the effective interionic interaction $v_{\text{eff}}(r)$, which is consistent with $g_{eI}(r)$, $g_{II}(r)$ and $B_{II}(r)$. In an effort to avoid truncation errors, the PDFs are extended beyond the truncation radius of the simulation by an efficient procedure [12]. More (numerical) details about this method have already been described in previous papers [10,12]. This method (QHNC–MD) is completely parameter-free and requires as input only the atomic number and the parameters of the thermodynamic states.

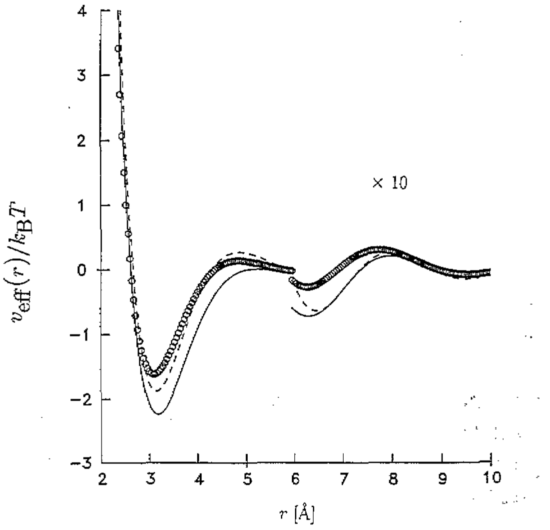

Fig. 1. Effective interatomic pair potential $v_{\text{eff}}(r)$ for liquid lithium at 470 K as a function of r as obtained from the QHNC–MD method (this paper; full line), as used in a previous study (symbols; [6]) and as obtained from the NPA method (broken line; [7]).

In this study we have investigated liquid lithium at a temperature of 470 K. In Fig. 1, we display the effective interatomic pair potential as obtained in QHNC–MD, along with the potential used in a recent study [6]. We observe rather large discrepancies, in particular near the first minimum, which is the more astonishing since results for the static structure obtained from both are in good agreement.

In our calculations for liquid lithium at 470 K, convergence of the above procedure was obtained after two steps; for the first MD run we used 16000 particles, while for the second one we restricted ourselves to 4000 particles.

2.2. The simulation and the models

Starting from the effective pair potential shown in Fig. 1, the dynamic CFs were obtained in standard microcanonical MD runs with 2048 particles; the runs were extended over 100 000 timesteps Δt (of 0.1 fs). The same accuracy requirements used in previous computer experiments [13] were imposed. For further details about the determination of the dynamic CFs from the positions and velocities of the particles, the averaging process and the models applied for the interpretation, we refer the reader to these papers [13].

3. Results

In Fig. 2, we show the results for the static structure factor: we compare data obtained in our computer experiment with neutron scattering data obtained by Ruppersberg and Egger [14]. As in previous studies of liquid lithium [5,6], we find excellent agreement, which indicates once more that the static structure is not too sensitive to the interatomic potential.

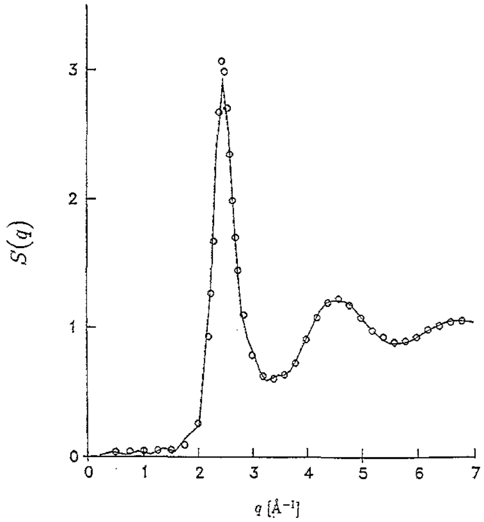

Fig. 2. Static structure factor $S(q)$ as a function of q as obtained in a computer experiment in the present study (full line) compared with experimental neutron scattering data [14].

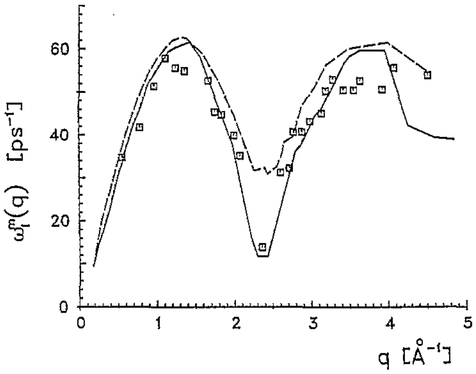

Fig. 3. Longitudinal dispersion relation $\omega_l^m(q)$ as a function of q: full line, present study; broken line, results from previous study [6]; symbols: results from ab initio simulations [9].

As reference data for our dynamic CFs we have chosen data from a recent ab initio simulation of liquid lithium performed by Kresse [9]. We have calculated the dynamic structure factor $S(q,\omega)$ and, based on those results, the longitudinal dispersion relation $\omega_l^m(q)$ of the longitudinal current CFs. The latter one is displayed in Fig. 3 along with the ab initio results and data from our previous study [6]. We find good agreement of the present data with the ab initio results.

Finally, in Fig. 4 we present the dynamic structure factor for three different q-values. The main peak of the static structure factor is positioned at $q_p = 2.6$ Å^{-1}. For qs smaller than q_p we typically observe discrepancies as the one displayed in Fig. 4(a). For qs larger than q_p we obtain in general rather good agreement (cf. Fig. 4(b) and (c)). In this context it is necessary to point out that the ab initio simulations were performed for 64 particle ensembles over a shorter time-range which should also explain the observed differences.

Finally, we have checked the value of the diffusion constant, which may easily be extracted from such a computer experiment: The value we found for D was $6.3 \pm 0.15 \times 10^{-3}$ nm^2/ps, which is in good agreement with the experimental value [15] of $6.4 \pm 0.5 \times 10^{-3}$ nm^2/ps.

At the moment we try to compare our results with experimental data obtained in X-ray experiments [4,16]; here the dynamic structure factor is obtained directly. We still encounter discrepancies, but for the moment it is not yet clear if they arise from the scattering or the computer experiment. As soon as these open questions are settled they will be presented elsewhere.

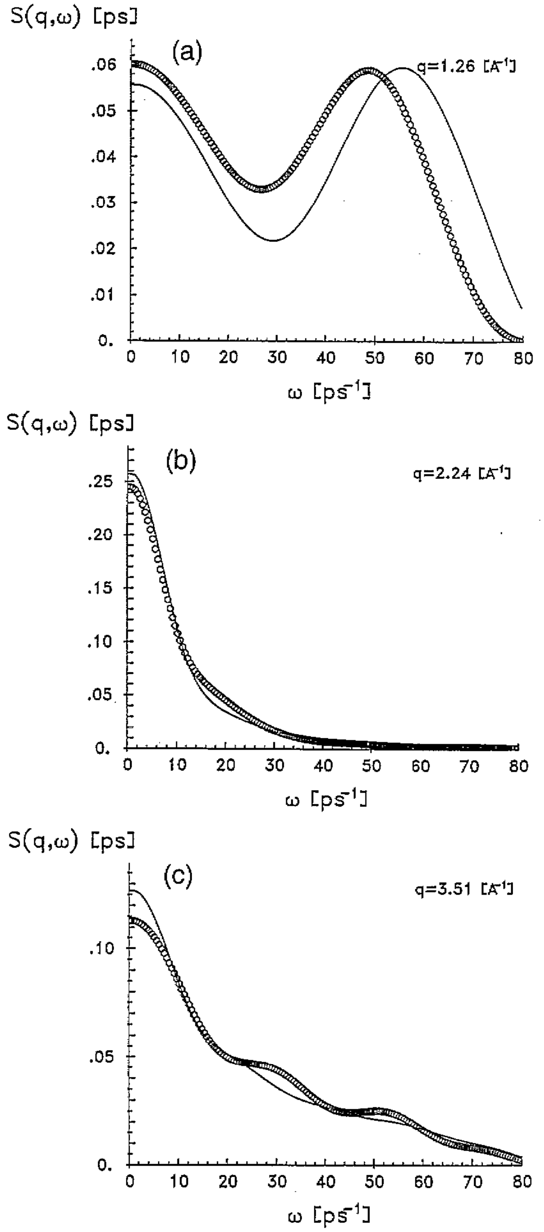

Fig. 4. Normalized dynamic structure factor $S(q,\omega)/S(q)$ as a function of ω for three different q-values (as indicated): full line, present study, symbols, results from ab initio simulations [9].

4. Conclusion

We have performed a computer experiments by means of a classical molecular dynamics simulation for liquid lithium. In contrast to previous studies, we have used an effective pair potential calculated by means of the quantal hypernetted-chain theory, a method which provides an interaction that is self-consistent with the radial distribution function. Our results are compared with ab initio simulation data. We find satisfactory results for the dynamic structure factor and the dispersion relation. However, further calculations on a larger scale (as, for example, different systems on a large temperature range) are required to prove the reliability of our approach.

Acknowledgements

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