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AT MODEL ELECTRODE/MOLTEN SALT INTERFACES

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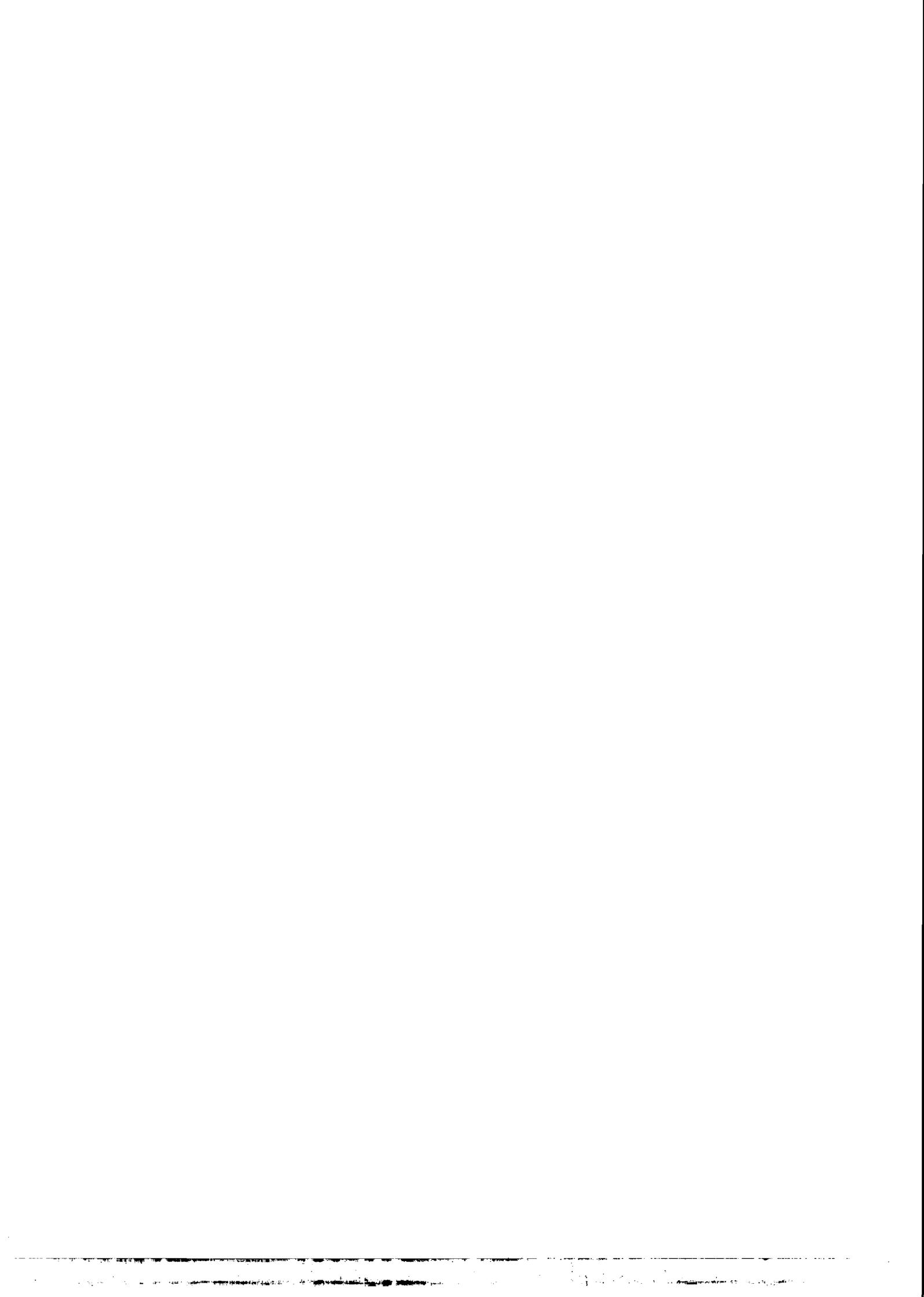and

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ABSTRACT

The anisotropic ionic diffusion coefficients in model electrochemical cells in the molten-salt regime for the electrolyte are evaluated from the ionic density profiles reported in simulation work of Grout and coworkers. A local description of the diffusion processes for counterions and coions in the electrical double layer is obtained from the data.

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Electrified metal-electrolyte interfaces have been of fundamental and applied interest for many years (see for example Trasatti 1989). Given the complexity of real electrochemical systems, computer simulation of greatly simplified models has had in this field the useful role of providing controlled data to test advances in statistical mechanical theories (Carnie and Torrie 1984).

In this perspective Esnouf, Smith and Grout (1988) have extended the computer simulation studies of model electrode/electrolyte interfaces to the molten salt regime of the electrolyte. They studied by molecular dynamics a slab of ionic liquid, enclosed between two oppositely charged hard walls and with pairwise interactions chosen to model molten KCl, at various values of the wall separation l, the wall charge qe/l^2 per unit area and the temperature T. The single-particle density profiles $\rho_\alpha(z)$ ($\alpha = K, Cl$) show layering of the charge density in the molten salt along the z direction perpendicular to the walls. Ionic diffusion in the slab is anisotropic and values for the self-diffusion coefficients $D_\parallel^{(\alpha)}$ and $D_\perp^{(\alpha)}$ are obtained from the mean square displacements of the ions along directions parallel and perpendicular to the walls, respectively. The same methods have recently been applied by the Oxford group to study this type of finite electrochemical system with a jellium model for the electrodes *in lieu* of a hard wall model (Williams 1990). The main consequences of allowing at this level for the spill-out of metallic electrons at the surface of the electrodes are found to be increased layering in the ionic density profiles, due to the spill-out aiding adsorption, as well as relative suppression of perpendicular diffusion.

The simulation results on self-diffusion coefficients have no immediate connection with the diffusion of ions in the electrical double layer, since each ionic species in the simulation samples is simultaneously acting as counterions at one electrode and as coions at the other. We aim in this letter (i) to theoretically show how the anisotropic self-diffusion coefficients in the simulation samples are related to the ionic density profiles for given pairwise ionic interactions, and (ii) to extract from the data information on how counterions and coions separately diffuse in the double layer formed at a single electrode.

We use for the above purposes a theoretical approach to diffusion which has been recently developed for monatomic classical liquids (Tankeshwar, Singla and Pathak 1991) and extended to ionic melts (Tankeshwar and Tosi 1991). The approach stems from work of Zwanzig (1983) and Mohanty (1985), who developed a simple model for dynamics in cold dense fluids to evaluate their transport coefficients directly from the Green-Kubo time correlation formulae. We refer the reader to the earlier work, and in particular to the article by Zwanzig (1983), for an adequate presentation of the ideas underlying the model. We simply recall here that diffusion is envisaged as occurring through jumping processes, so that in a bulk molten salt it is described at the simplest level of approximation in terms of Einstein vibration frequencies ω_α and jumping frequencies $1/\tau_\alpha$ for the two ionic species. The self-diffusion coefficients are defined through the appropriate velocity autocorrelation functions and are given by

$$D^{(\alpha)} \equiv \frac{k_B T}{m_\alpha} \int_0^\infty dt \, \frac{1}{N} \sum_{i=1}^{N}{}^{(\alpha)} <v_{i\alpha}(t).v_{i\alpha}(0)>/<v_{i\alpha}^2> \; = \; \frac{\pi k_B T \tau_\alpha}{2m_\alpha} \, \mathrm{sech}(\frac{\pi}{2}\omega_\alpha \tau_\alpha) \quad (1)$$

where m_α are the ionic masses. The vibration and jumping frequencies can be related to liquid structure and pair interactions through the sum rules governing the short-time behaviour of the velocity autocorrelation functions. Writing the latter as

$$\frac{1}{N} \sum_{i=1}^{N}{}^{(\alpha)} <v_{i\alpha}(t).v_{i\alpha}(0)>/<v_{i\alpha}^2> \; = \; 1 - \frac{1}{2}A_\alpha t^2 + \frac{1}{24}B_\alpha t^4 + ..., \quad (2)$$

one has $\omega_\alpha^2 = (5A_\alpha^2 - B_\alpha)/(4A_\alpha)$ and $\tau_\alpha^2 = (B_\alpha - A_\alpha^2)/(4A_\alpha)$. For bulk molten KCl, using the pair interactions and bulk pair distribution functions of the Oxford group at T = 1309 K, we find (in 10^{-5} cm^2 s^{-1}) $D^{(K)} = 12.1$ and $D^{(Cl)} = 13.4$, against the measured values $D^{(K)} = 14.8$ and $D^{(Cl)} = 13.4$ at 1273 K (Bockris, Nanis and Richards 1965).

Let us consider first the self-diffusion coefficients in the finite slab of melt studied in the simulation work. The formulae that we have summarily reported just above still apply, except that we have to introduce distinct vibration and jump frequencies for diffusion parallel

or perpendicular to the walls. Each diffusion coefficient is strongly inversely dependent on the appropriate mean square restoring frequency A, and we focus on the calculation of $A_{K\perp}$ for perpendicular motion of the K^+ ion from the appropriate sum rule. We write

$$A_{K\perp} = \int_{-1/2}^{1/2} dz_1\, \rho_K(z_1)\, A_{K\perp}(z_1) \Big/ \int_{-1/2}^{1/2} dz_1\, \rho_K(z_1) \tag{3}$$

and the local square restoring frequency $A_{K\perp}(z_1)$ for perpendicular motion of a K^+ ion at z_1 is given by

$$A_{K\perp}(z_1) = \frac{1}{m_K} \int_{-\infty}^{\infty} dx_{12} \int_{-\infty}^{\infty} dy_{12} \int_{-1/2}^{1/2} dz_2 \left[\frac{\rho_{KCl}(z_1, r_{12})}{\rho_K(z_1)} \frac{\partial^2 U_{KCl}(r_{12})}{\partial z_{12}^2} + \frac{\rho_{KK}(z_1, r_{12})}{\rho_K(z_1)} \frac{\partial^2 U_{KK}(r_{12})}{\partial z_{12}^2} \right] \tag{4}$$

where $\rho_{\alpha\beta}(z_1, r_{12})$ and $U_{\alpha\beta}(r_{12})$ are the two-particle distribution functions and the pair potentials. The two contributions in the bracket in (4) describe the backscattering from unlike and like neighbours, respectively. The local restoring force $A_{K\parallel}(z_1)$ for parallel motion is given by a similar expression involving the second derivative of the pair potentials with respect to x_{12}, and the expressions for the Cl^- ion follow from (3) and (4) by interchanging the suffixes K and Cl.

In the evaluation of integrals such as shown in (4) we relate the two-body functions in the inhomogeneous system to the single-particle density profiles by the approximation

$$\rho_{\alpha\beta}(z_1, r_{12}) = \rho_\alpha(z_1)\, \rho_\beta(z_2)\, g_{\alpha\beta}(r_{12}) , \tag{5}$$

$g_{\alpha\beta}(r)$ being the bulk distribution functions (see for example Croxton 1980). We then find that the backscattering of the diffusing ion by neighbouring unlike ions is dominant and becomes relatively less important for parallel diffusion than for perpendicular diffusion with increasing charge density on the electrode, leading to $D_\perp^{(\alpha)} < D_\parallel^{(\alpha)}$. Our numerical results for the diffusion coefficients, as calculated from the density profiles reported by the Oxford group and including the two-body contributions to the fourth-moment sum rules $B_{\alpha\parallel}$ and $B_{\alpha\perp}$ (see Tankeshwar and Tosi 1991), are shown in table 1 for both the hard wall and the jellium models of the electrodes at various values of the electrode charge density q. Compar-

ison with the simulation data of Esnouf *et al* (1988) and Williams (1990) on diffusion coefficients is made in table 1 whenever possible.

Clearly, there is good agreement between our results and the simulation data, and in particular the trends indicated by the data ($D_{\parallel}^{(\alpha)}/D_{\perp}^{(\alpha)}$ increasing with q and, for given q, on replacing the hard-wall electrodes with jellium electrodes) are accounted for by the theory. The reasons for these behaviours are to be found in the layering of the charge density in the, molten salt slab parallel to the walls, as shown by the density profiles. For any given ion in a layer, the most effective backscattering comes from unlike neighbours lying in the same layer for parallel diffusion and in the two neighbouring layers on either side of it for perpendicular diffusion. This gives rise to the indicated trends in the ratio $D_{\parallel}^{(\alpha)}/D_{\perp}^{(\alpha)}$, since layering increases with q and, for given q, with the increased adsorption allowed by electron spill-out in the jellium model. Increasing layering leads to decreasing backscattering by unlike neighbours in each layer and to increasing backscattering by unlike neighbours in the neighbouring layers.

The foregoing results refer to averages over all the ions of a given species inside the slab. As we have already remarked, in the particular configuration of the simulation sample in which the density profiles are determined, i. e. a finite slab confined by two oppositely charged walls, the ions of a given species simultaneously play the role of counterions with regard to one wall and of coions with regard to the other. However, in several of the simulation runs it is evident that the density profiles associated with the two walls may be taken as approximately independent from each other. This is especially the case for a hard-wall sample at q = 2 and T = 1298 K, where the density and potential profiles show only statistical fluctuations over a very substantial region of z around the middle of the sample (Esnouf *et al* 1988). In such situations we may use the simulated density profiles to approximately construct separate profiles for counterions and coions at a single electrode.

Choosing the wall at z = - 1/2 as the positively charged one, the counterion density profile $n_{Cl}(z)$ in the above mentioned sample is constructed by taking it equal to $\rho_{Cl}(z)$ in the range -1/2 < z < -1/4 and equal to the bulk density n thereafter. At distance 1/4 from the wall

one is already well outside the thickness of the double layer. Similarly, the coion density profile $n_K(z)$ is taken equal to $\rho_K(z)$ in the range $-1/2 < z < -1/4$ and equal to the bulk density n thereafter. Using these profiles in (5), the local square restoring frequency for perpendicular motion of a Cl$^-$ counterion at position z_1 is then given by

$$A_{Cl\perp}(z_1) = \frac{1}{m_{Cl}} \int_{-\infty}^{\infty} dx_{12} \int_{-\infty}^{\infty} dy_{12} \int_{-1/2}^{\infty} dz_2 \left[n_K(z_2) g_{KCl}(r_{12}) \frac{\partial^2 U_{KCl}(r_{12})}{\partial z_{12}^2} \right.$$
$$\left. + n_{Cl}(z_2) g_{ClCl}(r_{12}) \frac{\partial^2 U_{ClCl}(r_{12})}{\partial z_{12}^2} \right], \qquad (6)$$

with similar expressions for the other local A's. The dependence on the distance $z_1 + 1/2$ from the electrode can be explicitly seen by replacing the integration variable z_2 in favour of the variable z_{12}.

Obviously, the integral in (6) should reduce to its bulk value far away from the wall. Owing to the fact that the integrands have effectively rather short range, for $z_1 \approx -1/4$ we find that the anisotropy of the calculated restoring frequencies has disappeared and we recover their bulk values. Letting z_1 approach the electrode, the influence of the double layer gradually emerges. We thus have the possibility of examining the (parallel or perpendicular) diffusion of (positive or negative) counterions or coions in the double layer as a function of z_1, namely in dependence of distance from the electrode.

Illustrative results of these calculations are reported in figure 1 in the form of "local diffusion coefficients" for Cl$^-$ counterions and K$^+$ coions, in superposition with their density profiles constructed from the simulation data of Esnouf et al (1988) as described above. Evidently, while parallel diffusion in the double layer is affected by local structure only to a relatively minor extent, there is a strong correlation between the perpendicular diffusion processes and the local structure in the double layer. The correlation is similar for counterions and coions, except for their relative dephasing, and is simply summarized by the observation that perpendicular diffusion of each ionic species is slowed down in the regions where its

density piles up. This confirms our earlier interpretation of the numerical results in table 1.

In summary, we have been able to give a satisfactory quantitative interpretation of the available data on ionic diffusion in simulated electrochemical cells and to propose a detailed picture for the diffusion processes occurring in the electrical double layer in the molten-salt regime for the electrolyte.

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Table 1. Anisotropic self-diffusion coefficients for K^+ and Cl^- ions in model electrochemical cells in the molten-salt regime for the electrolyte. Values in parentheses are from the molecular dynamics results of Esnouf *et al* (1988) and Williams (1990).

q / T (K)	$D_\parallel^{(K)}$	$D_\perp^{(K)}$	$D_\parallel^{(K)}/D_\perp^{(K)}$	$D_\parallel^{(Cl)}$	$D_\perp^{(Cl)}$	$D_\parallel^{(Cl)}/D_\perp^{(Cl)}$
Hard wall:						
0 / 1309	9.0	8.9	1.01	10.6	10.5	1.01
1 / 1326	9.1	8.7	1.04	10.8	10.5	1.03
2 / 1320	8.9	8.4	1.06	11.3	10.5	1.07
2 / 1320				(9.3)[a]	(8.6)[a]	(1.08)[a]
9 / 1406	11.6	7.4	1.58	14.7	10.3	1.43
9 / 1406				(12.9)[a]	(8.9)[a]	(1.45)[a]
Jellium wall:						
1 / 1299	8.8	8.3	1.06	10.9	10.6	1.03
1 / 1327	(10.2)	(9.7)	(1.05)			
2 / 1358	9.5	8.5	1.12	11.5	10.5	1.10
9 / 1381	12.4	6.6	1.88	16.0	7.1	2.26
9 / 1381	(11.2)	(5.2)	(2.15)	(13.3)	(6.3)	(2.11)

[a] Averages for K^+ and Cl^-.

Figure caption

Figure 1. Local perpendicular and parallel diffusion coefficients D (in 10^{-5} cm^2 s^{-1}) for Cl^- counterions (middle drawing) and K^+ coions (top drawing), evaluated from local vibrational and jumping frequencies as functions of the distance z from a positively charged hard-wall electrode at q = 2 and T = 1298 K. The bottom drawing shows the corresponding density profiles n(z) (in Å^{-3}) as obtained from the simulation data of Esnouf *et al* (1988).