Solubility of KF in water by molecular dynamics using the Kirkwood integration method

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We have studied the solubility of potassium fluoride in aqueous solution at near ambient condition, using a simple modeling for the ion and water interactions and computing the values of the chemical potential by molecular dynamics within the framework of Kirkwood generalized thermodynamic integration approach for the evaluation of free energy differences. We report the details of the procedure we used, which is based—at variance with previous attempts—on the individual determination of the chemical potential for the ions in solution. We explore a wide range of salt concentrations up to more than 25 M and determine the solubility. The agreement with the experimental value is reasonable, taking account of the rather crude model used. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1498820]

I. INTRODUCTION

The prediction of ionic solid's solubility is of prime interest for environment sciences and geochemistry with regard to rocks solubility and water contamination in soils. However, it is advisable to distinguish solids having common ions or elements with water as Al_2O_3, SiO_2, etc., and the others as CaF_2, $Ca_3(PO_4)_2$, ... Compounds having common elements with water have acid-base properties and their dissolution often requires action of acids and bases. Other ionic compounds have even oxido-reduction properties and their dissolution brings about a variation of their oxidation degree. For example, $^{IV}UO_2$ becomes $^{VI}UO_2^{2+}$ in water. Even if we envisage, in the long term, to treat these kind of systems, in a first approach we will content ourselves with studying systems not presenting these difficulties. A preliminary study on KF solubility is the goal of the present paper. As a next step, we will treat systems close to it, as LiF, CaF_2, ThF_4, $MgSO_4$, $CaSO_4$, $BaSO_4$, etc., and we plan to check common ion effects, i.e., the solubility of a salt in the presence of another salt, by calculating lithium and/or calcium salt solubilities in the presence of a KF excess. The solubility of a salt in a solvent is measured by the concentration of the saturated solution in equilibrium with a precipitate, i.e., when, at a given temperature T and pressure P, the chemical potential of the solute in solution equals the chemical potential of the pure salt crystalline phase. In the case of aqueous electrolyte solutions the problem could be somewhat more complex, taking into account the possible occurrence of crystalline hydrate phases. In spite of the simple definition,[1,2] there are no recent attempts to define a simple theoretical procedure to see if it is possible to gain physical insight into such processes by numerical simulations, apart from an early approach for sodium chloride in supercritical water.[3] This approach contains somewhat restrictive *ad hoc* assumptions to simplify the calculation both for the solid and the solution phases, which are not valid if the solubility is high. Although the various ingredients needed are rather well known in literature[2–13] no direct attempt exists to perform such kind of calculations in the case of electrolyte solutions at high concentrations. In particular, accurate calculations of free energies of solvation have been attempted only for simple uncharged mixtures (rare gases) at finite concentrations[4,14] or near infinite dilution in the case of ionic solutes.[5,7–10,13] Furthermore it is required to compute the absolute chemical potential of the species under investigation in the solid phases with sufficient accuracy using rather different, and in any event uncorrelated, methods.[11,15] In this paper, extending established techniques for the calculation of the chemical potential of ionic species both in a dense liquid and in the pure crystalline phase we will show how it is possible to compute the solubility of an electrolyte salt dissolved in water. The test case we have chosen for our simulations is potassium fluoride salt in water, since its solubility is relatively high and thus requires to explore the case of solutions at high concentrations. In Sec. II we review the statistical mechanical theory. In Sec. III we define a microscopic model, while in Sec. IV we detail the conditions of

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the molecular-dynamics simulations and we present our results. Section V gives some concluding remarks.

II. THEORY

In order to determine the condition of phase equilibria we need to compare the values of the chemical potential for the electrolyte in solution with that in the solid phase at the given temperature and pressure. The density of both phases is too high to make feasible a direct calculation using Widom particle insertion method.[16] Therefore, we adopt the scheme originally proposed by Kirkwood in the thirties[2] of a generalized thermodynamic integration using a coupling parameter to describe a path from an analytically known ''reference condition'' to the point of interest. We generalize the original NVT Kirkwood approach for liquid solutions to the NPT case. For the solid phase we calculate the absolute free energy of crystals using the method proposed by Frenkel and Ladd.[11]

A. Electrolyte chemical potential in solution

For a generic electrolyte in solution, composed of r constituents, each constituent $j=1,\ldots,r$ having charge number q_j and formula weight number ν_j, the condition of electroneutrality imposes $\Sigma_{j=1}^{r} q_j \nu_j = 0$. Therefore, since the concentrations of ionic components cannot be varied independently, the definition of separate chemical potentials, although theoretically useful, does not have operational significance.[1] In our derivation we will drop, in the subscripts, the indication of ionic charges and will simply denote potassium ions by K instead of K^+ and fluoride ions by F instead of F^-, in order to increase the legibility of formulas. For example in the case of potassium fluoride one has simply $\nu_K = \nu_F = 1$ and the chemical potential μ of the electrolyte is defined as

$$\mu = \sum_{j=1}^{r} \mu_j \nu_j = \mu_K + \mu_F . \tag{1}$$

Starting from the finite difference ratio $\Delta F/\Delta N_j = \mu_j$ defining the chemical potential of species j as the change in free energy produced by the subtraction or addition of a molecule of type j from the system at fixed $T,V,N_{\alpha\neq j}$, Kirkwood originally derived the integral definition for the chemical potentials

$$\mu_j = k_B T \ln N_j/V + \int_0^1 \overline{U_j(\lambda')} d\lambda' + \varphi_j(T), \tag{2}$$

where $\overline{U_j(\lambda')}$ is the expected value of the potential energy of the subtracted particle in the ensemble in which the interaction is weighted by the parameter λ', and $\varphi_j(T)$ is the contribution from the momentum space integral.[2]

In our case we prefer to use the pressure P as a thermodynamic variable rather than the volume V, working in the isothermal–isobaric ensemble whose partition function is directly related to the Gibbs free energy. Specializing to the case of K^+F^- aqueous solutions, we can easily derive an expression for the chemical potentials in terms of Gibbs free energy differences. For example, the chemical potential μ_K of the potassium ion as a function of the temperature T and pressure P and in a solution with N_w water molecule, $N_K = N_F$ ion pairs, is given by

$$\mu_K(T,P,N_w,N_K,N_F) = \mathcal{G}(T,P,N_w,N_K+1,N_F) - \mathcal{G}(T,P,N_w,N_K,N_F). \tag{3}$$

In order to calculate the Gibb's free energy difference, following Kirkwood, we gradually add to the solution at (T,P,N_w,N_K,N_F) one extra ion I (I being either K or F) by coupling its interaction with the parameter λ varying in the interval $[0,1]$. We can write down the Hamiltonian for the composite system as

$$\mathcal{H}(\lambda) = \mathcal{K}(N_w,N_K,N_F) + \mathcal{U}_0(N_w,N_K,N_F) + \frac{\mathbf{p}_I^2}{2m_I} + \lambda \mathcal{U}_1(N_w,N_K,N_F,1_I), \tag{4}$$

where $\mathcal{U}_0$ is the potential energy term for the solution alone, $\mathcal{U}_1$ is the term corresponding to the interaction of the extra ion I with the solution, and with $\mathcal{K}(N_w,N_K,N_F)$ we indicate the kinetic energy of N_w water molecules, N_K potassium ions and N_F fluorine ions. We can now write down the expression for the isothermal–isobaric partition function

$$\mathcal{Q}(T,P,N_w,N_K,N_F,\lambda) = \frac{1}{N_w!N_K!N_F!}\int dV \exp(-\beta P V) \times \frac{1}{\Lambda_w^{3N_w}\Lambda_K^{3N_K}\Lambda_F^{3N_F}\Lambda_I^3} \times \int d\mathbf{r}^{N_w} d\mathbf{r}^{N_K} d\mathbf{r}^{N_F} d\mathbf{r}_I e^{-\beta\mathcal{U}_0} e^{-\lambda\beta\mathcal{U}_1}, \tag{5}$$

where the Λ's are the thermal de Broglie wavelengths, or more generally the molecular contributions from the momentum space integral. The Gibbs free energy of the composite system $\mathcal{G}(\lambda) = -k_B T \ln \mathcal{Q}(\lambda)$ is now a function of the coupling parameter λ, while the Gibbs free energy difference between the systems with $\lambda = 1$ and $\lambda = 0$ can be expressed in terms of the thermodynamic integration

$$\Delta\mathcal{G} = \mathcal{G}(\lambda=1) - \mathcal{G}(\lambda=0) = \int_0^1 d\lambda' \left[\frac{\partial \mathcal{G}}{\partial \lambda}\right]_{\lambda=\lambda'}. \tag{6}$$

Thanks to the linear coupling, the generalized thermodynamic force over λ has the simple expression

$$\left[\frac{\partial \mathcal{G}}{\partial \lambda}\right]_{\lambda=\lambda'} \equiv -k_B T \frac{1}{\mathcal{Q}(\lambda')}\left[\frac{\partial \mathcal{Q}(\lambda)}{\partial \lambda}\right]_{\lambda=\lambda'} = \langle \mathcal{U}_1 \rangle_{\lambda=\lambda'}. \tag{7}$$

We now specialize to the case of a gradual insertion of a potassium ion, i.e., $I=K$, in order to take properly into account the number counting associated with particle indistinguishability (the other case $I=F$ follows identically). The relation between the partition functions for the systems with N_K and N_K+1 potassium ions and the partition function defined as a function of the parameter λ, Eq. (5) is

$$\mathcal{Q}(\lambda=0)=\mathcal{Q}(T,P,N_w,N_K,N_F)\frac{\langle V\rangle}{\Lambda_K^3}, \tag{8}$$

$$\mathcal{Q}(\lambda=1)=(N_K+1)\,\mathcal{Q}(T,P,N_w,N_K+1,N_F), \tag{9}$$

giving in terms of Gibbs free energies

$$\mathcal{G}(\lambda=0)=\mathcal{G}(T,P,N_w,N_K,N_F)-k_BT\ln\left(\frac{\langle V\rangle}{\Lambda_K^3}\right), \tag{10}$$

$$\mathcal{G}(\lambda=1)=\mathcal{G}(T,P,N_w,N_K+1,N_F)-k_BT\ln(N_K+1). \tag{11}$$

The chemical potential of the ionic component $\mathbf{K}^+$ in the solution at the concentration specified by the numbers (N_w,N_K,N_F) is

$$\mu_K(T,P,N_w,N_K,N_F)=\mathcal{G}(\lambda=1)-\mathcal{G}(\lambda=0) - k_BT\ln\left(\frac{\langle V\rangle}{(N_K+1)\Lambda_K^3}\right). \tag{12}$$

Equation (12) is identical to the original Kirkwood expression, derived in the canonical ensemble, apart from the volume V replaced by the expected value of the volume in the isothermal–isobaric ensemble with (N_w,N_K,N_F) particles.

B. Chemical potential of the solid phase

We derive the chemical potential of the solid phase by computing, first, the absolute Helmholtz free energy of the crystal using the Frenkel and Ladd thermodynamic integration method[11] in terms of a coupling parameter $\lambda\in[0,1]$

$$\mathcal{F}(\lambda=1)=\mathcal{F}(\lambda=0)+\int_0^1 d\lambda'\left[\frac{\partial\mathcal{F}(\lambda)}{\partial\lambda}\right]_{\lambda=\lambda'}, \tag{13}$$

referring to a system with the Hamiltonian

$$\mathcal{H}(N_K,N_F,\lambda)=\mathcal{K}(N_K,N_F)+(\lambda\mathcal{U}_0(N_K,N_F) +(1-\lambda)\mathcal{U}_E(N_K,N_F), \tag{14}$$

where $\mathcal{U}_0$ is the potential energy of the physical system and $\mathcal{U}_E$ is that of a corresponding Einstein crystal, used as a reference system

$$\mathcal{U}_E=\sum_{i=1}^{N}\left[\frac{\gamma^{(K)}}{2}(r_i^{(K)}-\overline{r_i^{(K)}})^2+\frac{\gamma^{(F)}}{2}(r_i^{(F)}-\overline{r_i^{(F)}})^2\right], \tag{15}$$

where $\overline{r_i^{(K)}},\overline{r_i^{(F)}}$ are the equilibrium positions and $\gamma^{(K)},\gamma^{(F)}$ are the force constants of the harmonic crystal. In the canonical ensemble from the partition function

$$\mathcal{Q}(N,V,T;\lambda)=\frac{1}{h^{3N_K}h^{3N_F}}\int d\mathbf{r}^{N_K}d\mathbf{r}^{N_F}d\mathbf{p}^{N_K}d\mathbf{p}^{N_F} \times\exp\left(-\frac{\mathcal{K}+\lambda\mathcal{U}_0+(1-\lambda)\mathcal{U}_E}{k_BT}\right), \tag{16}$$

we derive the simple form for the thermodynamic force along the parameter λ

$$\left(\frac{\partial\mathcal{F}(\lambda)}{\partial\lambda}\right)_{\lambda=\lambda'}=-k_BT\frac{1}{\mathcal{Q}(\lambda')}\left(\frac{\partial\mathcal{Q}(\lambda)}{\partial\lambda}\right)_{\lambda=\lambda'} \tag{17}$$

$$=-\frac{k_BT}{\mathcal{Q}(\lambda')}\frac{1}{h^{3N_K}h^{3N_F}}\int d\mathbf{r}^{N_K}d\mathbf{r}^{N_F}d\mathbf{p}^{N_K}d\mathbf{p}^{N_F} \times\left[\frac{\partial}{\partial\lambda}\exp\left(-\frac{\mathcal{K}+\lambda\mathcal{U}_0+(1-\lambda)\mathcal{U}_E}{k_BT}\right)\right]_{\lambda=\lambda'}$$

$$=\langle\mathcal{U}_0-\mathcal{U}_E\rangle_{\lambda=\lambda'}. \tag{18}$$

To get the exact relation between the free energy of the λ coupled systems and the physical system we have to take into account the difference between the localized Einstein model, with distinguishable particles, and the physical system with indistinguishable particles. From the canonical partition function for the Einstein crystal

$$\mathcal{Q}(N,V,T)=(\mathcal{Q}_E^{(K)}(V,T))^{N_K}(\mathcal{Q}_E^{(F)}(V,T))^{N_F}, \tag{19}$$

where $N\equiv N_K=N_F$

$$\mathcal{Q}_E^{(K)}(V,T)=\frac{V}{\Lambda_K^3}\left(\frac{2\pi k_BT}{\gamma^{(K)}V^{2/3}}\right)^{3/2}, \tag{20}$$

$$\mathcal{Q}_E^{(F)}(V,T)=\frac{V}{\Lambda_F^3}\left(\frac{2\pi k_BT}{\gamma^{(F)}V^{2/3}}\right)^{3/2}, \tag{21}$$

and the canonical partition function for the physical model

$$\mathcal{Q}_0(N,V,T)=\frac{1}{N_K!\Lambda_K^{3N_K}N_F!\Lambda_F^{3N_F}} \times\int d\mathbf{r}^{3N_K}d\mathbf{r}^{3N_F}\exp\left(-\frac{\mathcal{K}+\mathcal{U}_0}{k_BT}\right), \tag{22}$$

we get for the physical Helmholtz free energy

$$\mathcal{F}(\lambda=0)=\mathcal{F}_E,\quad \mathcal{F}(\lambda=1)=\mathcal{F}-k_BT\ln(N_K!N_F!), \tag{23}$$

$$\mathcal{F}=\mathcal{F}_E+k_BT\ln(N_K!N_F!)+\int_0^1 d\lambda'\langle\mathcal{U}_0-\mathcal{U}_E\rangle_{\lambda=\lambda'}. \tag{24}$$

By transforming Eq. (24) into the Gibbs free energy, function of N,P,T, and dividing by the number of ion pairs, we obtain the chemical potential of the ionic crystal

$$\mu\equiv\mu_K+\mu_F\equiv\frac{\mathcal{G}(N,P,T)}{N}=\frac{\mathcal{F}(N,P,T)}{N}+\frac{P\langle V\rangle}{N}. \tag{25}$$

III. MODELING THE AQUEOUS K^+F^- SOLUTION

Solvation of ions in water is a very active field of research. Water is historically the system for which more computational studies exist and, consequently, many effective potential models have been proposed and tested for water.[17] For most ions, effective potential models for the interaction with water exist. The model parameters, optimized with reference to a specific solvent model, have usually been derived by fitting *ab initio* calculated properties of a number of configurations of small clusters of water around a central ionic solute. These potential models have been used extensively to characterize solvation structures, ionic mobilities, and the

TABLE I. Potential parameters for aqueous potassium fluoride solution.

$i-j$	σ_{ij} [Å]	ε_{ij} [kJ/mol]	$i-j$	A_{ij} [kJ/mol]	ρ_{ij} [Å]	C_{ij} [kJ/(mol Å^6)]	D_{ij} [kJ/(mol Å^8)]
O–O	3.166	0.6502	K–K	146 455.0	0.338	1463.3	1445.3
O–K	3.250	0.5216	K–F	50 562.9	0.338	1174.3	1264.6
O–F	3.143	0.6998	F–F	16 365.6	0.338	1120.1	1324.8

electrostatic contributions to the free energies of solvation in the so-called limit of infinite dilution. Recently, also a few simulations at finite concentrations have appeared with a focus on the concentration dependence of the structural and dynamical properties of hydrogen bonding in solution.[18,19] A question that remains open is how far the crude, fixed charge, effective model description can be extended to highly charged systems. In particular, is it well founded to compute the ion–ion pair interaction parameters using the so-called ''standard mixing rules'' starting from those optimized from the single ion interaction with water or blending parameters and models developed for rather different thermodynamic conditions? For example is it justified to use the molten salt Born–Huggins–Mayer potential with Tosi–Fumi parameters[20] for the interaction of ions in solution?

In this first attempt to describe our K^+F^- aqueous solution our main goal is to provide a sound method for the calculation of solubility, and therefore, we will be content with the most simple, hopefully realistic, model. For water we chose the simple point charge (SPC/E) model[21] and for ion–water interactions the model developed by Dang and co-workers[22] with parameters optimized for SPC/E water

$$V_{ij}(r_{ij})=4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]+\frac{e^2}{(4\pi\epsilon_0)}\frac{Z_iZ_j}{r_{ij}}, \quad (26)$$

while for ion–ion interactions we choose the earlier Born–Huggins–Mayer potential with Tosi–Fumi (TF) parameters[20]

$$V_{ij}^{\mathrm{TF}}(r_{ij})=A_{ij}e^{-r_{ij}/\rho_{ij}}-\frac{C_{ij}}{r_{ij}^6}-\frac{D_{ij}}{r_{ij}^8}+\frac{e^2}{(4\pi\epsilon_0)}\frac{Z_iZ_j}{r_{ij}}. \quad (27)$$

Our decision to disregard electrical polarization effects was eased by the high rigidity (''hardness'') of the fluoride ion. Nevertheless the model chosen for ion–ion interactions is known to work only moderately well for KF. However densities and energies of the crystalline phase around room temperature and pressure are roughly correct and, in any event, much better reproduced than using a Lennard-Jones potential with parameter extrapolated back from standard mixing rules. The parameters used in our calculations are reported in Table I.

Extensive investigations, by molecular dynamics with the model described, of the properties of aqueous solution of potassium fluoride are reported elsewhere.[23] They show a slowing down of the dynamics with increasing salt concentration, more pronounced than in the experimental case. The solution is closer to a gel than to a liquid. To avoid the statistical problems associated with the slowing down we decided to simulate a thermodynamic point with the somewhat higher temperature $T=320$ K.

Holonomic constraints present in the water model were treated as usual with SHAKE.[24] To simulate isothermal–isobaric, NPT, conditions we implemented Nosé–Hoover's thermostat[25] and a variant of the Andersen's barostat described in Ref. 26. The barostat uses the molecular virial to calculate pressure[27] in order to decouple the constraints from the volume fluctuations. The resulting equations of motion, solved with the total momentum $\mathbf{p}_{\mathrm{tot}}=0$, sample the phase space according to the $(N-1)PT$ ensemble distribution.[28] Long-range Coulomb interactions were treated using the Ewald summation method.[29]

IV. MOLECULAR-DYNAMICS CALCULATIONS AND RESULTS

To perform successful molecular-dynamics simulation of our model we have to define completely the conditions of our computations. In particular we have: (i) To fix the parameters defining the Einstein crystal; (ii) to treat the long-range forces and possible size dependencies associated with the insertion of charged particles; finally, although a minor issue, (iii) to get rid of the corrections needed to account for the fact that we work in ensembles with total momentum, $\mathbf{p}_{\mathrm{tot}}$, constant and equal to $\mathbf{0}$.

(i) For an Einstein crystal simulations at constant pressure are meaningless, since the volume is by definition fixed once the equilibrium positions of the particles are chosen. Instead the best way to get the parameters for the physical system is to work under NPT conditions. Thus we first performed NPT calculations for the K^+F^- crystal starting from the experimental lattice at 298 K computing, after a suitable equilibration, the average density of the solid. We used a system with $N=2048$ ion pairs at $T=320$ K and $P=0.1$ MPa and found an average volume per particle, $\langle V\rangle/N=38.627$ Å^3. Then we started a NVT calculation for the same system with the volume fixed to the average value reported above and calculated the mean-square deviations of the ions from their equilibrium lattice positions $\langle\Delta\mathbf{R}_{(K)}^2\rangle=0.063\,26$ Å^2 and $\langle\Delta\mathbf{R}_{(F)}^2\rangle=0.075\,31$ Å^2. To optimize the sampling[15] the Einstein crystal was chosen by fixing the harmonic constants in such a way to reproduce the calculated Debye–Waller factors, i.e., $\gamma_{(I)}=3k_BT/\langle\Delta\mathbf{R}_{(I)}^2\rangle$, where I stands for K^+ or F^-. A total of 21 molecular-dynamics independent calculations were successively performed for the composite system defined by the Hamiltonian in Eq. (14). The values of the parameter $\lambda\in[0,1]$ were taken at constant separation $\delta\lambda=0.05$. The molecular dynamics

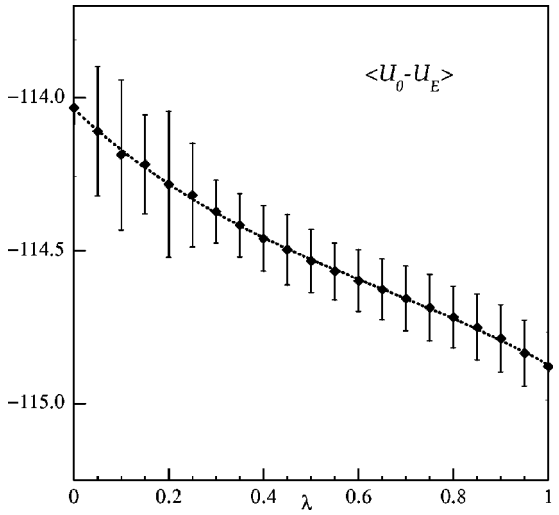

FIG. 1. λ dependence of the thermodynamic force $\langle \mathcal{U}_0 - \mathcal{U}_E \rangle_\lambda$ in the calculation of the Helmholtz free energy of the crystalline phase of potassium fluoride. The error bars in the figure represent the standard deviation of the instantaneous values.

(MD) averages were computed over equilibrium trajectories of 100 ps. The results are shown graphically in Fig. 1 together with their instantaneous standard deviations. These are really only a marginal overestimate of the errors since, even disregarding the reducing factor on the standard deviations coming from counting properly the independent contributions to the mean values, we get the free energy value with sufficiently high precision. From Eq. (25) we get the value $\mu = -116.10$ kJ/mol for the chemical potential of the electrolyte in the solid phase at $T = 320$ K;

(ii) To compute the chemical potential in the solution phase we have to decide how to account for the effects of the long range interactions both for electroneutrality and for possible size dependencies. The major problem in our MD simulations of the solution phase is the insertion of charged particles. A first attempt to introduce simultaneously a pair of particles with opposite charges, maintaining overall electroneutrality, was unsuccessful, due to the difficulty to obtain sufficient sampling of the relative configurations for the inserted pairs (the distance distribution), especially for small values of λ. Therefore, we had to work with the insertion of a single ion, performing an independent calculation of the chemical potential for each species, K^+ and F^-. The electro-neutrality of the system was maintained by considering a neutralizing uniform background. It has been suggested[7,10,30] that the periodicity of the system would imply a more dramatic size dependence than desirable. Those authors have suggested a size dependent correction for this effect inversely proportional to the dielectric constant. In our case the correction is small and largely within our statistical error. Therefore, we did not include it in our results. Without such correction the size dependence of our simulation can be seen in Fig. 2 both for the insertion in pure water [Fig. 2(a)] and in a highly concentrated solution [Fig. 2(b)].

(iii) We also need to account for the fact that the calculations both in the solid phase and in the solutions are performed in an ensemble at constant total momentum $\mathbf{p}_{\text{tot}} = 0$. In Ref. 12, Polson *et al.* have shown how to estimate the corrections coming from this situation.

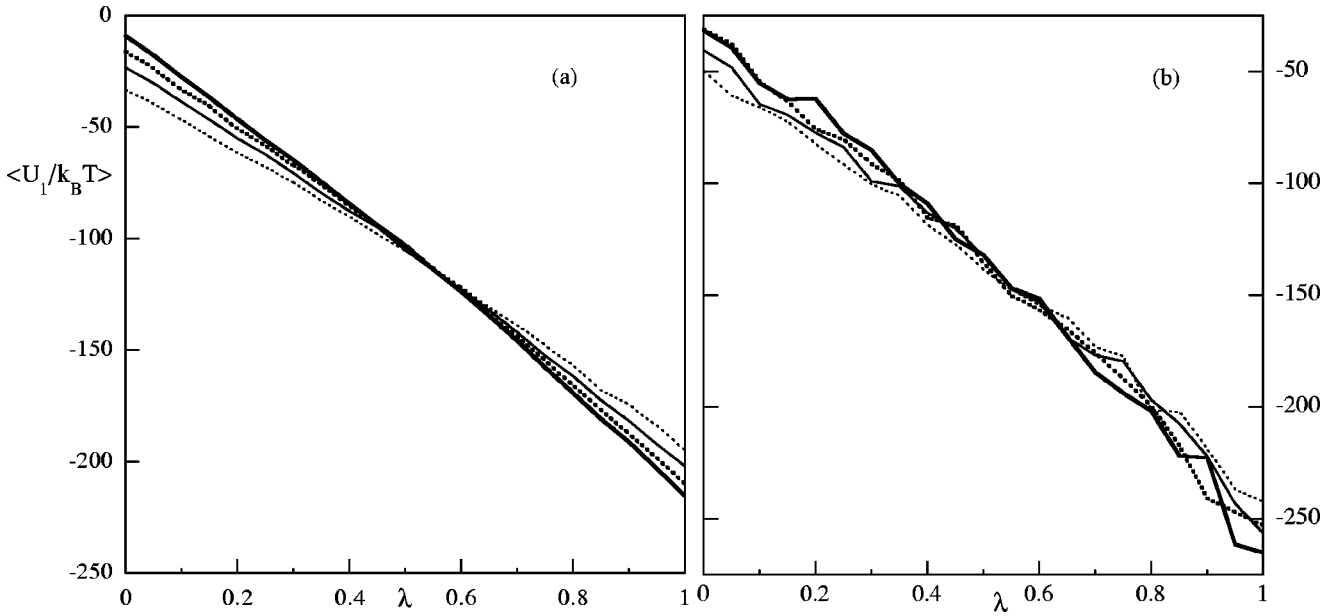

FIG. 2. Size dependence of the Coulomb contribution to the thermodynamic force $\langle \mathcal{U}_1^{\{\text{Coulomb}\}} \rangle_\lambda$ in the calculation of the chemical potential for the potassium ion in solution, for two cases: (a) Pure water and (b) 24.2 M KF solution. In both panel curves are representative of system with a given number of water molecules: $N_w = 1024$ thick straight line; $N_w = 512$ thick dotted line; $N_w = 256$ thin straight line; $N_w = 128$ thin dotted line. The change in slope is counterbalanced by the presence of a central fixed point, so that the excess chemical potential obtained by integration over λ shows variations within 0.1 kJ/mol, i.e., within the statistical errors of our calculation.

TABLE II. Electrolyte chemical potential: Individual contribution vs salt molar concentration. For completeness we also include the average volume and the number of ion pairs in each system.

c [M]	$\langle V\rangle$ [Å^3]	$N_K=N_F$	$\mu_K^{(ex)}$ [kJ/mol]	$\mu_F^{(ex)}$ [kJ/mol]	$\mu^{(ex)}$ [kJ/mol]	$\mu^{(id)}$ [kJ/mol]	μ [kJ/mol]
0.0	15 300	0	−39.5	−75.1	−114.6	−11.0	−125.6
5.28	10 061	32	−42.5	−73.7	−116.2	−8.1	−124.3
8.40	12 686	64	−44.0	−71.5	−115.5	−7.8	−123.3
11.6	12 905	90	−45.5	−69.6	−115.1	−7.5	−122.6
14.1	13 213	111	−46.9	−67.5	−114.4	−7.4	−121.8
17.9	13 925	150	−48.3	−64.1	−112.4	−7.2	−119.6
24.2	17 148	250	−49.4	−61.4	−110.8	−7.0	−117.8
26.5	12 029	192	−51.8	−56.8	−108.6	−6.9	−115.5

We have checked that in our case the corrections are definitively small and there is no need to include them.

A number of systems at different concentrations were set up by choosing the triplet (N_w, N_K, N_F) corresponding to a set of predefined molal concentrations ranging from the ''infinite dilution'' to very high molality. The systems were equilibrated using a series of NPT molecular dynamics runs with heating–cooling cycles until we reached a satisfactory equilibrium at the desired value $T=320$ K. For each concentration the individual chemical potentials of the two ionic components were calculated using the method discussed. As before the values of the parameter $\lambda\in[0,1]$ were taken with the uniform spacing $\delta\lambda=0.05$, and 20 independent MD runs at constant NPT for each ion were performed. In this case the value $\lambda=0$ is not directly computable. The λ dependent thermodynamic forces were averaged over equilibrium trajectories of 100 ps. Individual results for the chemical potential are listed in Table II with the relevant thermodynamic properties as a function of concentration, separating ideal and excess contributions defined as

$$\mu_I^{(\mathrm{id})}=k_BT\log\left(\frac{(N_I+1)\Lambda_I^3}{\langle V\rangle_{N_w,N_K,N_F}}\right), \tag{28}$$

$$\mu_I^{(\mathrm{ex})}=\mathcal{G}(\lambda=1)-\mathcal{G}(\lambda=0), \tag{29}$$

where the average volumes in Eq. (28) were computed in separate NPT runs of the various concentrated solutions.

One, for us unexpected, feature of the individual excess chemical potential for the ions is shown in Fig. 3. While the excess chemical potential μ_F for the fluorine ion increases with salt concentration, μ_K behaves in the opposite way, that is potassium ion is preferentially solvated in concentrated solution, while the fluorine ion has a high affinity for water, probably related to its capacity to make strong hydrogen bonds. As a result, the variation of the electrolyte chemical potential is the sum of two, large, opposite contributions, and has a relatively smooth behavior, rising slowly with concen-

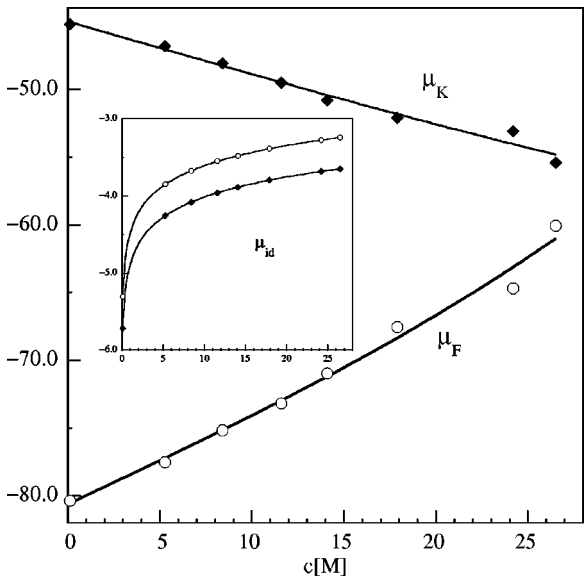

FIG. 3. Behavior of the individual contributions to the electrolyte chemical potential. The values of $\mu_K^{(\mathrm{ex})}$ and μ_F^{ex} are shown. Lines represent a simple polynomial (degree=3) fit to the data. In the inset the individual ideal chemical potential are shown: Their behavior with concentration results simply from the variation of the ion density, with the line showing the analytical log-dependence.

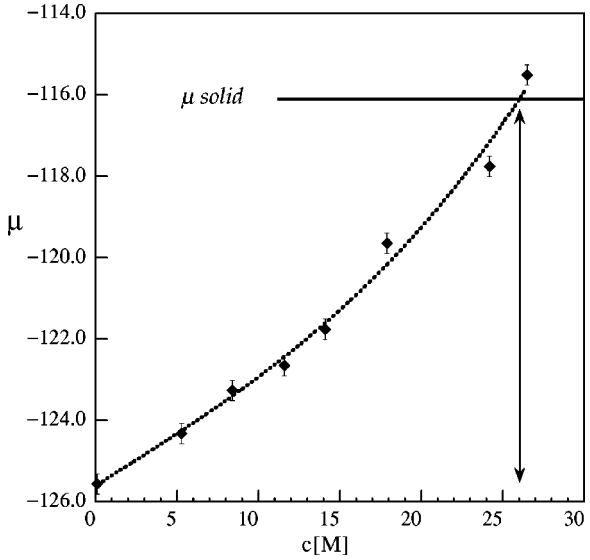

FIG. 4. Graphical determination of KF solubility in water. The horizontal line shows the value of the electrolyte chemical potential in the solid phase, while the diamonds are those in the solution. As a guide to the eye we include the fit with a polynomial of degree 3 and a vertical arrow showing the extrapolated molar concentration of the saturated solution, starting from an experimental value of 24.4 for the molality (Ref. 31) which is very close, for our model, to the solution with $c=17.9$ M.

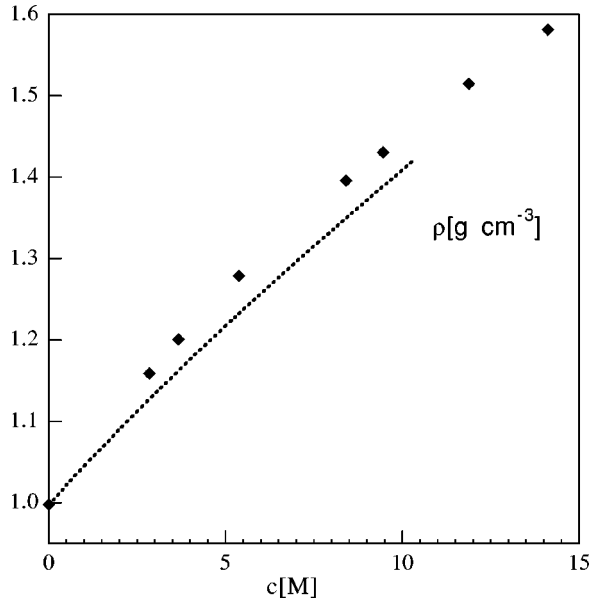

FIG. 5. Behavior of density vs molar concentration for our model (diamonds) compared with the experimental values (line).

tration. The behavior of the ideal term is shown in the inset of the same figure. In Fig. 4 we show the curve of chemical potential versus the concentration of the solution, fitted by a simple polynomial of order 3, together with the horizontal line corresponding to the chemical potential of the solid (crystalline) phase. The intersection is found at the concentration $s \approx 26$ M which is, therefore, the saturation value of our *KF* aqueous solution at $T = 320$ K. Our value compares reasonably with the experimental solubility, $s \approx 17$ M.[31] The agreement goes beyond our expectation, since the model we have chosen fails to reproduce quantitatively the density behavior of the concentrated solutions; see Fig. 5.

V. CONCLUDING REMARKS

This paper is a successful attempt to apply well-known procedures to get free energies by computer simulation to obtain information on solubility, one of the most important properties of concentrated electrolyte solutions. By taking advantage of simulations at constant temperature and pressure coupled with the charging procedure first suggested by Kirkwood, and of other more standard approaches to compute global free energies we have demonstrated not only the feasibility of such a calculation but also the absence of major computational difficulties in the approach. However the reliability of the results is strongly dependent on the accuracy of the interaction potential models to represent a realistic system of physical importance. Here, progress will come from different approaches, such as *ab initio* simulations. The important point we want to stress is that the statistical mechanics theory of solubility does not present numerical or conceptual difficulties.

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