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## Statistical mechanics of solutions

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**Abstract.** The theoretical calculation of the properties of the ionic solutions is discussed from the viewpoint of numerical simulations. We consider the simple case of the mixture of a solvent of polar molecules and ions and also, briefly, the case where both solvent molecules and ions are polarizable.

In a simulation of an ionic solution, the computation of the generalized frequency dependent dielectric constant  $\Sigma(\omega)$  is not as straightforward as, for instance, the calculation of the transport coefficients of neutral and non-polar molecular systems. Due to the long range of the electric interactions, the expression for  $\Sigma(\omega)$  in terms of  $\hat{\mathbf{P}}$ , the microscopic polarisation, and  $\hat{\mathbf{J}}$ , the microscopic electric current in the system, depends on the shape and boundary conditions of the volume enclosing the solution [1]. The first part of this paper will be devoted to the general outline of the method allowing to solve this problem and to its application to the systems which are localized in a cubic volume with periodic boundary conditions [2, 3]. In the second part we present the results of a computation of  $\Sigma(\omega)$  [4] and discuss the problem of the convergence of the statistical averages in the simulation of ionic solutions.

We first deal with the derivation of formulae for  $\Sigma(\omega)$ . The ensemble averages  $\mathbf{P}$  and  $\mathbf{J}$  of  $\hat{\mathbf{P}}$  and  $\hat{\mathbf{J}}$  are defined by

$$\mathbf{P}(\mathbf{r}, t) \equiv \langle \hat{\mathbf{P}} \rangle = \left\langle \sum_s \boldsymbol{\mu}_s(t) \delta(\mathbf{r} - \mathbf{r}_s(t)) \right\rangle \quad (1)$$

$$\mathbf{J}(\mathbf{r}, t) \equiv \langle \hat{\mathbf{J}} \rangle = \left\langle \sum_i q_i \mathbf{v}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t)) \right\rangle \quad (2)$$

where the indices  $s$  and  $i$  correspond respectively to the solvent molecules and ions,  $\boldsymbol{\mu}_s$  is the dipole of a solvent molecule and  $q_i$  is the charge of an ion.  $\mathbf{P}$  and  $\mathbf{J}$  give an estimate of the macroscopic polarisation and current in the solution. These macroscopic quantities are related to the Maxwell electric field  $\mathbf{E}(\mathbf{r}, t)$  by equations which define the time dependent dielectric constant and conductivity tensors  $\boldsymbol{\epsilon}(\mathbf{r}, \mathbf{r}', t)$  and  $\boldsymbol{\sigma}(\mathbf{r}, \mathbf{r}', t)$

$$4\pi\mathbf{P}(\mathbf{r}, t) = \int_{-\infty}^t dt' \int_V d\mathbf{r}' (\boldsymbol{\epsilon}(\mathbf{r}, \mathbf{r}', t-t') - \mathbf{1}) \cdot \mathbf{E}(\mathbf{r}', t') \quad (3)$$

$$4\pi\mathbf{J}(\mathbf{r}, t) = \int_{-\infty}^t dt' \int_V d\mathbf{r}' \boldsymbol{\sigma}(\mathbf{r}, \mathbf{r}', t-t') \cdot \mathbf{E}(\mathbf{r}', t') \quad (4)$$

where  $V$  the volume of the system and  $\mathbf{1}$  is an unit tensor local in space and time.

Assuming a local and isotropic form for the tensors  $\sigma$  and  $\epsilon$ , the formulae (3) and (4) become after Fourier-Laplace transform on  $t$

$$4\pi\mathbf{P}(\mathbf{r}, \omega) = (\epsilon(\omega) - 1)\mathbf{E}(\mathbf{r}, \omega) \quad 4\pi\mathbf{J}(\mathbf{r}, \omega) = \sigma(\omega)\mathbf{E}(\mathbf{r}, \omega). \quad (5)$$

$\mathbf{E}(\mathbf{r}, \omega)$  can be obtained from the solution of Maxwell's equations in the limit, valid for the considered systems, where the propagating modes are neglected. In the presence of an external electric field  $\mathbf{E}_{\text{ex}}(\mathbf{r}, \omega)$  and for a system surrounded by empty space, this solution has the form

$$\begin{aligned} \mathbf{E}(\mathbf{r}, \omega) &= \mathbf{E}_{\text{ex}}(\mathbf{r}, \omega) + \int_V \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \left[ \frac{3(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^2} - \mathbf{1} \right] \cdot \left( \mathbf{P}(\mathbf{r}', \omega) + \frac{i}{\omega}\mathbf{J}(\mathbf{r}', \omega) \right) \\ &\equiv \mathbf{E}_{\text{ex}} + \mathbf{G}_0 \circ (\mathbf{P} + \frac{i}{\omega}\mathbf{J}) \end{aligned} \quad (6)$$

where  $\mathbf{1}$  is an unit tensor local in space,  $\circ$  represents both convolution in  $\mathbf{r}$  space and tensor multiplication and  $\mathbf{G}_0$  denotes the Green function associated with Maxwell's equations in the electrostatic limit.

Using the relations (5), equation (6) can be written

$$\mathbf{E} = \mathbf{E}_{\text{ex}} + \Sigma\mathbf{G}_0 \circ \mathbf{E} \quad (7)$$

where

$$\Sigma(\omega) = (\epsilon(\omega) - 1) + \frac{4\pi i}{\omega}\sigma(\omega). \quad (8)$$

The formal solution of equation (7) is

$$\mathbf{E} = \mathbf{E}_{\text{ex}} + \Sigma\mathbf{G}_0 \circ (\mathbf{1} - \Sigma\mathbf{G}_0)^{-1} \circ \mathbf{E}_{\text{ex}} \equiv \mathbf{E}_{\text{ex}} + \Sigma\mathbf{G} \circ \mathbf{E}_{\text{ex}}. \quad (9)$$

With this expression for  $\mathbf{E}$  the relations (5) become

$$4\pi\mathbf{P}(\mathbf{r}, \omega) = (\epsilon(\omega) - 1)(\mathbf{E}_{\text{ex}} + \Sigma\mathbf{G} \circ \mathbf{E}_{\text{ex}}) \quad 4\pi\mathbf{J}(\mathbf{r}, \omega) = \sigma(\omega)(\mathbf{E}_{\text{ex}} + \Sigma\mathbf{G} \circ \mathbf{E}_{\text{ex}}). \quad (10)$$

On the other hand, expressions of  $\mathbf{P}$  and  $\mathbf{J}$  can be derived from the linear response theory in presence of the external field  $\mathbf{E}_{\text{ex}}$

$$4\pi\mathbf{P}(\mathbf{r}, \omega) = \beta[\langle \hat{\mathbf{P}}\hat{\mathbf{P}} \rangle + i\omega\langle \hat{\mathbf{P}}\hat{\mathbf{P}} \rangle_\omega + \langle \hat{\mathbf{P}}\hat{\mathbf{J}} \rangle_\omega] \circ \mathbf{E}_{\text{ex}} \quad (11)$$

$$4\pi\mathbf{J}(\mathbf{r}, \omega) = \beta[\langle \hat{\mathbf{J}}\hat{\mathbf{J}} \rangle_\omega + i\omega\langle \hat{\mathbf{J}}\hat{\mathbf{P}} \rangle_\omega] \circ \mathbf{E}_{\text{ex}}$$

where  $\beta = 1/kT$ ,  $\langle \hat{\mathbf{P}}\hat{\mathbf{P}} \rangle_\omega$ ,  $\langle \hat{\mathbf{P}}\hat{\mathbf{J}} \rangle_\omega, \dots$  are the Fourier-Laplace transforms of the time-dependent correlation functions  $\langle \hat{\mathbf{P}}(\mathbf{r}, 0)\hat{\mathbf{P}}(\mathbf{r}', t) \rangle$ ,  $\langle \hat{\mathbf{P}}(\mathbf{r}, 0)\hat{\mathbf{J}}(\mathbf{r}', t) \rangle, \dots$  and  $\langle \hat{\mathbf{P}}\hat{\mathbf{P}} \rangle = \langle \hat{\mathbf{P}}(\mathbf{r}, 0)\hat{\mathbf{P}}(\mathbf{r}', 0) \rangle$ . The time-dependent correlation functions are easily computable by numerical simulations as an integral on  $t$  along the trajectories of the molecules, for instance

$$\langle \hat{\mathbf{P}}(\mathbf{r}, 0)\hat{\mathbf{P}}(\mathbf{r}', t) \rangle \propto \int dt' \hat{\mathbf{P}}(\mathbf{r}, t')\hat{\mathbf{P}}(\mathbf{r}', t + t'). \quad (12)$$

The comparison between the two sets of equations (10) and (11) allows one to eliminate  $\mathbf{E}_{\text{ex}}$ ,  $\mathbf{P}$  and  $\mathbf{J}$  and to obtain the general expression of  $\Sigma$  in terms of the correlation functions of  $\hat{\mathbf{P}}$  and  $\hat{\mathbf{J}}$ , and of  $\mathbf{G}$ . Obviously  $\mathbf{G}$  is a rather complicated quantity which clearly depends on the shape and boundary conditions of the system through  $\Sigma\mathbf{G}_0$ . However it can be computed in a few cases, for instance for the infinite system and, fortunately, for the systems with periodic boundary conditions used in the numerical simulations. In these systems the Coulomb potential must be replaced by the Ewald potential which takes into account the effect of the periodic boundary conditions

$$\frac{1}{r} \Rightarrow \Psi(\mathbf{r}) = \Psi_E(\mathbf{r}) + \frac{2\pi}{2\epsilon' + 1} \frac{r^2}{V} \quad (13)$$

where  $\Psi_E(\mathbf{r})$  is a known periodic function and the last term is the contribution of the dielectric medium supposed to surround the infinite set of periodic replicas of the simulation cell [5]. Then the Green function  $\mathbf{G}$  satisfies

$$\int_V d\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = -\frac{1}{\Sigma(\omega) + 2\epsilon' + 1} \mathbf{U}. \quad (14)$$

where  $\mathbf{U}$  is the unit tensor. Using these results and the definitions

$$\bar{\mathbf{P}}(t) = \int_V d\mathbf{r} \hat{\mathbf{P}}(\mathbf{r}, t) \quad \bar{\mathbf{J}}(t) = \int_V d\mathbf{r} \hat{\mathbf{J}}(\mathbf{r}, t)$$

we obtain for  $\epsilon' = 1$

$$\frac{\epsilon(\omega) - 1}{4\pi} \frac{3}{3 + \Sigma(\omega)} = \frac{\beta}{3V} [\langle \bar{\mathbf{M}}^2 \rangle + i\omega \langle \bar{\mathbf{M}} \cdot \bar{\mathbf{M}} \rangle_\omega + \langle \bar{\mathbf{M}} \cdot \bar{\mathbf{J}} \rangle_\omega] \quad (15)$$

$$\sigma(\omega) \frac{3}{3 + \Sigma(\omega)} = \frac{\beta}{3V} [\langle \bar{\mathbf{J}} \cdot \bar{\mathbf{J}} \rangle_\omega + i\omega \langle \bar{\mathbf{J}} \cdot \bar{\mathbf{M}} \rangle_\omega] \quad (16)$$

and for  $\epsilon' = \infty$

$$\frac{\epsilon(\omega) - 1}{4\pi} = \frac{\beta}{3V} [\langle \bar{\mathbf{M}}^2 \rangle + i\omega \langle \bar{\mathbf{M}} \cdot \bar{\mathbf{M}} \rangle_\omega + \langle \bar{\mathbf{M}} \cdot \bar{\mathbf{J}} \rangle_\omega] \quad (17)$$

$$\sigma(\omega) = \frac{\beta}{3V} [\langle \bar{\mathbf{J}} \cdot \bar{\mathbf{J}} \rangle_\omega + i\omega \langle \bar{\mathbf{J}} \cdot \bar{\mathbf{M}} \rangle_\omega]. \quad (18)$$

It is worth noticing the important differences between the values of the correlation functions for different boundary conditions, for instance

$$\int_0^\infty dt \langle \bar{\mathbf{J}}(0) \cdot \bar{\mathbf{J}}(t) \rangle = 0 \quad \epsilon' \neq \infty \quad (19)$$

$$\int_0^\infty dt \langle \bar{\mathbf{J}}(0) \cdot \bar{\mathbf{J}}(t) \rangle \propto \sigma(0) \quad \epsilon = \infty.$$

These differences, obviously, do not imply different values of  $\epsilon(\omega)$  and  $\sigma(\omega)$ .

For ionic solutions where both solvent molecules and ions are polarizable, the previous formulae (17) and (18) remain valid if the following substitutions are made [3]:

$$\epsilon(\omega) - 1 \Rightarrow \epsilon(\omega) - \epsilon(\infty) \quad \bar{\mathbf{M}} = \sum_s \boldsymbol{\mu}_s \Rightarrow \sum_s \mathbf{m}_s + \sum_i \mathbf{m}_i$$

where  $m_s$  and  $m_i$  are the total dipole moments of solvent molecules and ions.

We now move on to numerical simulations.  $\Sigma(\omega)$  has been evaluated by numerical simulations for a system of 1024 solvent molecules and 256 ions [4]. The solvent molecules were polarizable and but without permanent dipole moment. The short range interaction potentials between the solvent molecules and ions were Lennard-Jones (LJ) potentials. The polarizability  $\alpha$  of the solvent molecules was in reduced units  $\alpha^* = \alpha/\sigma_s^3 = 0.12$  and the charge  $q$  of the ions  $q^* = q/(\epsilon_+\sigma_+) = 12$ , where  $\sigma_s$ ,  $\epsilon_+$  and  $\sigma_+$  are the parameters of the solvent-solvent LJ potential and of the positive ion LJ potential. The other parameters of LJ potentials were given by the relations  $\sigma_s/\sigma_- = 2.5$ ,  $\sigma_s/\sigma_+ = 2.0$ ,  $\epsilon_+/\epsilon_s = 1/15$  and  $\epsilon_+ = \epsilon_-$  and by Berthelot rules for the interactions between ions and solvent and between unlike ions. If  $\sigma_-$  is the unit of length the density was 0.0597 and the time unit was  $(m\sigma_-^2/\epsilon_s)^{1/2}$  where  $m$  is the mass, assumed equal, of the solvent molecules or ions.

The simulations were performed using the Ewald potential for the electric interactions and the two values  $\epsilon' = 1$  and 0 (in this last case, the factor 3 must be replaced by 1 in the right-hand sides of (16) and (17)). The values of  $\sigma(0)$ , in reduced units, were  $0.4 \pm 0.1$  and  $0.45 \pm 0.1$  for  $\epsilon' = 1$  and 0 respectively, and of  $\epsilon(0)$   $3.3 \pm 0.3$  and  $3.2 \pm 0.3$ . A similar agreement was obtained for the other values of  $\omega$ . These results show that within the limit of the statistical error, the value of  $\Sigma(\omega)$  is independent of the boundary conditions if the adequate relations between  $\sigma(\omega)$ ,  $\epsilon(\omega)$  and the correlation functions of  $\bar{M}$  and  $\bar{J}$  are used.

However, the statistical error on the data is large, being  $\sim 10$ -20%. This result is due to the very slow convergence of the statistical averages in the numerical simulations of ionic solutions for a ionic concentration of a few percent. The physical origin of this slow convergence is clearly due to the slow diffusion of the ions in the solvent. Then the number of integration steps in a molecular dynamics simulation or of generated configurations in a Monte Carlo simulation must be sufficiently large in order to sample correctly the phase space of the system. This point is discussed in details in [6] where it is established that  $10^5$  trial moves per particle are needed in a Monte-Carlo simulation to obtain good accuracy on the equilibrium correlations functions of the ions.

In conclusion, the formalism summarized in the first part provides all the formulae needed for a correct interpretation of the simulation data of ionic solutions; however, the realization of such simulations is hampered by a very difficult problem of convergence.

## References

- [1] Martin P C 1968 *Many-body Physics* ed C DeWitt and R Balian (New York: Gordon and Breach)  
Fulton R L 1978 *J. Chem. Phys.* **68** 3089, 3095
- [2] Caillol J M, Levesque D, and Weis J J 1986 *J. Chem. Phys.* **85** 6645
- [3] Caillol J M, Levesque D, and Weis J J 1989 *J. Chem. Phys.* **91** 5544
- [4] Caillol J M, Levesque D, and Weis J J 1986 *J. Chem. Phys.* **91** 5555
- [5] de Leeuw S W, Perram J W and Smith E R 1980 *Proc. R. Soc. A* **373** 27, 57
- [6] Caillol J M, Levesque D, and Weis J J 1990 *Mol. Phys.* **69** 199