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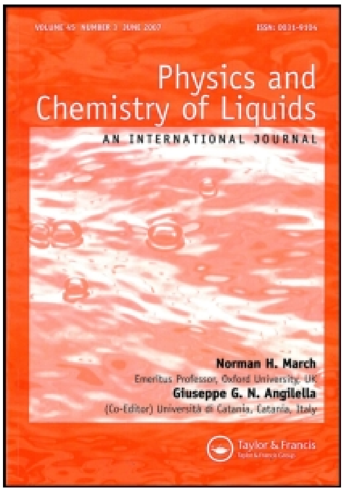

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VACANCY DYNAMICS IN MOLTEN RbCl

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A method has been developed for the study of vacancy dynamics in molecular dynamics simulations of either liquids or solids. This has been applied to the case of molten RbCl to show that vacancies may be considered to exist in the liquid state using either static or dynamic criteria, but that these do not represent a significant proportion of the free volume.

KEY WORDS: Vacancy, molten salt, molecular dynamics.

1 INTRODUCTION

It is well known from the theory of imperfect crystalline solids that defects and vacancies have great importance, since they determine various transport properties. Some theories of melting are based on defect behaviour. There are many accepted methods, mainly experimental, for studying the dynamics of defects and vacancies. There are not yet, however, any methods for examining the dynamical behaviour of the equivalent free volume in liquids.

It has recently been shown that the presence of vacancies in liquids is a characteristic feature of the static structure.[1] Here a vacancy is defined as a void large enough to accommodate a particle. These have been identified using a method based on the vertices of the Voronoi polyhedra associated with the particle positions,[2,3] and applied to Monte Carlo simulated configurations of molten CsF and RbBr. Radial distribution functions have been calculated and found to be similar to those of unlike ions.

Since these vacancies are identified only in static configurations it is not obvious that they have any significant lifetime, and may therefore only be due to random fluctuations. In order to investigate this it is necessary to develop a method that is equally applicable to both solids and liquids, so that vacancies in the two phases are treated on the same basis. In this paper we describe the development of such a method.

2 IDENTIFICATION OF STATIC VACANCIES

For the purposes of this study we have used a molecular dynamics simulation of molten RbCl at 1050 K. 216 ions are contained in a cubic box of side 21.384 Å, corresponding to the experimentally measured density at this temperature. Periodic boundary conditions have been applied and the Ewald summation used to correct for the long range Coulomb force. The interionic potential was that due to Fumi and Tosi.[4] The time step chosen, 5 fs, was relatively short for such a simulation. The system has been well equilibrated over 20,000 timesteps and a section of 1100 timesteps then used for the vacancy study.

At each timestep the Voronoi polyhedra describing the geometric structure of the liquid have been calculated.[3] The vertices of each polyhedron are points that are equidistant from 4 ions, with no other ions being closer. If the distance between the vertex and the ions is larger than the radius of an ion (in this case Rb^+ and Cl^- are assumed equivalent) then the vertex defines the centre of a void large enough to accommodate an ion, and hence a vacancy by our definition. While this method will not necessarily identify all possible vacancy sites it is computationally efficient. We find 4519 vacancies in 1100 configurations, an average of 4 vacancies for 216 ions. The minimum number in any configuration is 2 and the maximum is 11. Since the volume change on melting is $\simeq 20\%$ for RbCl[5] it is clear that the vacancies do not account for all the additional free volume in the liquid relative to the crystal.

3 IDENTIFICATION OF DYNAMIC VACANCIES

We now have to find a method by which vacancies can be traced between consecutive timesteps. The first criterion proposed is based on the Delauney tetrahedron (DT), which is the set of four particles that defines a Voronoi polyhedron vertex, and hence a vacancy. Since the timestep, 5 fs, is short compared to the time between collisions of ions it can be supposed that if at least some of the ions in the DT defining a vacancy are identical to those in the previous timestep then the vacancy is the same. Using this criterion we have determined the lifetimes of vacancies for which three ions in the DT remain the same. The lifetime distributions are given in Table 1. Of the 4519 vacancies found in 1100 configurations using a static criterion 735 are 'independent', but 50% of these exist for just a single timestep, and only 4 exist for more than 100 timesteps. Using a two ion criterion the number of independent vacancies decreases to 673 and the average lifetime increases slightly, as might be expected.

Because the average lifetime is much less than the period of a typical density fluctuation the result is not surprising. Oscillations of the ions may cause vacancies to 'disappear' for a number of timesteps, and then to 'reappear' later (see Figure 1). The same would be true in a crystal. Also if we consider the motion of a vacancy from one site to another then it can be seen that the vacancy does not 'exist', using our definition, while it is moving. For this reason we have altered our dynamical criterion so that the vacancy is considered the same if it occurs with two or three identical ions in the DT within a given number of timesteps, not just in consecutive timesteps.

Table 1 Percentage of independent vacancies with a given lifetime found by different methods.

Number of timesteps (0.005 ps)	*1*	*2–15*	*16–40*	*41–100*	*101–*
3 neighbour/ 1 timestep	50	40	6	3.4	0.6
2 neighbour/ 1 timestep	50	40	5	4	1
3 neighbour/ 5 timesteps	10	60	20	8	2
2 neighbour/ 5 timesteps	8	55	20	12	5
$\Delta r = 3$ Å/ $\Delta t = 0.5$ ps	3	17	25	25	30

Results for an interval of 5 timesteps, 25 fs, are given in Table 1. Again the number of independent vacancies decreases, to 261 for the three ion and 213 for the two ion case, and the average lifetime increases.

From a study of the motions of the ions in this simulation we find that they oscillate around a mean position for times of order 0.5–1.0 ps, and then 'hop' rapidly to a nearby site. Sites in this sense are positions separated by distances corresponding to the first peak in the radial distribution function for unlike ions, $\simeq 3$–4 Å. Assuming that vacancies behave in a similar fashion then increasing our interval to 5–10 timesteps would account for those that 'disappear' during hops, but would not

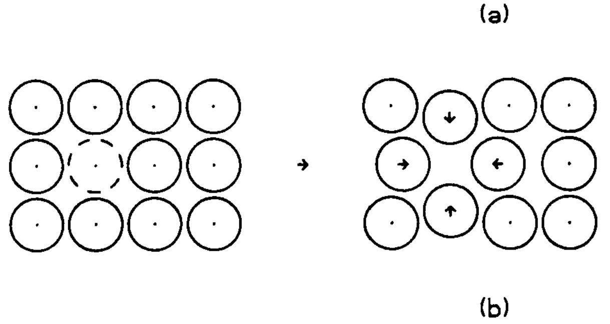

Figure 1 Temporary 'disappearance' of a vacancy during (a) motion from one site to another and (b) oscillation of the neighbouring atoms.

account for oscillations of the neighbours. The time period of appropriate oscillations can be estimated from the optic phonon frequencies at the Brillouin zone edge in the equivalent crystal, i.e. $\simeq 0.5$ ps or 100 timesteps. Increasing the time interval for identical vacancies by this amount would be possible, but is computationally very time consuming using the DT method, so we must develop a simpler criterion.

To do this we have defined vacancies as the same in configurations n and m ($m > n$) if $t_m - t_n \leq \Delta t$ and $|r_m - r_n| \leq \Delta r$ where t_i is the time of configuration i and r_i is the position of the vacancy in that configuration. Δt is then chosen to be 0.5 ps and Δr to be 3 Å, since this is approximately the separation of two ions. Applying these criteria we now find only 61 independent vacancies, of which 18 have lifetimes longer than 0.5 ps (Table 1), the maximum being 1.5 ps. We may therefore consider that these 18 are 'true' vacancies since they exist for longer than a typical density fluctuation. This corresponds to about one vacancy per configuration (taking into account their lifetime), compared to the four found using a purely static criterion.

4 DYNAMICS OF VACANCIES

Having established the existence of long lived vacancies it is of interest to study their motion and to compare it to that of ions in the liquid. For diffusion of ions we expect a mean square displacement proportional to time, but no such simple correlation is found for the vacancies. The derivation of a precise relation is difficult because of their small number, but in general those with intermediate lifetimes have large displacements compared to those with long lifetimes. At the two extremes there is one vacancy with a lifetime of 0.625 ps that moves 0.7 Å, and one of lifetime 0.295 ps that moves 3.27 Å. The former corresponds to a diffusion coefficient of 0.08 10^{-5} cm^2 s^{-1}, and the latter of 3.6 10^{-5} cm^2 s^{-1}, comparable to that of ions in the liquid.[5]

We have also studied the mean radius of every vacancy. It has previously[3] been found that vacancies with larger radii have lower energies, as might be expected, and are therefore more 'stable'. The energy is defined as that of either a positive or negative ion placed at the vacancy position, the lower of the two values being taken. In this way the 'charge' of the vacancy may also be determined. We find that vacancies with longer lifetimes tend to have larger radii, in agreement with the above conclusion. The larger size of the longer lived vacancies may also explain why their displacements are relatively small.

5 CONCLUSIONS

We have studied the dynamics of the free volume in molten RbCl and find that voids sufficiently large to accommodate an ion may exist for times longer than the period of the average density fluctuation, and may therefore be termed 'vacancies' in the same sense as in crystals. These voids correspond to only about 0.5% of the total volume, and to 2.5% of the volume change on melting. It is consequently not possible to consider that the excess free volume in the liquid is predominantly due to vacancies. It is reasonable to suggest that the method of identifying vacancies used here, based on the Delauney tetrahedron, produces an underestimate of their significance. However to perform a more complete calculation would be computationally expensive and is unlikely to alter the conclusion.

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