Estimation of the Chemical Potential and the Activity of NaCl in Molten $DyCl_3$-NaCl by Molecular Dynamics Simulation

Masanori Sakurai, Ryuzo Takagi, Ashok K. Adya[a], and Marcelle Gaune-Escard[b]

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguroko, Tokyo 152, Japan

[a] University of Abertay Dundee, Division of Applied Chemistry, School of Molecular and Life Science, Bell Street, Scottland, DD1 1HG, UK

[b] IUSTI, CNRS UMR 6595, Technopole Chateau-Gombert, 5 rue Enrico Fermi, 13453 Marseille, France

Z. Naturforsch. **53a,** 655–658 (1998); received April 18, 1998

Molecular dynamics simulations of molten $DyCl_3$-NaCl were carried out at liquidus temperatures of the phase diagram. The chemical potential and the activity of NaCl was successfully estimated with the method proposed by Powles et al., which requires only positional data of the ions at the temperatures in question.

1. Introduction

Spent metallic nuclear fuels are to be reprocessed in a molten salt in the Integral Fast Reactor (IFR) program proposed by the Argonne National Laboratory (ANL) [1]. Since fission products (FP) consist of many elements, and knowledge of the thermodynamic properties of their salts is needed to recover them, it is of interest to see if such properties can be estimated computationally. In this work we performed a successful estimation of the chemical potential and the activity of NaCl in molten $DyCl_3$-NaCl with the molecular dynamics (MD) method proposed by Powles *et al.* [2], which requires only the positional data of the ions at the temperature in question. The activity a_i of the component i in a mixture is described by

$$RT \ln a_i = \mu_i(x_i) - \mu_l(i),$$

where $x_i/100$ is the mole fraction of the component i, $\mu_i(x_i)$ is the chemical potential of i in the mixture and $\mu_l(i)$ is the chemical potential of the pure component i.

The thermodynamic properties of NaCl are known from experiments, so that we can check the calculated results.

2. Computation

In order to obtain a canonical ensemble, we made the MD simulation proposed by Nose [3] with the 7 points predictor-corrector method, using periodic boundaries. The time increment was 0.5 fs as in [4]. We employed the Born-Mayer-Huggins pair potential, excluding the dipole-quadrupole term:

$$\Phi_{ij} = \frac{z_i z_j e^2}{4\pi\varepsilon_0 r} + A_{ij} b \exp\left[(r_i^0 + r_j^0 - r)/\sigma\right] - \frac{c_{ij}}{r^6}, \tag{1}$$

where r, z, e, ε_0, b, A, r^0, and σ are the distance between the ions i and j, the valency, the elementary charge, the dielectric constant of vacuum, the pre-exponential factor, the Pauling factor, the ionic radius and a softness parameter, respectively. The Coulomb potential was evaluated by the Ewald method [5]. The potential parameters of Na^+ and Cl^-, given by Tosi and Fumi [6], were employed. The potential parameters of the trivalent cations are not available, so that they have to be evaluated. The ionic radius $r^0_{Dy^{3+}}$ and the softness parameter σ are determined such that the experimental pair correlation functions [7] and the mixing enthalpy [8] in the molten $DyCl_3$-NaCl (50:50) system at 1100 K are reproduced. We obtained $r^0_{Dy^{3+}} = 0.153$ nm and $\sigma = 3.3\ \text{nm}^{-1}$. The parameter c_{ij} was estimated from the ionic polarizability [9, 10]. The side length of the periodic cell corresponded to the available density [11]. After the system was well annealed, data acquisition was made during 5000 time steps.

The excess chemical potential was estimated from the positional data of the ions recorded every 20 MD time steps with the method proposed by Powles *et al.* [2]. Powles *et al.* showed that the intercept of a linear plot of $L(u)$ vs. u gives the excess chemical potential:

$$L(u) \equiv \ln(f(u)/g(u)) = \beta u - \beta\mu^{\text{ex}}. \tag{2}$$

Reprint requests to M. Gaune-Escard;
E-mail: mge@iusti.univ-mrs.fr
Fax: +33 (0) 4 91 11 74 39

0932-0784 / 98 / 0800-0655 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

The function of $f(u)$ is a distribution function of the energy u, which is the energy difference between the original system and the system with inserted fictitious particles to the original system [12]. The function of $g(u)$ is a distribution function of the energy u, which is the energy difference between the original system and the system with removed particles from the original system [13]. μ^{ex} is the excess chemical potential. Equation (2) means that a plot of $L(u)$ vs, βu has a slope of unity. The chemical potential is given by

$$\mu = \mu^{ideal} + \mu^{ex}, \tag{3}$$

where μ^{ideal} is the chemical potential of the ideal gas. The chemical potential of the ideal gas is calculated from (4) and (5):

$$\mu^{ideal} = kT \log\left(\frac{N}{V}\Lambda_i^3\right) + kT \log\left(\frac{N}{V}\Lambda_j^3\right), \tag{4}$$

$$\Lambda_i = \sqrt{\frac{h^2}{2\pi m_i\, kT}}, \tag{5}$$

where h, m, N, and V are the Planck constant, the mass of an ion, Avogadro's number and the molar volume, respectively. We concluded in [14] that the function $L(u)$ depends on the size of the system and gives a reasonable value of the chemical potential if the cell contains more than 1000 ions. In this work we employed 1728 ions.

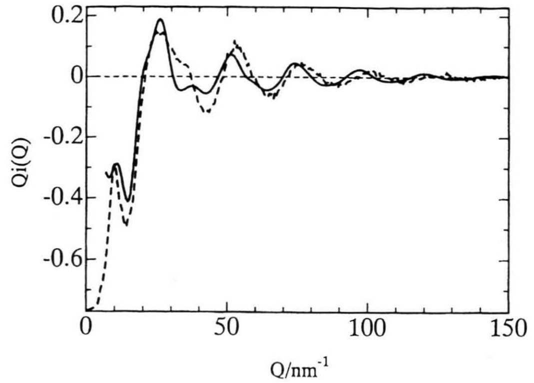

Fig. 1. Total structure factor of the molten $DyCl_3$-NaCl (25:75) system. Solid line: computed; dashed line: experimental [7].

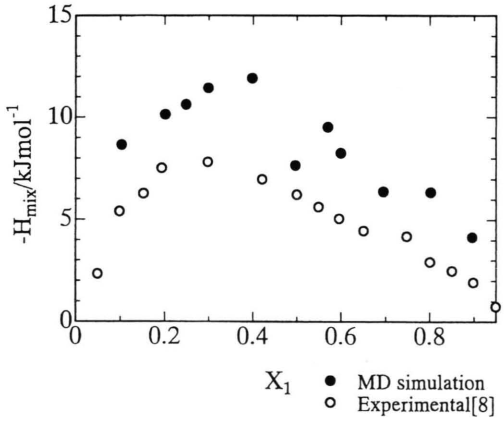

Fig. 2. Mixing enthalpy in the molten $DyCl_3$-NaCl system at 1100 K.

3. Results and Discussion

The isobaric specific heat (C_p) is calculated by

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P, \tag{6}$$

where H and T is the enthalpy and the temperature, respectively. The isobaric specific heat of molten $DyCl_3$ is found to be 129.8 J/mol K, while the experimental one is 159.4 J/mol K [15].

With these potential parameters, the MD simulation of the molten binary system $DyCl_3$-NaCl was carried out. The total structure factor of the molten $DyCl_3$-NaCl (25:75) system, estimated by the MD, is shown in Fig. 1, together with the experimental results [7]. The coincidence is satisfactory. It is remarkable that the MD simulation reproduced the first sharp diffraction peak (FSDP) quite well (Q = 10.5 nm^{-1} from the MD; Q = 10.0 nm^{-1} from the measured structure factor). The FSDP has been interpreted as the Dy-Dy correlation due to chlorine-sharing linkage between the octahedral units [16]. The mixing enthalpy of the molten $DyCl_3$-NaCl system at 1100 K is shown in Fig. 2 together with the experimental one [8]. The coincidence is satisfactory.

In order to calculate the chemical potential of NaCl in the molten $DyCl_3$-NaCl system, we made MD simulations at liquidus temperatures of the phase diagram [17]. The conditions of the MD simulations are shown in Table 1. Additionally, in order to estimate the activity of NaCl, we made a MD simulation of NaCl in the supercooled state at this temperature. The densities of the molten NaCl were extrapolated to this temperature. In order to obtain the energy distributions $f(u)$ and $g(u)$ in (2), 500 combinations of pairs of Na^+ and Cl^- ions were removed from or added to the system randomly. The fictitious pairs of Na^+ and Cl^- are put at regular 10 × 10 × 10 grids in

Table 1. Conditions of MD simulations.

System $DyCl^3$-NaCl (x_1:x_2)	Number of ions			Temperature (K)	Density (g/cm^3)
	Dy^{3+}	Na^+	Cl^-		
(10:90)	79	706	943	1019.0	1.9553
(20:80)	144	576	1008	893.7	2.3394
(0:100)	0	864	864	1019.0	1.5860
(0:100)	0	864	864	893.7	1.6540

x_1: $DyCl_3$ and x_2: NaCl.

Table 2. The chemical potentials and the activity coefficients of NaCl in the molten $DyCl_3$-NaCl system, estimated by MD simulation.

System $DyCl_3$-NaCl (x_1:x_2)		(10:90)	(20:80)
$\mu_l(2)$	(kJ/mol)	−886.18	−864.16
$\mu_l(x_2)$	(kJ/mol)	−888.52	−873.86
$RT \ln a_2$	(kJ/mol)	−2.34	−5.86
a_2		0.75	0.45
Experimental (a_2) [17, 18]		0.80	0.49

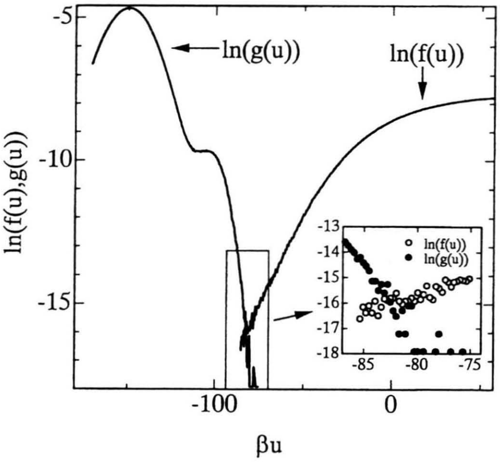

Fig. 3. Energy distribution functions $f(u)$ and $g(u)$ of NaCl in the molten $DyCl_3$-NaCl (10:90) system.

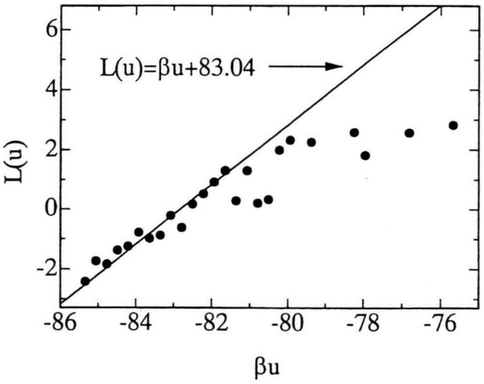

Fig. 4. The function of $L(u)$ defined by (2) in the molten $DyCl_3$-NaCl (10:90) system.

the basic cells. The energy distribution functions of NaCl in the molten $DyCl_3$-NaCl (10:90) system, $f(u)$ and $g(u)$, are depicted in Figure 3. $L(u)$ defined by (2) is depicted in Fig. 4, where a linear line with a slope of unity is drawn at the point $L(u) = 0$ where $f(u)$ and $g(u)$ cross. The excess chemical potential of NaCl is estimated from the intercept of this linear line. By the same procedure, carried out for the molten $DyCl_3$-NaCl (20:80) system, we obtained the chemical potential of NaCl. The chemical potentials of the ideal gas of NaCl in the molten binary system are $\mu^{\text{ideal}} = -187.26$ kJ/mol ($T = 1019.0$ K) and $\mu^{\text{ideal}} = -162.15$ kJ/mol ($T = 893.7$ K), as calculated by (4) and (5). The coincidence is satisfactory.

The activity of NaCl in the molten $DyCl_3$-NaCl system is calculated by

$$RT \ln a_2 = \mu_l(x_2) - \mu_l(2), \tag{7}$$

where T and a_2 are the liquidus temperature and the activity of NaCl. $\mu_l(x_2)$ is the chemical potential of NaCl in the molten binary system and $\mu_l(2)$ is the chemical potential of the pure supercooled NaCl at the liquidus temperature. The excess chemical potential of NaCl was also estimated with the method proposed by Powles *et al.* The chemical potentials of the ideal gas of NaCl at two liquidus temperatures are $\mu^{\text{ideal}} = -185.60$ kJ/mol ($T = 1019.0$ K) and $\mu^{\text{ideal}} = -159.23$ kJ/mol ($T = 893.7$ K) as calculated by (4) and (5). The chemical potentials of NaCl at the liquidus temperature estimated by MD simulation $\mu_l(2)$ and the activity of NaCl a_2 are listed in Table 2 together with the experimental ones [17, 18]. The activity of NaCl in the molten $DyCl_3$-NaCl system estimated by MD simulation is close to the experimental one.

4. Conclusion

It is demonstrated that reasonable values of the chemical potential and the activity of NaCl were obtained by MD simulations with the method proposed by Powles *et al.*

[1] Y. I. Chang, L. C. Walters, J. E. Battles, D. C. Wade, and M. J. Lineberry, ANL-IFR-125 (1990).

[2] J. G. Powles, W. A. B. Evans, and N. Quirke, Mol. Phys. **46**, 1347 (1982).

[3] S. Nose, Mol. Phys. **52**, 255 (1984).

[4] W. F. Gunsteren and H. J. C. Berendsen, Mol. Phys. **34**, 1311 (1977).

[5] P. P. Ewald, Ann. Phys. **64**, 253 (1921).

[6] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids **25**, 45 (1964).

[7] A. K. Adya, R. Takagi, Y. Sato, M. Gaune-Escard, A. C. Barnes, and H. Fischer, to be submitted.

[8] R. Takagi, L. Rycerz, and M. Gaune-Escard, Denki Kagaku **62**, 240 (1994).

[9] Y. Iwadate, J. Mochinaga, and K. Kawamura, J. Phys. Chem. **85**, 3708 (1981).

[10] B. Larsen, T. Forland, and K. Singer, Mol. Phys. 26, 1521 (1973).

[11] G. J. Janz, J. Phys. Chem. Ref. Data **17**, 1 (1988).

[12] B. Widom, J. Chem. Phys. **39**, 2808 (1963).

[13] K. S. Shing and K. E. Gubbins, Mol. Phys. **46**, 1109 (1982).

[14] R. Takagi and M. Sakurai, Z. Naturforsch. **53a**, 13 (1998).

[15] M. Gaune-Escard and L. Rycerz, to be published.

[16] M. L. Saboungi, D. L. Price, C. Scamehorn, and M. P. Tosi, Europhys. Lett. **15**, 283 (1991).

[17] H. J. Seifert and J. Sandrock, Acta Chemica Scan. **49**, 653 (1995).

[18] M. Gaune-Escard and F. Da Silva, private communication.