

Contact Theorems for Rough Interfaces

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Contact theorems for rough surfaces are discussed. Simple relations for the average contact density are obtained for neutral and charged walls. When the walls are not planar there are new contributions proportional to the field gradients near the charged wall.

KEY WORDS: Interphases, solid-liquid; exact results; rough interphases, surfaces.

1. INTRODUCTION

Contact theorems are very useful to estimate the accuracy of integral equations and computer simulations for inhomogeneous systems near neutral or charged walls.

We have derived^(1,2) sum rules for liquids near charged planar surfaces in which the total contact density was given as a function of the charge on the wall and the bulk pressure of the fluid.

In recent times, and due to the rapid increase in computer performance, simulations of more realistic systems are possible. Nonspherical solute molecules, and metal surfaces with crystal structures, are accessible to simulations of interfaces with discrete (and also nonspherical) solvent (water) molecules. In these simulations it is very important to use a potential with a correct equation of state (pressure). In general, in the models of water the interaction is either adjusted to the experimental value of the density and there is an error in the pressure, or (in a few cases) the interaction is adjusted to the pressure and there is a generally slight error in the density. For the simulation of interfaces, we think that the latter situation is preferable. The contact sum rules are based on force balance considera-

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tions between the bulk pressure and the forces exerted by the molecules on the container walls. Although a formal derivation could be obtained by integration of the Born–Green–Yvon equation, it can be shown that all pair (or higher multiplet) interactions of molecules in the fluid phase cancel and therefore only singlet densities count. Our results are extensions of previous work.⁽³⁻⁵⁾

There are two kinds of dynamic relations that are interesting in electrochemistry: those for the normal pressure and those for the stress and strain along the interface, which have been measured experimentally.⁽⁶⁾ We discuss in this paper the first ones for surfaces that are planar on the average, but not necessarily locally. This includes rough surfaces, but more interestingly interfaces between a single crystals and solutions.

The most general definition of a planar interface is obtained by requiring that the average force acting on an individual molecule of the fluid of species $i = 1, \dots, m$ is integrated to a constant for arbitrarily large surfaces. The surface defined by $z_1(x, y; A)$ represents the contact surface, and is the solution of the equation

$$w_i(x, y, z) = A \quad (1)$$

where $w_i(\mathbf{r}) = w_i(x, y, z)$ is the interaction of the wall with molecule i for given x, y , and finite A . Then

$$\frac{1}{S} \int_S dx dy z_1(x, y; A) = B_i \quad (2)$$

and our condition simply is that Eq. (2) is satisfied for every component of the mixture. This is a planar surface on the average.

For hard-core potentials we clearly choose $z_1(x, z)$ to be the hard-core surface, and the requirement is that the average z_1 over the entire, infinite surface is a constant.

2. NEUTRAL SYSTEMS

Consider the total energy of the interface

$$W = \int d\mathbf{r}_1 \frac{d\Omega_1}{8\pi^2} \sum_i w_i(1) \rho_i(1) \quad (3)$$

where $w_i(1) \equiv w_i(\mathbf{r}_1; \{b\}, \Omega_1)$ is the total interaction potential of the wall and a particle of species i situated at position \mathbf{r}_1 with orientation Ω_1 (Ω_1 are the Euler angles that define the molecular orientation). $\{b\}$ is a set of parameters which define the position of the surface: if we produce an

arbitrary but small deformation of the surface, we get from Eq. (3) the Taylor expansion

$$\delta W = \int d\mathbf{r}_1 \frac{d\Omega_1}{8\pi^2} \sum_i \rho_i(1) \frac{\delta w_i(1)}{\delta b} \delta b + \frac{1}{2} \left\langle \frac{\delta^2 W}{\delta b \delta b'} \delta b \delta b' \right\rangle_S + \dots \quad (4)$$

We are interested in a particular deformation of the interface: a uniform displacement in the z direction. Then

$$P = P_0 = -\frac{1}{S} \frac{\partial W}{\partial z} = -\frac{1}{8\pi^2 S} \int_S dx_1 dy_1 d\Omega_1 \int dz_1 \sum_i \rho_i(1) \frac{\partial w_i(1)}{\partial z_1} \quad (5)$$

which expresses the force balance equation in the z direction.

Let us consider first the case of hard walls near a fluid with hard convex molecules. The simplest case is that of a planar wall. The hard-core interaction is best expressed by the force relation

$$\frac{\partial w_i(1)}{\partial z_1} = -k_B T \delta [F_i(\mathbf{r}_1, \Omega_1) - 1] \quad (6)$$

where the solution of $F_i(\mathbf{r}_1, \Omega_1) = 1$ yields the position of contact of the molecule at the wall⁽⁸⁾ when the orientation is given by the Euler angles $\Omega_1 \equiv (\psi_1, \theta_1, \phi_1)$. Then we obtain $z_1(\Omega_1)$ as the solution of

$$F_i(z_1, \Omega_1) = 1 \quad (7)$$

For a hard ellipsoid of main axes A, B, C , for instance, we get⁽⁸⁾

$$\begin{aligned} z_1(\Omega_1) &= [1/(R_{13}^2/A^2 + R_{32}^2/B^2 + R_{33}^2/C^2)]^{1/2} \\ &= 1/[\cos^2 \theta_1/C^2 + \sin^2 \theta_1 (\sin^2 \phi_1/A^2 + \cos^2 \phi_1/B^2)]^{1/2} \end{aligned} \quad (8)$$

Where R_{ij} are the matrix elements of Euler's rotation matrix.

Replacing into Eq. (5), we get

$$P = P_0 = k_B T \sum_i \int \frac{d\Omega_1}{8\pi^2} \rho_i[z_1(\Omega_1), \Omega_1] \cos \theta_1 \quad (9)$$

where $z_1(\Omega_1)$ is given by Eq. (8) When $A = B = C$ we get from Eq. (8)

$$z_1 = A = \sigma/2 \quad (10)$$

and we recover the well-known relation

$$P = P_0 = kT \sum_i \rho(\sigma_i/2) \quad (11)$$

When the walls are not flat, then we have to discuss the normal components of the pressure tensor and the tangential components of the stress tensor. Consider only crystal surfaces, which are more interesting experimentally. The equation for the contact distance is more complicated, since we have to solve a rather more complex equation involving convex and concave regions

$$F_i(x_1, z_1, y_1; \Omega_1) - 1 = 0 \quad (12)$$

which is solved to yield

$$z_1(1) \equiv z(x_1, y_1, \Omega_1) \quad (13)$$

To compute the force, we need to know the equation for the normal to the tangent plane more specifically,

$$\cos \beta_s(x_1, y_1) = \mathbf{n}_s \cdot \mathbf{e}_z \quad (14)$$

where \mathbf{n}_s is the direction of the tangent plane of the molecule. As an example, consider the triangular lattice of lattice constant d and height h : The simplest form of the surface is⁽⁷⁾

$$z(x, y) = (h/2)(\cos a + \cos b) \quad (15)$$

where

$$a = \frac{2\pi}{d} \left(x - \frac{y}{\sqrt{3}} \right) \quad \text{and} \quad b = \frac{2\pi}{d} \left(\frac{2y}{\sqrt{3}} \right)$$

The components of the normal vector $\mathbf{n}_s \equiv \mathbf{n}_s(x, y)$ are easily computed from $\partial z / \partial x$ and $\partial z / \partial y$:

$$\cos \beta_s = \left\{ \frac{1}{1 + (\pi h/d)^2 [\sin^2 a + (1/3)(\sin a - 2 \sin b)^2]} \right\}^{1/2} \quad (16)$$

The normal pressure sum rule is then

$$P_0 = k_B T \sum_i \bar{p}_i(\text{con}) \quad (17)$$

where

$$\bar{p}_i(\text{con}) = \frac{1}{S_A} \int dx_1 dy_1 \int \frac{d\Omega_1}{8\pi^2} \rho_i[z_1(1)] \cos \beta_s(x_1, y_1) \cos \theta_n \quad (18)$$

where now θ_n is the angle between the tangent plane at contact and the direction of the line joining the contact point and the center (also center of mass) of molecule i .

3. CHARGED SYSTEMS

The interaction $w_i(\mathbf{r})$ is now the sum of two contributions: a Coulomb or electrostatic term plus a nonelectrostatic, covalent term such as discussed above:

$$w_i(\mathbf{r}) = w_i^{\text{cov}}(\mathbf{r}) + w_i^{\text{es}}(\mathbf{r}) \quad (19)$$

Consider different situations:

1. The uniformly charged electrode facing a primitive model (continuum dielectric) electrolyte. In this case

$$w_i(\mathbf{r}) = w_i^{\text{hc}}(\mathbf{r}) + w_i^{\text{es}}(\mathbf{r}) \quad (20)$$

The electrostatic contribution is in this case

$$w_i^{\text{es}}(z) = -e_i E_0 z / 2 \quad (21)$$

where e_i is the charge of i , and E_0 is the bare electric field. Using the electroneutrality relation

$$q_S = -\int_0^\infty q(z) dz = \frac{E_0 \epsilon}{4\pi} \quad (22)$$

where q_S is the surface charge density of the electrode, we immediately get

$$P = P_0 - \frac{\epsilon}{8\pi} [E_0]^2 \quad (23)$$

where P_0 is given by Eq. (17).

It expresses the fact that the total pressure must be equal to the kinetic term due to the collisions of the molecules at the wall minus the attractive electrostatic contribution of a planar capacitor with charge density $q_S = \epsilon E_0 / 4\pi$.

2. The flat electrode facing a nonprimitive model electrolyte. If the solvent consists of neutral molecules with a dipole (or higher multipoles), there will be no net force since the dipoles interact with the gradient of the

applied field ∇E_0 , which in this case is zero. Therefore, only the hard repulsive interactions count, and we get now

$$P = P_0(\text{solute}) + P_0(\text{solvent}) - \frac{1}{8\pi} [E_0]^2 \quad (24)$$

where $P_0(\text{solute})$ and $P_0(\text{solvent})$ are the bulk pressure terms given by Eq. (17). Notice that now the dielectric constant has disappeared from this relation. This means that the electrostatic contribution in a solvent of high dielectric constant like water is now much smaller than in the primitive model, and that the covalent (hard-core) solvent term P_0 plays a much larger role in the makeup of the concentration profile near the electrode.

3. The rough or structured electrode near a primitive electrolyte. The situation is now more complicated, since the charge distribution at the electrode surface will not be uniform, and therefore both contact densities (for hard surfaces as well as for soft surfaces) will be functions of z as well as the position on the surface x, y . There will be a simple relation only for average quantities such as the average contact density near a hard plane, Eq. (18).

It is clear that the electrostatic forces along the surface are of vanishing magnitude for a random rough surface, or zero for a periodic crystal surface. We assume that the surface has a fixed charge distribution, and since we are neglecting images, it is not metallic.

Assume now a capacitor in vacuum, in which one plate is our surface S , with its charge distribution, and the second plate is very far, and has a uniform charge density $-q_S$, such that there is no field sufficiently far behind the first plate of our capacitor. From Gauss' theorem, and since the transverse components of the field $E_x^0(1), E_y^0(1)$ are asymptotically zero at the sides of our capacitor,

$$\langle E_z^0 \rangle_S = (1/S) \int dx_1 dy_1 E_z^0(1) = (4\pi/\epsilon) q_S \quad (25)$$

Since the faraway electrode creates a field $-(1/2)\langle E_z^0 \rangle_S$ which does not contribute to the pressure on the first electrode, the electrostatic contribution to the pressure P_e is given by

$$\begin{aligned} P_e &= 1/S \int d1 \sum_{i=1}^m e_i \rho_i(1) [E_z^0(1) - (1/2)\langle E_z^0 \rangle_S] \\ &= 1/S \int d1 \sum_{i=1}^m e_i \rho_i(1) (1/2)\langle E_z^0 \rangle_S \\ &\quad + 1/S \int d1 \sum_{i=1}^m e_i \rho_i(1) [E_z^0(1) - \langle E_z^0 \rangle_S] \end{aligned} \quad (26)$$

Using charge electroneutrality, we get

$$P_e = -\frac{\epsilon}{8\pi} \langle E_z^0 \rangle_S^2 + 1/S \int d1 \sum_{i=1}^m e_i \rho_i(1) [E_z^0(1) - \langle E_z^0 \rangle_S] \quad (27)$$

where the first term is the Maxwell stress tensor contribution present in the flat electrode case, while the second term is a new one arising from fluctuations in the bare field. The integration should cover only a narrow region near the electrode surface.

The other single-particle term containing the short-range interactions between the molecules and ions and the wall yields

$$\left\langle \rho_i(1) \frac{\partial w_i^{\text{cov}}(1)}{\partial z_1} \right\rangle_S = 1/S \int_S dx_1 dy_1 \rho_i(1) \nabla_1 w_i^{\text{cov}}(1) \quad (28)$$

where

$$\left\langle \rho_i(1) \frac{\partial w_i^{\text{cov}}(1)}{\partial z_1} \right\rangle_S = 1/S \int_S dx_1 dy_1 \int_{z_s(x_1, y_1)}^{L_1} dz_1 \rho_i(1) \frac{\partial w_i^{\text{cov}}(1)}{\partial z_1} \quad (29)$$

Putting it all together yields the general contact theorem for a planar on the average, but not necessarily smooth, surface:

$$P = P_0 - \frac{\epsilon}{8\pi} \langle E_z^0 \rangle_S^2 + 1/S \int d1 \sum_{i=1}^m e_i \rho_i(1) [E_z^0(1) - \langle E_z^0 \rangle_S] - \sum_{i=1}^m \left\langle \rho_i(1) \frac{\partial w_i^{\text{cov}}(1)}{\partial z_1} \right\rangle_S \quad (30)$$

This theorem is a generalization of the previously derived contact theorems to the realistic case of nonsmooth electrode surfaces. It contains the previous results as particular cases.

For a surface with an array of sticky adsorption sites, such as in the case of the sticky site model (SSM) discussed elsewhere,⁽⁹⁾ the adsorption potential has the form

$$\exp[-\beta w_a(\mathbf{r})] = 1 + \lambda(\mathbf{R}) \delta(z) \quad (31)$$

with

$$\lambda(\mathbf{R}) = \sum_{n_1, n_2}^M \lambda_a \delta(\mathbf{R} - n_1 \mathbf{a}_1 - n_2 \mathbf{a}_2) \quad (32)$$

Here $\mathbf{R} = x, y$ is the position at the electrode surface, and z the distance to the contact plane, which is at a distance $\sigma/2$ from the electrode. In (32), n_1, n_2 are integers, there are M sites on the electrode of area S , and $\mathbf{a}_1, \mathbf{a}_2$ are the lattice vectors of the adsorption sites on the surface. The parameter λ_a

represents the fugacity of an adsorbed atom of species a . Define now the regular part of the density function

$$y_i(1) = [\rho_i(1)/\rho_i] e^{\beta w_i^{\text{cov}}(1)} \quad (33)$$

Replacing into the general contact theorem (30) gives⁽⁵⁾

$$P = k_B T \sum_{i=1}^m \bar{\rho}_i(\sigma_i/2) - \varepsilon/8\pi [E_z^0(0)]^2 + (M\lambda_d/S) \sum_{i=1}^m \left\langle \frac{\partial y_i(1)}{\partial z_1} \right\rangle \rho_i \quad (34)$$

This theorem has been verified recently in ref. 4 for the exactly solved model of a one-component plasma in two dimensions.

4. The rough electrode near a nonprimitive (for example, with a solvent of dipolar hard spheres) electrolyte. Now we have to include the effect of electric field gradients, which are not zero near the electrode. The total electrostatic force is⁽¹⁰⁾

$$-\frac{\partial w_\alpha^{\text{es}}(\mathbf{r})}{\partial \mathbf{r}} = e_\alpha \mathbf{E}_0 + \boldsymbol{\mu}_\alpha \cdot (\nabla \mathbf{E}_0) + (1/6) q_\alpha : (\nabla \nabla \mathbf{E}_0) \quad (35)$$

where μ_α is the dipole moment of α , q_α its quadrupole moment, and so on. We remark that now the solvent single-particle density $\rho_s(1)$ is a function not only of \mathbf{r}_1 , but also of the orientation of the molecules with respect to the electrode, which in the case of the linear dipoles is given by θ_1 , ϕ_1 . Therefore we expand

$$\rho_s(1) = \sum_{l,m} \rho_{s,m}^l Y_m^l(\theta_1, \phi_1) = \rho_{s,0}^0 + \sum_m \rho_{s,m}^1 Y_m^1 + \dots \quad (36)$$

The dipole contribution to the pressure is

$$\left\langle \rho_s(1) \frac{\partial w_s^{\text{es}}(1)}{\partial z_1} \right\rangle_s = -\frac{4\pi\mu_s}{3} \int_0^\infty dz_1 \frac{1}{S} \int dx_1 dy_1 \rho_s(1) \frac{\partial \mathbf{E}_0(1)}{\partial z_1} \quad (37)$$

which after a short calculation leads to

$$P = P_0(\text{solute}) + P_0(\text{solvent}) - \frac{1}{8\pi} \langle E_z^0(0) \rangle^2 + 1/S \int d1 \sum_{i=1}^m e_i \rho_i(1) [E_z^0(1) - \langle E_z^0(0) \rangle] - \frac{4\pi\mu_s}{3} \left\langle \sum_m \rho_{s,m}^1 \frac{\partial E_{-m}^1(\mathbf{r}_1)}{\partial z_1} \right\rangle_s \quad (38)$$

where we have used

$$\mathbf{E}_0(1) = \sum_m E_m^1(\mathbf{r}_1) \mathbf{e}_m^1 \quad (39)$$

where \mathbf{e}_m^1 are the polar components of the unit vector.

The last term of Eq. (38) corresponds to an electrostriction effect which vanishes for uniform external field \mathbf{E}_0 .

5. The rough electrode near a nonprimitive electrolyte: Most of the models of water employed in the computer simulations consist of neutral molecules with embedded point charges.

The sum over the charges q_v in each molecule is indicated by the index v and is zero for each molecule. Each of these charges is located at the position \mathbf{b}_v relative to a molecular reference frame. From Eq. (30) we get

$$\begin{aligned} P = & P_0(\text{solute}) + P_0(\text{solvent}) - \frac{1}{8\pi} \langle E_z^0(0) \rangle^2 \\ & + 1/S \int d1 \sum_{i=1}^m e_i \rho_i(1) [E_z^0(1) - \langle E_z^0(0) \rangle] \\ & + \left\langle \rho_s(1) \sum_v q_v E_z^0(\mathbf{r}_1 + \mathbf{b}_v) \right\rangle_s \end{aligned} \quad (40)$$

where $\bar{\rho}_s(1)$ is now the orientation-dependent density function of the solvent with embedded charges at contact.

These relations point to the importance of using a model potential for liquid water that has the correct equation of state (pressure) rather than the correct bulk density (which may be off by a few percent) when computing density profiles near planar or rough electrodes.

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