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Integral equations and molecular dynamics in liquid metals; a complementary approach applied to molten Li

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Abstract. We explore how the use of molecular dynamics simulations with relatively small systems can be viewed as a complementary tool to provide key input (bridge functions) for an accurate integral-equation formalism. Our results do indeed show that an efficient description of the microscopic structure of liquid metals can thus be attained by means of inexpensive MD runs with a small number of sample particles.

1. Introduction

In a previous work, two of the authors [1] in collaboration with Alvarez and Stell studied in detail the behaviour of bridge functions extracted from MD results for metallic systems like aluminium and caesium. A rather surprising conclusion drawn from that work was the relative insensitivity in the reference hypernetted chain equation (RHNC) results in changes in the cutoff distance of the simulated pair distribution function (PDF) used when extracting bridge functions from MD data. This immediately suggests the possibility of using much smaller sample sizes (in [1] 1372 particles were used) to generate equally useful bridge functions. This idea is certainly not new and it has already been exploited to some extent by Linse [2] in the case of asymmetric electrolytes. Note that in this type of approach, the simulation sample is viewed as the 'reference system', which when utilized in the RHNC scheme will lead to results for an infinite, non-periodic and homogeneous fluid, the liquid metal.

In [1] it was argued that the short- and medium-range structure of the bridge function, $B(r)$, contains the information required for the description of $g(r)$ over a wide range of distances, thus explaining the lack of sensitivity to changes in the cutoff radius of the simulated PDF (and consequently, one might assume, to changes in the sample size), since these affect essentially the long-range behaviour of $B(r)$.

In order to fully assess these assumptions, in this work we present a series of MD simulations for molten lithium using 250-, 432- and 1458-particle samples. The choice of lithium as a system of interest makes the scope of this work twofold. On one hand we will test the validity of the above-mentioned assumption and, on the other, comparison between our 'experimental' bridge functions and hard-sphere ones, in particular the Labík–Malijevský (LM) formula [3], will explain why in this case Percus–Yevick (PY) type approximations for $B(r)$ yield accurate results, whereas in systems like Al or Cs they fail badly [1,4].

The next section is devoted to a description of the model and a brief summary of the theory. Finally, in section 3 we discuss the most significant results.

2. The potential model. A brief outline of the theory

The potential model considered here for liquid lithium is due to Rasolt and Taylor (RT) [5], and is an interionic potential derived from first principles in the context of the nearly-free electron approximation (NFE). Essentially, the system is considered as a liquid of positively charged particles which interact via an effective potential

$$u(r) = \frac{(Ze)^2}{r} - \frac{1}{(2\pi)^3} \int \hat{v}_c(q) F(q) \exp(-iq \cdot r) dq \quad (1)$$

where Z is the cation valence, e the electron charge and $\hat{v}_c(q)$ is the Fourier transform of the cation-cation Coulomb potential given by

$$\hat{v}_c(q) = 4\pi(Ze)^2/q^2. \quad (2)$$

The energy-wavenumber characteristic function $F(q)$ contains the electron-mediated part of the interaction, including both local and non-local components in the Rasolt-Taylor treatment. Explicit expressions for this function can be found in the appendix of [1], and a complete description of the theory is available in the original works by Rasolt and Taylor [5] and Dagens, Rasolt and Taylor [6]. Specific potential parameters are found in [6] and, as in [1], the potential model M2 is used [6]. This approach has proven to be efficient in treating group I, II and III metals, but is too simple to deal with transition metals.

The system considered here has already been studied by Jacucci, Klein and Taylor [7] who showed that MD data using the RT potential agree reasonably well with experimental structure factors. Foiles, Ashcroft and Reatto [8] later obtained integral-equation results (RHNC and crossover approximations) which accurately reproduced the simulation data. We have thus a model which can safely be used to account for the experimental structural properties of liquid Li and at the same time is suitable for an accurate theoretical description with handy numerical procedures.

Following Jacucci, Klein and Taylor [7] the density of the system was set to 0.504 g cm^{-3} and the systems equilibrated in our NVE molecular dynamics calculation at $T = 573 \pm 3 \text{ K}$ depending on the sample. We have used 250, 432 and 1458 particles initially on a BCC lattice. This lattice is melted by means of small random displacements from the starting configuration, and then between 5000 and 10000 steps were allowed for thermalization. Averages were performed along a 25000 step run. A typically time step used is $2.5 \times 10^{-16} \text{ s}$. This small time step and an appropriate choice of the interaction potential cutoff guarantee energy conservation throughout the run. By appropriate choice we mean that the cutoff is chosen to be a value of r for which the interaction potential vanishes due to the long-range oscillations. Throughout this work we have used as unit length the size of the unit cell in solid Li at approximately the same density as the liquid, namely $a = 3.483 \text{ \AA}$. Our MD results are consistent with those found in [7].

Now following the procedure suggested in [1], we extend the MD generated pair distribution function following the procedure devised by Verlet some time ago [9], i.e. we solve the Ornstein-Zernike (OZ) equation

$$\gamma(r_{12}) = \rho \int c(r_{13}) [c(r_{32}) + \gamma(r_{32})] dr_3 \quad (3)$$

coupled with the closure

$$c(r) = \begin{cases} g^{\text{MD}}(r) - 1 - \gamma(r) & \text{if } r < R_c \\ -\beta u(r) & \text{if } r > R_c \end{cases} \quad (4)$$

with $\gamma(r) = g(r) - 1 - c(r)$ as usual; $g^{\text{MD}}(r)$ denotes the simulated pair distribution function. Again we take the cutoff distances R_c so that $g^{\text{MD}}(R_c) - 1 = 0$. Besides, to be consistent with the MD we set $u(r) = 0$ for $r > R_m$, where R_m is the cutoff of the interaction potential in the simulation, which not necessarily has to be equal to R_c in equation (4), and is chosen to fulfill $u(R_m) = 0$ to improve energy conservation along the MD run.

The bridge function can now be obtained using the relation

$$B(r) = \gamma(r) - \log g(r) - \beta u(r) \quad (5)$$

As in [1], $B(r)$ cannot be reliably determined for small values of r due to the statistical uncertainties in the simulated PDF. Finally we solve equation (3) coupled with

$$c(r) = \exp[-\beta u(r) + \gamma(r) - B_{\text{ref}}(r)] - 1 - \gamma(r) \quad (6)$$

where $B_{\text{ref}}(r)$ is any of the bridge functions obtained from the simulation, or a hard-sphere bridge function calculated using the Verlet-Weis parameterization of the hard-sphere distribution function [10] and the Henderson-Grundke [11] parameterization of $y(r)$. In this latter case, once more as in [1] the hard-sphere diameter is chosen to fulfill the optimization condition [12]

$$4\pi \int_0^\infty (g(r) - g_{\text{HS}}(r; d)) \frac{\partial B_{\text{HS}}(r; d)}{\partial d} r^2 dr = 0. \quad (7)$$

As mentioned before, it is also possible to use the Percus-Yevick based empirical formula proposed by Labík and Malijevský [3] which turns out, in this case, to be a suitable choice for the reference bridge function.

3. Results

The interaction potential described in the previous section is plotted in figure 1. One can easily identify a rather typical metallic potential with the characteristic long-range oscillations, without the peculiarities present in the Al potential [1]. The pair distribution function obtained for the largest sample (1458 particles) is shown in figure 2 together with the results obtained from the RHNC integral equation when the MD data for the 1458-particle sample are used to generate the bridge function, using the largest possible cutoff in equation (4) ($R_c = 4.4a$). As it was the case in [1], when this is done the agreement between simulation and theory is complete. In figure 3 we have plotted radial distribution functions obtained for various sample sizes focusing in the region where discrepancies become more apparent. One readily notices that for small r values (first and second coordination shells) discrepancies are negligible and for larger values of r the influence of the sample size (and consequently the

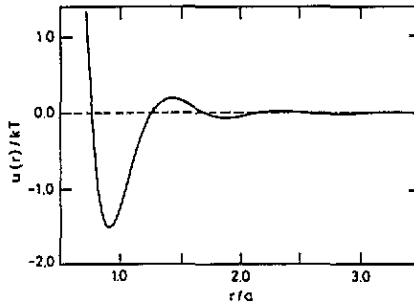


Figure 1. Effective ion-ion potential for liquid lithium.

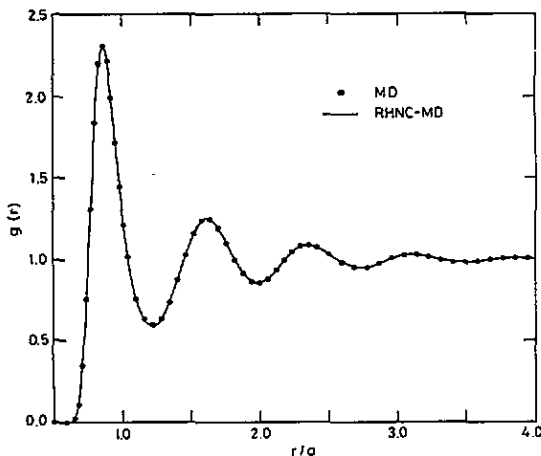


Figure 2. Pair distribution function for liquid Li from MD simulation and RHNC equation using a bridge function extracted from MD data (RHNC-MD).

interaction potential cutoff) is more noticeable. Thus, we will then let the MD $g(r)$ account for the short-range structure in the closure relation equation (4) and rely on the MSA-like approach implicit in equation (4) for the rest of interaction range.

In figure 4(a) several $B(r)$ functions are plotted for a variety of sample sizes using a PDF cutoff which includes first and second coordination shells ($R_c = 1.82a$). Results for the largest cutoff available ($R_c = 4.44a$) are also shown. We see that the curves exhibit the same qualitative behaviour, with the largest deviations corresponding to the smallest sample. The flat maximum present around $r = 3.6a$ when the largest cutoff is used vanishes for smaller cutoffs, i.e. is not reproduced by the MSA-like relation (4). However the maximum around $r = 2a$ is present in all curves. (Use of a hypernetted chain-type approximation in the extension of $g(r)$ would predict a $B(r)$ vanishing at $r = R_c$.) In figure 4(b) we present the Verlet-Weis-Grundke-Henderson bridge function (vw) for hard spheres together with the Labík-Malijevský approximation, both obtained after optimization of the RHNC equation using equation (7). Contrary to what happened in the Al and Cs cases studied in [1], here the 'experimental' bridge functions do not reach appreciably negative values. This might explain why in

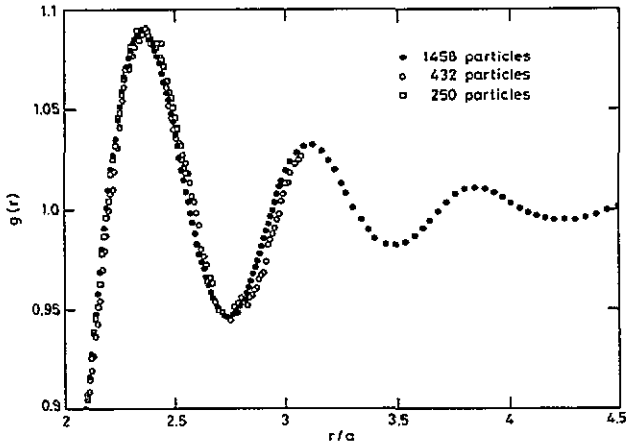


Figure 3. Sample size dependence in the radial distribution function for liquid Li. Deviations for lower r values are negligible.

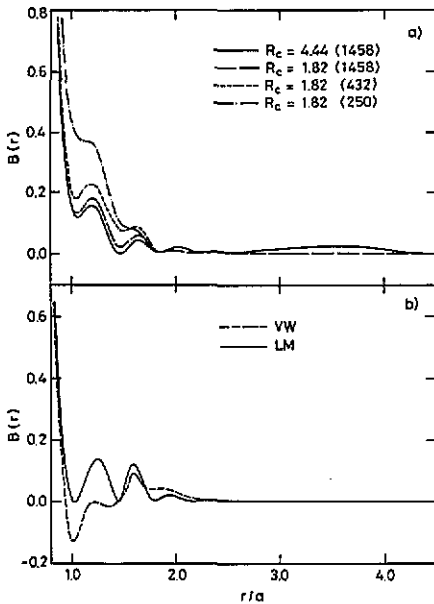


Figure 4. (a) Bridge functions extracted from MD pair distribution functions for different sample sizes and PDF cutoff radii. (b) Hard-sphere bridge functions obtained from the Verlet-Weis-Grundke-Henderson parameterization and the Labík-Malijevský empirical formula, satisfying optimization condition equation (7).

this case it is possible to perform the optimization procedure using the LM formula since, being PY-related, it remains always positive. For Al and Cs the optimization procedure in this latter case failed, whereas for the vw bridge function it did not pose particular problems. The qualitative behaviour of the hard-sphere functions (positions of maxima and minima) agrees quite well with the extracted $B(r)$.

Now in figure 5 we analyse in detail the influence of the sample size in the results of $g(r)$ generated by equations (3) and (6) using the bridge function shown in figure 4(a). For the sake of clarity we have only plotted the most extreme cases,

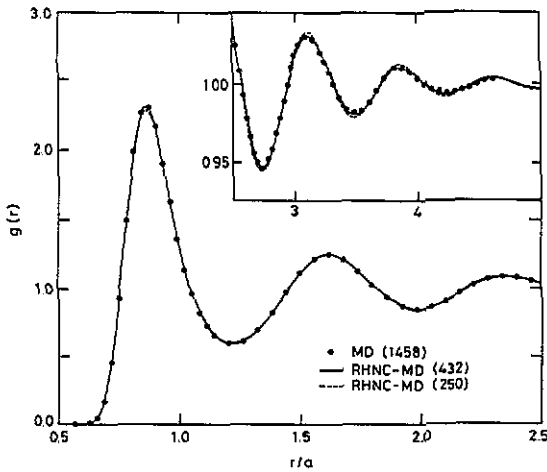


Figure 5. Pair distribution function for molten Li from simulation versus RHNC-MD results using some of the bridge functions depicted in figure 4(a).

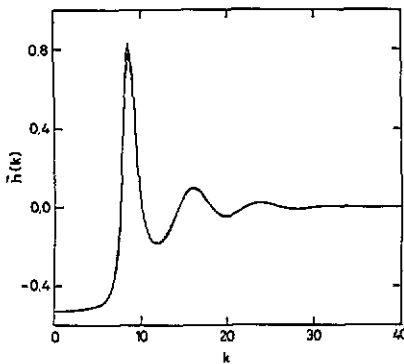


Figure 6. Fourier transform of the total correlation function, $\hat{h}(k)$ from RHNC-MD results, (bridge functions from 1458- and 250-particle samples denoted by solid and dashed lines respectively) and by Verlet's extension of the MD results for a 1458-particle sample (dash-dotted line).

i.e. 1458-particle sample with $R_c = 4.44$ and 250 particles with $R_c = 1.82$. Other results are hardly distinguishable from the first. MD data are plotted for the largest sample. We can appreciate that the discrepancies for the small sample results are slim, even in the long-range detail. One might ask what would be the effect of these tiny departures on a quantity of great interest, i.e. the structure factor. The answer to this question can be seen in figure 6, where we have plotted $\hat{h}(k) = [\hat{S}(k) - 1]/\rho$ computed from the extracted $B(r)$ as in figure 4 (solid and dashed line correspond to using bridge functions extracted from 1458- and 250-particle samples respectively) and also we include the $\hat{h}(k)$ resulting from Verlet's extension procedure (dash-dotted line). It is readily apparent that discrepancies in the structure factors are altogether

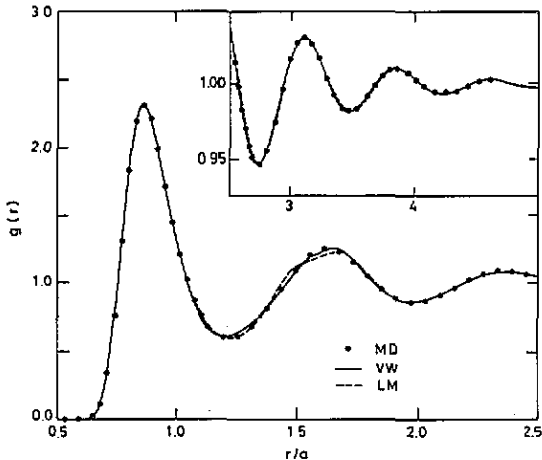


Figure 7. Radial distribution functions computed from the optimized RHNC equation using Verlet-Weis and Labík-Maličevský hard-sphere bridge functions (ORHNC-VW and ORHNC-LM on the figure respectively) compared with MD results.

negligible, as is consistent with the results found for pair distribution functions.

Finally, the results of the RHNC when hard-sphere reference bridge functions are used with optimization of the hard sphere diameter can be found in figure 5. As pointed out by Foiles, Ashcroft and Reatto [8] the agreement is excellent, aside from a small deviation in the second maximum (which appears to be characteristic of the use of this type of bridge functions [1]). The success of these theories can be understood in terms of the remarkable qualitative similarities found between the hard-sphere bridge functions and those extracted from MD.

We conclude thus that the combined use of MD simulation of relatively small samples with RHNC-type equations yields a powerful tool in the determination of liquid metal microscopic structures. Note in this respect that the CPU time required for the 1458-particle MD amounts to 24 hours on a VAX-9210 whereas a 250-particle sample needs approximately one hour. The solution of the integral equations involved in extracting the bridge function and generating a new $g(r)$ barely take a couple of minutes of CPU time. And finally, as a last observation we should stress that we appreciate again a considerable variability in the shape of bridge functions depending on the interaction potential as was the case when we considered potential models for Al and Cs.

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