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LETTERS TO THE EDITOR

NOTES

Contact theorems for models of the sticky electrode

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In recent times there have been a number of experiments which reveal the detailed nature of the metal–electrolyte interface. It is then of interest to incorporate the details of the surface structure into the theoretical models of the electrode interface.[1] A rather basic way of doing this is to use the sticky potential of Baxter,[2] which has been used to study adsorption phenomena at interfaces.[3] A model of a structured interface in which the atoms of the metallic electrode are represented by sticky sites was discussed in a previous publication.[4]

On the other hand, one knows that in spite of the relative complexity of the interactions at charged, flat interfaces, there is a sum rule, which derives from momentum conservation which is the so-called contact theorem[5] which relates the contact density near a hard wall to the excess charge on that wall. In the absence of image forces we have, for the primitive model, in which the ions are hard spheres of diameter σ_i, embedded in a continuum dielectric media,

$$k_B T \sum_{i=1}^{s} \rho_i(\sigma_i/2) = P + \frac{\epsilon E^2}{8\pi}, \tag{1}$$

where $\rho_i(\sigma_i/2)$ is the contact density of the ion i ($i = 1,...,s$), k_B is the Boltzmann constant, T the absolute temperature, P is the pressure, ϵ the dielectric constant, and E the external applied field. Equation (1) represents the force balance equation. For the nonprimitive model in which the solvent is represented by a collection of hard spheres of diameter σ_n ($n = 1,...,M$) with an electric dipole (or, in general, a multipole), the contact theorem (1) becomes

$$k_B T \sum_{i=1}^{s} \rho_i(\sigma_i/2) + k_B T \sum_{n=1}^{M} \rho_n(\sigma_n/2) = P + \frac{E^2}{8\pi}, \tag{2}$$

where we have lost the dielectric constant ϵ in the last term, and we got an extra term in the left-hand side.

In the present note we extend the contact theorems (1) and (2) to the case in which the electrode wall has an arrangement of sticky spots represented by the interactions

$$e^{-\beta v_i(\mathbf{r}_1)} = 1 + \lambda \delta(x_1) F(\mathbf{R}_1), \tag{3}$$

where $\beta = 1/k_B T$ is the Boltzmann factor, $v_i(\mathbf{r}_1)$ is the adsorption potential, $\mathbf{r}_1 = x_1, y_1, z_1$ is the coordinate of particle 1, $\mathbf{R}_1 = y_1, z_1$ is the position in the adsorbing plane, while x_1 is the distance to that plane. For a regular lattice of adsorbing sites,[4]

$$F(\mathbf{R}_1) = \sum_{\mathbf{m} \equiv m_y, m_z} \delta(\mathbf{R}_1 - \mathbf{R}_\mathbf{m}), \tag{4}$$

where $R_\mathbf{m}$ indicates the position of the sticky sites, indexed by the entire numbers m_y, m_z. But, in general, $F(\mathbf{R})$ is an arbitrary function. The parameter λ is just an order parameter.

The number density of particles of species i at $\mathbf{r}_1$ is $\rho_i(\mathbf{r}_1)$. We define the regular part of this function by means of the relation

$$\rho_i(\mathbf{r}_1) = e^{-\beta v_i(\mathbf{r}_1)} y_i(\mathbf{r}_1) = y_i(\mathbf{r}_1)[1 + \lambda\delta(x_1)F(\mathbf{R}_1)]. \tag{5}$$

Consider now the Born–Green–Yvon equation for a mixture near a planar interface:

$$k_B T \frac{\partial}{\partial x_1} \rho_i(\mathbf{r}_1)$$

$$= y_i(\mathbf{r}_1)\lambda F_i(\mathbf{R}_1)\frac{\partial}{\partial x_1}\delta(x_1) - \rho_i(\mathbf{r}_1)\frac{\partial}{\partial x_1}u_i(x_1)$$

$$- \rho_i(\mathbf{r}_1)\sum_j \int d\mathbf{r}_2 \rho_j(\mathbf{r}_2)g_{ij}(1,2)\frac{\partial}{\partial x_1}u_{ij}(r_{12}), \tag{6}$$

where $u_i(x_1)$, $u_{ij}(r_{12})$ are the 1 and 2 body forces, $g_{ij}(1,2)$ is the inhomogeneous pair correlation function.

If we integrate Eq. (6) over $\mathbf{r}_1$, divide by S, the area of the interface, and use the definitions

$$\bar{\rho}_i(x_1) = \frac{1}{S}\int d\mathbf{R}_1 \rho_i(\mathbf{r}_1), \tag{7}$$

$$\bar{Y}_i(x_1) = \frac{1}{S}\int d\mathbf{R}_1 y_i(\mathbf{r}_1)F(\mathbf{R}_1), \tag{8}$$

we get, after a short calculation,

$$k_B T \sum_i \left[\bar{\rho}_i(\infty) - \bar{\rho}_i(0) \right]$$

$$= -\lambda \sum_i \frac{\partial}{\partial x} \overline{Y}_i(x) \bigg|_{x=0}$$

$$- \frac{1}{S} \sum_i \int d\mathbf{r}_1 \rho_i(\mathbf{r}_1) \frac{\partial}{\partial x_1} u_i(x_1)$$

$$- \frac{1}{S} \sum_{ij} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2) g_{ij}^{(1,2)} \frac{\partial}{\partial x_1} u_{ij}(r_{12}) \quad (9)$$

and

$$k_B T \sum_i \bar{\rho}_i(0)$$

$$= \lambda \sum_i \frac{\partial}{\partial x} \overline{Y}_i(x) \bigg|_{x=0}$$

$$+ P - \frac{1}{S} \sum_i \int d\mathbf{r}_1 \rho_i(\mathbf{r}_1) \frac{\partial}{\partial x} u_i(x) , \quad (10)$$

where P is the bulk pressure. The last term depends on the explicit form of the wall particle interaction. For a flat, charged wall, we get using

$$u_i(x) = e_i \times E_0 , \quad (11)$$

where e_i is the charge, and E_0 is the bare field at the surface. Using electroneutrality, we get, after a short calculation,

$$k_B T \sum_i \bar{\rho}_i(0) = \lambda \sum_i \frac{\partial}{\partial x} \overline{Y}_i(x) \bigg|_{x=0} + P + \frac{\epsilon E_0^2}{8\pi} \quad (12)$$

which is the extension of the contact theorem[5] to a sticky surface with an arbitrary sticky potential $\lambda F(\mathbf{R})$. The new term can be put in a slightly more explicit form for a surface with a sticky point lattice [Eq. (4)]

$$\lambda \sum_i \frac{\partial}{\partial x} \overline{Y}_i(x) \bigg|_{x=0} = \frac{\lambda}{\omega} \sum_i \frac{\partial}{\partial x} y_i(x,0) \bigg|_{x=0} , \quad (13)$$

where we have assumed that the sticky point is at the origin of the lattice, and ω is the area of the unit cell.

Equation (13) also applies to the case of a mixture of ions and hard solvent molecules, in which case the dielectirc constant is $\epsilon = \epsilon_0 = 1$ in the Gaussian system.

The above procedure can be used to extend the contact theorem previously derived for an ideally polarizable interface.[6] The result is [using the notation of Ref. 6, for the left (L) and right (R) phases]

$$P^L - P^R = \alpha^L \left[\bar{\phi}(0) - \phi^L \right] - \alpha^R \left[\bar{\phi}(0) - \phi^R \right]$$

$$+ k_B T \sum \left[\bar{\rho}_i^L(-\sigma_i/2) - \bar{\rho}_i^R(\sigma_i/2) \right]$$

$$- k_B T\lambda \frac{\partial}{\partial x} \left\{ \sum \overline{Y}_i^L(-\sigma_i/2 - x) \right.$$

$$\left. - \overline{Y}_i^R(\sigma_i/2 + x) \bigg|_{x=0} \right\} . \quad (14)$$

In a recent publication, F. Cornu[7] has verified these theorems for the case of the two-dimensional one component plasma.

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Study of the thermodynamic properties of the TiIr intermetallic molecule

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The Engel–Brewer theory of metal bonding[1] predicts very high thermodynamic stability for the metal alloys between a d electron deficient transition metal and a transition metal which contains filled d orbitals. According to this approach, an increase in the number of bonds and thus in the bond strength results from the transfer of electrons from the platinum group metal to the vacant d orbitals of the d electron deficient metal. Several experimental investigations[2-5]