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# A molecular dynamics simulation of the diffusion of the solute (Au) and the self-diffusion of the solvent (Cu) in a very dilute liquid Cu–Au solution

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## Abstract

The identification of the manner in which a solute diffusion coefficient ( $D$ ) might vary with temperature ( $T$ ) in a fused metal or semimetal has led to considerable experimental study and some theoretical analysis. However, the conclusions of this work are inconsistent. In the present work, molecular dynamics studies of diffusion of a very dilute solute (Au) in liquid Cu are presented. Using the simple Enskog theory of diffusion, it is shown that the ratio of the diffusion constant of the solute to the diffusion constant of the solvent for a very dilute solution is approximately constant. This prediction is confirmed by molecular dynamics simulations although the values of ratios agree only within 20%–25%. In agreement with experiment, current simulations predict that within the usually investigated temperature range, the diffusion coefficient is linearly dependent on temperature. A very small contribution of parabolic behavior can only be observed for a temperature range much wider than that available for physical experiments due to materials limitations.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

It has been noted [1, 2] that, in order to achieve optimum control of crystal growth and casting processes involving multi-component alloys on earth, it is necessary to develop numerical control models. The usefulness of these will depend on the quality/accuracy of the diffusion data incorporated; unfortunately, current data, where available, are often widely inaccurate.

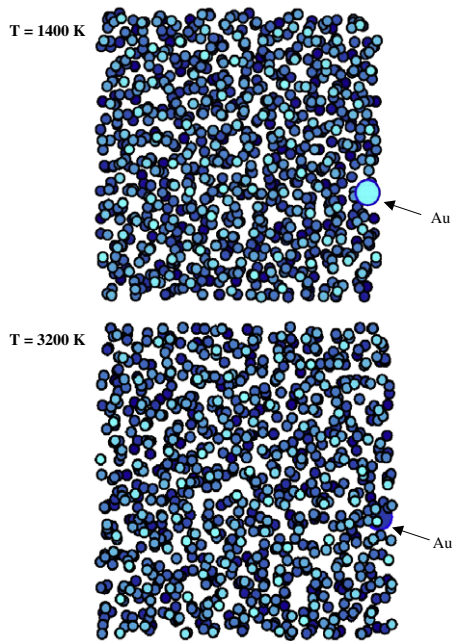
Summaries of the most often quoted theoretical predictions of this dependence are available [1–3]: each prediction arises from a particular description of the liquid state and the associated diffusion mechanism. Those most commonly quoted are:  $D$  proportional to:  $\exp(-\frac{1}{T})$ ;  $T$ ;  $\sqrt{T}$ ;  $T^2$ ;  $T^{(1.7 \rightarrow 2.3)}$ .

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Hence it was suggested that, by comparing the measured temperature dependence with the theoretical predictions, some indication of the operative diffusion mechanism should be apparent and provide insight into the structural nature of the host solvent.

In this work the diffusion of Au in a very dilute liquid Cu–Au solution is studied. The rate of self-diffusion of Cu in its liquid state is also calculated.

First a few comments on the nature of the molecular dynamics modeling used here. In the case of liquid diffusion, an assembly of like atoms is selected, the solvent, into which one foreign atom, the solute, is introduced to study diffusion in a very dilute liquid solution. The system is allowed to ‘react’, i.e. the solute atom ‘diffuses’ by atomic collisions, as do the solvent atoms. The manner in which the collisions take place to effect the displacement of all the atoms is dependent upon the interatomic potential fields seen by the solute and solvent atoms. Thus the critical component of a realistic molecular



**Figure 1.** The structure of simulated liquid copper at temperatures of 1400 and 3200 K. The larger diameter sphere represents the single Au atom. The positions of copper atoms lying more deeply in the cluster are given darker shades to indicate their relative distances from the displayed surface.

dynamic simulation of the motion of the solute atom is having a good description of the interatomic potential.

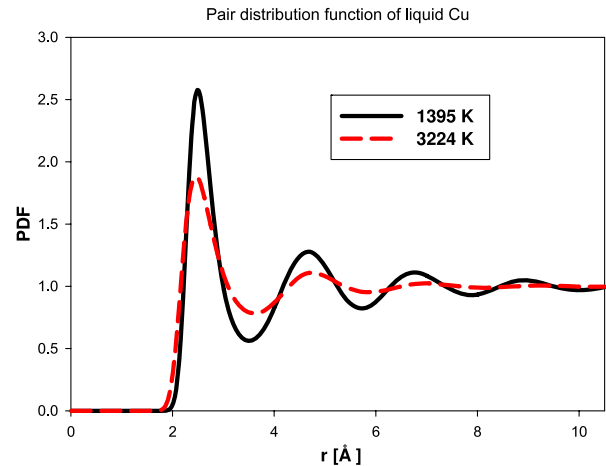
The embedded atom method (EAM) functions have been developed [4], which describe very well the energetic, structural and mechanical properties of solid metals and their alloys. The EAM method is commonly used to study the properties of metals and alloys because, in contrast to pair potential methods (zero Cauchy discrepancy), it predicts correctly the elastic properties, since it includes many body interactions (through the energy term that is dependent on the electron density). Furthermore it also has been demonstrated that the same potentials describe very well interactions in liquid metals: Cu, Au, Ag and Ni and, in particular, the static structure factors calculated at 1420 K for Cu and Au agree very well with experiment [5]. Although EAM functions could be further refined for use in the study of liquids, in their present forms they seem able to describe the liquid state realistically. These potentials have also been used successfully in studying nano-crystals [6].

## 2. Molecular dynamics simulations

The diffusion in this dilute liquid solution is modeled using a cubic cluster with 863 Cu atoms and a single Au atom. Periodic boundary conditions are used. EAM, Au–Cu potentials, are used that were developed by Foiles *et al* [4] as discussed above.

Examples of the liquid structure for a cluster at 1400 and 3200 K are shown in figure 1.

The pair distribution function, calculated for simulated liquid copper at 1395 and 3224 K average temperature, are



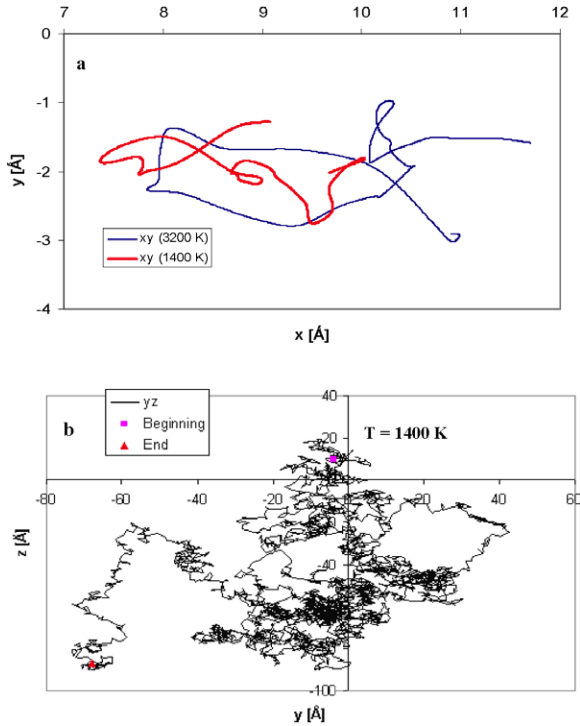
**Figure 2.** Pair distribution function calculated for simulated liquid copper at 1395 and 3224 K temperatures.

shown in figure 2. The pair distribution function at 1395 K agrees very well with experimental data [7] and the calculated by MD simulation pair distribution function for liquid Cu shown in [5]. At short distances some order is present due to hard sphere exclusion. This order is lost at larger distances where the pair distribution function becomes flat. As observed experimentally [7], pair distribution functions become flatter with rising temperature (e.g. at 3224 K, as shown below).

### 2.1. Mean square displacement method of calculation of diffusion constant

When compared with what happens in a solid, diffusion in a liquid is very fast. In figure 3(a) a two-dimensional projection of trajectories (created during 2.5 ps) of the movement of the Au atom at 1400 and 3200 K are shown. The overall diffusion paths in figure 3 represent diffusion of one atom only and it should not be compared with those associated with the changes of solute concentration in a typical liquid diffusion couple that is measured on the large assembly of atoms. The figure 3(a) also demonstrates that a large number of configurations should be used. An insufficient statistical basis, as is suggested in figure 3(a) where the effective diffusion during random walk is almost the same for both temperatures, may provide misleading results. The simulation time-step used is equal to 2 fs; therefore the recorded time 2.5 ps corresponds to 1250 configurations. The diffusion length during this short time (2.5 ps) is significant. In figure 3(b) the trajectory of the Au atom is shown during 10k ps at 1400 K (average temperature 1395 K). At this temperature, the Au atom diffuses a distance that is many times larger than the dimensions of the original cluster ( $\sim 22$  Å), therefore the propagating error due to the use of periodic boundary conditions for a simple liquid is observed.

In our simulation, we have only one Au atom while in an actual experiment, the diffusion is measured over many atoms in a liquid state that does not have a periodic structure. The traditional method of calculating a diffusion constant ( $D$ ) as a limit of the average value of the mean square displacement (msd) at such a long time may lead to a less accurate result.



**Figure 3.** (a) The two-dimensional trajectories (created during 2.5 ps) of the Au atom at 1400 and 3200 K are indicated. (b) The two-dimensional projection of the trajectory of the Au atom is shown during 10k ps at 1400 K (average temperature 1395 K). The position of the atom at the beginning of simulation is shown as a rectangle, whilst the triangle indicates the position of the Au atom after 10k ps.

Therefore, to eliminate any propagating errors, the diffusion constant was calculated as an average over diffusion jumps for the times equal to the recorded time-step ( $t_{rec} = 2.5$  ps) with the number of configurations ( $n$ ) equal to 1250. The diffusion constant for atom ‘ $i$ ’ was calculated using the average over all the recorded configurations ( $N = 4000$ ), i.e.,

$$D_i = \frac{1}{6t_{rec}} \frac{1}{N} \sum_{j=1}^N \sum_{k=1}^3 (x_{k+n}^j - x_k^j)^2. \quad (1)$$

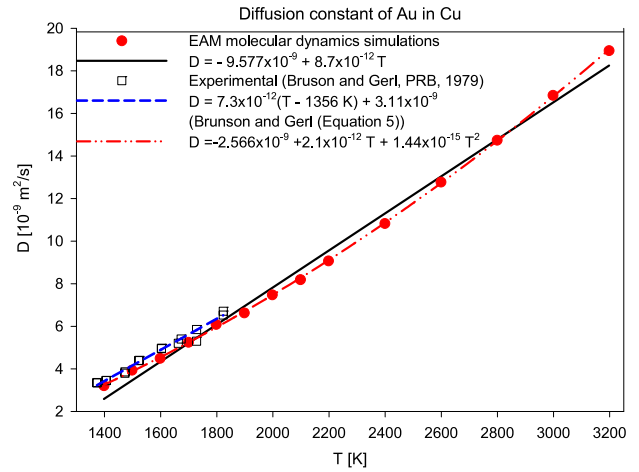
Altogether  $5 \times 10^6$  ( $=n \times N = 1250 \times 4000$ ) configurations were used.

Whilst we have considered only one Au atom per cluster, the value of  $D_{i=Au}$  should represent a figure close to that of an experimentally measured diffusion constant since that would be averaged over the diffusion of all the Au atoms in the Cu in a dilute Cu–Au liquid.

The same method was used to calculate the diffusion of Cu atoms. However, there are  $N_{Cu}$  (863) atoms per simulated cluster, therefore the self-diffusion of Cu is calculated by the additional averaging over the number of Cu atoms, i.e.,

$$D_{Cu(self)} = \frac{1}{N_{Cu}} \sum_{i=1}^{N_{Cu}} D_i. \quad (2)$$

In figure 4, EAM molecular dynamics simulations of the diffusion of one Au atom in the cluster of 863 Cu atoms are shown for the temperatures slightly above the boiling



**Figure 4.** EAM molecular dynamics simulations of the diffusion of Au in Cu for the temperatures from 1400 K to slightly above the boiling temperature for Cu (3200 K). The simulations show only small parabolic deviation from the linear fit shown by the solid line. The experimental data [8] together with the linear fit provided are shown by black squares and a broken line respectively.

temperature of Cu (3200 K). The simulations agree very well with the existing experimental data [8] but the latter are only available for a narrow temperature range. The deviation from the linear fit is not noticeable for the temperature range that is used in experimental measurements (less than 1000 K) [8]. The correlation coefficient for the presented parabolic fit is 0.9999 and it is only slightly better than the respective correlation coefficient for linear fit: 0.9965. The calculated residuals for parabolic fit are very small, with the largest relative residual at low temperature equal to 1.4% while at high temperature it is 0.3%. The relative deviations for the linear fit are one order of magnitude larger and are equal to 19% and 4%, for the low and high temperatures respectively. The relative standard deviation of temperature is equal to 2% for 1400 K temperature and 1.6% for 3200 K, therefore statistical fluctuations are smaller than the observed deviation from the linear fit at these temperatures. The linear fit to the experimental data that was developed by Brunson and Gerl [8] is also shown in figure 4 by a broken line and it agrees well with the simulated points for the temperature range used in their experiments.

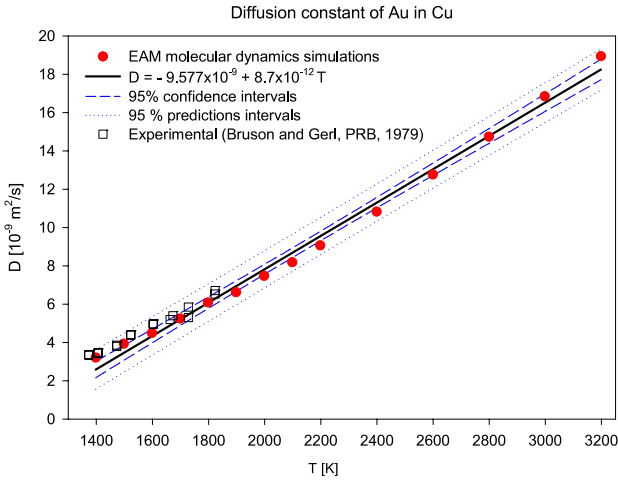
The 95% confidence intervals for the linear fit are shown in figure 5 by the dashed lines while the dotted lines indicate prediction intervals.

### 3. Enskog model for a very diluted solute

It can be shown from the Enskog theory of diffusion [9] that, for a very dilute solution, the ratio of the solute diffusion constant,  $D_i$ , to the solvent self-diffusion constant,  $D_s$ , is

$$\alpha = \frac{D_i(T)}{D_s(T)} = \left[ \frac{8 * \sqrt{ms + mi}}{(\sigma_s + \sigma_i)^3 \sqrt{ms} \times mi} \right] / \left[ \frac{\sqrt{2}}{\sigma_s^3 \sqrt{ms}} \right] \\ = 4\sqrt{2} \left( \frac{\sigma_s}{\sigma_s + \sigma_i} \right)^3 \sqrt{\frac{ms + mi}{mi}}, \quad (3)$$

where  $\sigma$  represents the hard spheres diameters and  $m$  the masses of solvent ( $s$ ) and solute ( $i$ ), respectively. This



**Figure 5.** EAM molecular dynamics simulations for the diffusion of Au in Cu up to slightly above the boiling temperature for Cu (3200 K). The linear fit to simulated points ( $R^2 = 0.993$ ) is shown by the solid line. The 95% confidence intervals are shown by dashed lines, while dotted lines indicate prediction intervals.

relation is useful since it is almost temperature independent (see appendix for approximations) and, knowing the self-diffusion constant of the solvent, it allows an estimation of the temperature dependence of the solute diffusion constant in a very dilute solution. Self-diffusion can be very accurately calculated using MD and often experimental data are available. Knowing  $D_s(T)$ , one can get an approximate value of the solute/impurity diffusion constant from the relation:  $D_i(T) = \alpha D_s(T)$ , where  $\alpha$  is approximately temperature independent. Since for another solute/impurity ‘j’, we can write a similar expression:  $D_j(T) = \beta D_s(T)$ , we can conclude that the ratios of the diffusion constant of all very dilute solutions (in the same solvent) are not temperature dependent (e.g.  $D_i(T)/D_j(T) = \alpha/\beta$ ). In the following sections the comparison of this prediction with molecular dynamics simulations and experiment will be given.

### 3.1. Enskog model and molecular dynamics prediction

In table 1 EAM molecular dynamics calculations are shown of the diffusion constant of Au (also presented above in figure 4) and the self-diffusion constant of the solvent Cu at various temperatures. Although the diffusion constant is an order of magnitude higher at the higher temperature than at a temperature close to the melting point of Cu (1358 K), it may be seen that the ratio of the diffusion constant of Au (solute) to the diffusion constant of the solvent (Cu) is almost temperature independent (last column in table 1).

However the ratios of the diffusion constants of Au solute and Cu solvent calculated by EAM molecular dynamics do not agree well with Enskog predictions when the diameters of Cu and Au are assumed to be equal to the values of diameters,  $\sigma_o$ , tabulated in [10]. Only when it is assumed that Au and Cu have the same hard sphere diameter does the agreement becomes better, as shown in table 2.

It may be concluded that, in this dilute state, the difference in the hard sphere diameters of Au and Cu (both elements

**Table 1.** EAM molecular dynamics calculations of diffusion constant (in  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) of Au and self-diffusion constant of solvent Cu at various temperatures, and the respective ratios of the diffusion constants of solute (Au) to the diffusion constants of the solvent (Cu).

EAM molecular dynamics calculations			
$T$ (K)	$D_{\text{Cu}}$	$D_{\text{Au}}$	$D_{\text{Au}}/D_{\text{Cu}}$
1398	3.69	3.21	0.87
1498	4.42	3.93	0.89
1598	5.19	4.49	0.87
1699	5.99	5.25	0.88
1798	6.84	6.09	0.89
1898	7.73	6.63	0.86
1998	8.66	7.48	0.86
2098	9.61	8.19	0.85
2198	10.61	9.07	0.85
2399	12.70	10.83	0.85
2599	14.92	12.77	0.86
2799	17.26	14.74	0.85
2998	19.76	16.85	0.85
3198	22.37	18.95	0.85

**Table 2.** The calculated ratios (equation (3)) of the diffusion constants for Cu and Au using various values for the ionic diameter of Au.

Atom	Mass	$\sigma_o$ (Å) [10]	$D_i/D_{\text{Cu}}$
Au	196.96	2.88	0.68
Au	196.96	2.58	0.81
Cu (solvent)	63.546	2.58	1

**Table 3.** The calculated ratios (equation (3)) of diffusion constants of various very dilute impurities in a liquid Cu to the self-diffusion constant of liquid Cu.

Atom	Mass	$\sigma_K$ (Å) [11]	$D_i/D_s$
Sb	63.546	3.18	0.71
Ag	107.868	2.9	0.74
Au	196.96	2.88	0.68
Sn	118.71	3.1	0.65
Cu (solvent)	63.546	2.56	1.00

from the IB group in periodic table) does not have much effect on the diffusion and only the differences in atomic mass are significant.

### 3.2. Comparison of the Enskog prediction with experiment

In table 3, the diffusion constants ratios of various elements as impurities in Cu (solvent) are calculated using equation (3). The values for the hard sphere radii as tabulated by Kittel [11] are used due to the data for Sb in [10] not being available. It can be seen that the respective diameters for Sn, Au and Ag are very close to that provided in [10] and also shown in table 2 above.

Bruson *et al* [8] provide a linear fit to their experimental data of diffusion constants: i.e.  $D = A'(T - T_m) + B'$ . However they did not measure the self-diffusion of Cu in the liquid state. In table 4 (below), the respective ratios for the provided fits versus the Au diffusion constant are shown as



**Table 4.** The ratios of diffusion constants calculated from the expressions obtained from fitting the experimental data [8] for Cu solvent and from the equation (3).

The ratios of diffusion constants for fits of experimental data [8] for Cu solvent			
$T$ (K)	$D_{Ag}/D_{Au}$	$D_{Sn}/D_{Au}$	$D_{Sb}/D_{Au}$
1400	0.94	0.95	1.22
1500	0.98	1.07	1.20
1600	1.01	1.16	1.19
1700	1.03	1.22	1.18
1800	1.05	1.27	1.17
1900	1.06	1.31	1.17
Enskog	1.08	0.96	1.05

a function of temperature. The ratios of diffusion constants do not vary much for Ag and Sb. The variation is larger for Sn (40%) but it is still smaller than the variation of diffusion constant of Sn for this temperature range (120% change). The respective values calculated using equation (3) agree with experiment to within 40%.

#### 4. Discussion

As it is apparent from section 2, that molecular dynamics simulations can lead to reliable estimates of the mass diffusion coefficient that fit closely the experimental shear-cell-derived data of Bruson and Gurl [8]. The relationship between the diffusion coefficient and temperature appears to depend only very weakly on a quadratic term. Over a very large temperature range within the liquid region, the relationship between the mass diffusion coefficient and temperature is effectively linear. In view of this, one might ask what other experimental evidence is available to support this contention. Other work by these authors [12] of self-diffusion in liquid tin using the shear-cell technique reveals again a linear relationship between  $D$  and  $T$ .

As noted elsewhere [1], a ' $D \propto T$ ' relationship is found also for the fluidity and diffusivity in non-ionic aqueous liquids if buoyancy-driven flows are suppressed. This view has been championed by a number of researchers, particularly Hildebrand [13].

The current molecular dynamics simulations show that the ratio of the solute diffusion constant of very dilute solutions to the self-diffusion constant of the solvent are not dependent on temperature. This is in agreement with Enskog's prediction.

#### 5. Conclusions

- (1) Molecular dynamics modeling has been used to estimate the mass diffusion coefficient of gold in liquid copper at selected temperatures. It was observed that the relationship between the mass diffusion coefficient and temperature over the entire liquid range of copper is effectively linear and may be fitted to the relationship:  $D = -9.577 \times 10^{-9} + 8.7 \times 10^{-12}T$ , where  $T$  is in K and  $D$  is in  $m^2 s^{-1}$ . The correlation coefficient for the presented parabolic fit ( $D = -2.566 \times 10^{-9} + 2.1 \times$

$10^{-12}T + 1.437 \times 10^{-15}T^2$ ) is 0.9999 and is only slightly better than the respective correlation coefficient for the linear fit: 0.9965. The very small parabolic deviation would not be observed within the narrow temperature range normally available to obtain experimental data [8].

- (2) This work gives further support to the conclusions from the QUELD II/MIM/MIR mission [1] that, for the dilute alloy systems and temperature range used, the solute diffusion coefficient increases linearly with temperature if measured in a low earth-orbiting laboratory in the absence of significant solute transport induced by the ambient g-jitter.
- (3) These two approaches i.e. the measurement of desired diffusion coefficients in the absence of buoyancy-induced contamination, and the equivalent molecular dynamics simulation experiments, can provide benchmark reference values for accurate diffusion coefficient data necessary for use in the modeling of terrestrial liquid metal processing systems.
- (4) The ratio of the solute diffusion constant in a very dilute solution to the self-diffusion constant of the solvent, as predicted by the Enskog's theory to be temperature independent, is supported by current EAM molecular dynamics simulations.

#### Acknowledgments

We would like to thank Sandia National Laboratories (S M Foiles, M I Baskes) for help and for providing EAM code and Au-Cu potentials.

The use of SUN computer facilities at Queen's University is gratefully acknowledged.

#### Appendix

In the above derivation of equation (3), it is assumed, that the radial distribution function of unlike atoms upon contact is not dependent on the particular solute, which means that  $|1.5(\sigma_i - \sigma_s)/(\sigma_i + \sigma_s)|$  is much smaller than 1 and 'y', the total packing fraction used in [10], is not changed. Also the actual radial distribution function is predicted not to be dependent on the particular solute for a dilute alloy system.

Protopas [10] proposed that  $\sigma$  has a temperature dependent factor:  $(1 - 0.112(T/T_{\text{melting}})^{1/2})$  which implies that the hard sphere radius decreases with temperature (equivalent to a more vigorous collision at higher temperature). On taking this into account, we get

$$\alpha(T) = 4\sqrt{2} \left( \frac{\sigma_s}{\sigma_s + \frac{1-0.113\sqrt{T/T_{mi}}}{1-0.113\sqrt{T/T_{ms}}}\sigma_i} \right)^3 \sqrt{\frac{ms+mi}{mi}}, \quad (\text{A.1})$$

where  $\sigma_i$  and  $\sigma_s$  are the hard spheres diameters at 0 K and  $T_m$  are the melting temperatures respectively of the solvent ( $s$ ) and the solute ( $i$ ). The temperature dependence of the above coefficient is negligible and when the melting temperatures of solute and solvent are comparable the temperature dependence cancels out.

**References**

- [1] Smith R W 1998 *Microgravity Sci. Technol.* **11** 78–84
- [2] Smith R W, Scott P J and Szpunar B 2009 *Acad. Sci.* **16** 526–36
- [3] Malmejac Y and Frohberg G 1986 *Mass Transport by Diffusion* ed H U Walter (Berlin: Springer) chapter V (Fluid Sciences and Materials Science in Space) p 159
- [4] Foiles S M, Baskes M L and Daw M L 1986 *Phys. Rev. B* **33** 7983–91
- [5] Foiles S M 1985 *Phys. Rev. B* **32** 3409–15
- [6] Szpunar B, Lewis L J, Swainson I and Erb U 1999 *Phys. Rev. B* **60** 10107–13
- [7] Waseda Y 1980 *The Structure of Non-Crystalline Materials: Liquids and Amorphous Solids* (New York: McGraw-Hill)
- [8] Bruson A and Gerl M 1979 *Phys. Rev. B* **19** 6123–9
- [9] Chapman S and Cowling T G 1939 *The Mathematical Theory of Nonuniform Gases* (Cambridge: Cambridge University Press) p 327
- [10] Protopapas P, Andersen H C and Parlee N A D 1973 *J. Chem. Phys.* **59** 15–25
- [11] Kittel C 1986 *Introduction to Solid State Physics* 6th edn (New York: Wiley) p 646
- [12] Bruson A and Gerl M 1980 *Phys. Rev. B* **21** 5447–54
- [13] Hildebrand J L 1977 *Viscosity and Diffusivity* (New York: Wiley) chapter 1, p 688