Charge Fluctuations and Shear Stress of Thin Films

S. A. Safran

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

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We consider the effects of lateral charge fluctuations on the linear shear response of thin films. These fluctuations break the in-plane symmetry of the system and at short enough times cause the interaction energy to depend on the relative positions of the top and bottom surfaces of the film. This gives rise to a shear stress which can be significant depending on the time scale of charge reequilibration and on the charge and thickness of the film. The results have implications for the shear of charged membranes as well as the shear and frictional properties of electrolytes between two charged surfaces. [S0031-9007(98)07669-8]

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Recent interest in membrane adhesion and the intercalation of (charged) DNA molecules into lipid bilayers has motivated a renewed interest in the effects of charge fluctuations on binding and stability. While a homogeneous, mean-field, model of interactions between similarly charged membranes, surfaces, or linear molecules results in repulsive interactions, theoretical considerations of the effects of charge fluctuations, which produce inhomogeneity in the system, can generate attractive interactions [1,2]. Such attractions have been seen in computer simulations [3]; their origin lies in the correlations of the charge fluctuations—oppositely charged groups tend to be correlated across the thickness of the film and lead to attractions.

These fluctuations uniquely enable systems of charged, thin films to show a finite, linear shear response, at least when the nonequilibrium [4] nature of the system is considered. The existence of lateral charge fluctuations means that the interactions between the two surfaces (membranes) bounding the thin film, and even the charge distributions within the electrolyte itself, depend on the relative in-plane positions of the charges. Motion of those surfaces results in a finite shear response at least up to such times that the charges all reequilibrate and the resistance to such motion disappears. One therefore expects a shear stress for the system that depends on the characteristic time scale for the motion of the charged species and the fluctuation-induced, interaction energy density of the film.

In this paper we relate the shear stress on two bounding surfaces or membranes to the correlation function for charge fluctuations in the top and bottom layers bounding the film. This particular correlation function vanishes in the equilibrium case, and we find its contribution to the shear stress within a simple model for the dynamics of the layer charges in the system. The electrostatic contribution of the surface layers can be significant in the limit where the surface layer charges have long relaxation times compared with the molecules of the bulk fluid.

In order to derive an expression for the shear stress of a charged, thin film, we consider the thermodynamic potential G which is a functional of the free energy density f [5]:

$$G = \int d\vec{r}\{f[n(\vec{r})] - \mu n(\vec{r})\} = -\int d\vec{r}\,\Pi[n(\vec{r})], \quad (1)$$

where μ is the chemical potential and $\Pi[n(\vec{r})]$ is the osmotic pressure of the system. This applies to systems where the number of particles is either fixed or in equilibrium with a bath whose chemical potential is controlled by other means.

In addition to changes in the local volumes induced by expansions or dilations of the systems, a solution is also affected by deformations in that the solute particles themselves are rearranged by the deformations. One can compute the change in free energy due to these effects—which include shear deformations—by writing the density in terms of the particle positions:

$$n(\vec{r}) = \sum_m \delta(\vec{r} - \vec{R}_m), \quad (2)$$

where $\vec{R}_m$ is the position of the particle labeled by the index m. Upon a shear deformation, the α component of the particle position vector $\vec{R}_m$ is modified: $R_{m,\alpha} \rightarrow R_{m,\alpha} + \epsilon_{\alpha\beta}R_{m,\beta}$, where the shear strain is given by $\epsilon_{\alpha\beta}$ where $\alpha \neq \beta$. This change in the particle position vectors gives rise to a change in the local density. Since the thermodynamic potential is a functional of the local density, it, too, is modified by the shear strains, and we write

$$\Delta G = -\epsilon_{\alpha\beta} \int d\vec{r}\, \frac{\delta \Pi[n(\vec{r})]}{\delta n(\vec{r})} \sum_m R_{m,\beta}\, \frac{\partial \delta(\vec{r} - \vec{R}_m)}{\partial R_{m,\alpha}}\,. \quad (3)$$

Using the equality implied by the delta function, performing one partial integration, and neglecting boundary terms in the thermodynamic limit, one finds

$$\Delta G = -\epsilon_{\alpha\beta} \int d\vec{r}\, \frac{\partial}{\partial r_\alpha} \left(\frac{\delta \Pi}{\delta n(\vec{r})}\right) r_\beta n(\vec{r})\,. \quad (4)$$

The local shear stress $\sigma_{\alpha\beta}$ is defined by $\Delta G = -\epsilon_{\alpha\beta} \int d\vec{r}\,\sigma_{\alpha\beta}$ so that we can write

$$\sigma_{\alpha\beta} = \left\langle r_\beta n(\vec{r})\, \frac{\partial}{\partial r_\alpha} \left(\frac{\delta f}{\delta n(\vec{r})}\right)\right\rangle, \quad (5)$$

where we used the fact that the chemical potential μ is a constant. This formula agrees, in the continuum limit, with the expression derived by Doi [6] for discrete particles in solution using a somewhat different approach. The thermodynamic average is important in systems with density fluctuations. These averages may involve the nonequilibrium, but steady-state, distribution of particles. This is indeed the case in the charged, thin films considered here where the derivative of the local free energy per unit volume, $f[n(\vec{r})]$, is a constant in equilibrium (and equal to the chemical potential). It is only the shear flow in the system that causes any deviation of this derivative from zero.

We now apply this general formula to the case of two charged sheets whose layer charges are allowed to fluctuate in thermal equilibrium. The charged sheets (which can be thought of as two bilayer membranes or two charged surfaces in a surface force experiment) are separated by a polar fluid which contains the counterions. For simplicity, and to demonstrate the most dramatic effect, we consider the case of no added salt. We first consider the contribution of the charged sheets and then the counterion effects [7].

For two fluctuating charged sheets, where the free energy includes both the translational entropy of the charges (and possibly excluded volume and two-body interaction effects [8]) and their Coulomb interactions, one can express the free energy density f as a function of the fluctuating layer charge density $\sigma_1(\vec{\rho})$ for the layer located at $z = -D/2$ and $\sigma_2(\vec{\rho})$ for the layer located at $z = D/2$, where $\vec{\rho} = (x, y)$ is the two-dimensional position vector within the layer [2]. For the zx component of the shear stress, we consider the motion of the layer located at $z = -D/2$ with a constant velocity (in the $\hat{x}$ direction) $v = \dot{\gamma}D/2$, where D is the layer spacing and $\dot{\gamma}$ is the shear rate, while the layer located at $z = D/2$ moves with the same velocity in the $-\hat{x}$ direction. Assuming a simple, macroscopic shear flow, $\vec{v}(z) = \dot{\gamma}z\hat{x}$, implies that the fluid at $z = 0$ remains at rest. The volume average of the local shear stress is then written

$$\sigma_{xz} = \frac{-1}{2} \sum_{i=1,2} (-1)^i \left\langle \sigma_i(\vec{\rho}) \frac{\partial}{\partial x} \left(\frac{\delta f_s}{\delta \sigma_i(\vec{\rho})} \right) \right\rangle, \quad (6)$$

where f_s is the free energy per unit area. The result is most simply expressed in terms of the Fourier transforms of the layer charge densities, $\sigma_1(\vec{q})$ and $\sigma_2(\vec{q})$, where $\vec{q}$ is the two-dimensional wave vector. We shall use the fact that the correlation function is translationally invariant in rewriting the stress in terms of the Fourier components.

The free energy per unit area f_s due to the charge fluctuations (the uniform terms do not contribute to the shear stress) can be written within the harmonic approximation [2]

$$f_s = \frac{k_B T}{2A_0} \sum_{\vec{q}} A(\vec{q}) [|\sigma_1(\vec{q})|^2 + |\sigma_2(\vec{q})|^2] + 2B(\vec{q})\sigma_1(-\vec{q})\sigma_2(\vec{q}). \quad (7)$$

Here, A_0 is the area and the coefficients $A(\vec{q})$ and $B(\vec{q})$ arise from the intralayer interactions and entropy and interlayer effects, respectively. The intralayer effects give $A(\vec{q}) = \chi + 2\pi\ell/q$. For an ideal gas χ (which, in general, is proportional to the second derivative [8] of the local free energy not including the Coulomb terms) is given by $1/\sigma_0$, where σ_0 is the average charge density of the layer charges. The second term in the expression for $A(\vec{q})$ arises from the Coulomb interactions where $\ell = e^2/(\epsilon k_B T)$ is the Bjerrum length for a medium with dielectric constant ϵ. The interaction term is proportional to the product of layer charge densities and the coefficient $B(\vec{q})$, where $B(\vec{q}) = 2\pi\ell e^{-qD}/q$.

Even under shear, the steady-state correlation function $\langle|\sigma_2(\vec{q})|^2\rangle$ is isotropic; its integral with q_x therefore vanishes by symmetry. This is to be expected since the motion of the layer cannot affect the fluctuations within the layer to first order. On the other hand, the interlayer correlation function is no longer isotropic when the shear is applied—it contains a term linear in q_x and linear in the shear rate. Its integral with q_x does not vanish and contributes to the shear stress due to the charge fluctuations. Thus, only the interaction term in f_s will contribute and

$$\sigma_{xz} = \frac{k_B T}{A_0} \sum_{\vec{q}} i q_x B(\vec{q}) \langle \sigma_2(\vec{q}) \sigma_1(-\vec{q}) \rangle. \quad (8)$$

Although we have not written the explicit time dependence of the fluctuating charge densities $\sigma_i(\vec{q}, t)$, we note that the macroscopic shear stress is related to the equal time correlation functions of the system in steady state.

In order to find the effects of the shear on the interlayer correlations, an equation of motion for the charge density is required. To demonstrate that the charge fluctuations give rise to a finite shear stress in the simplest possible circumstances, we neglect hydrodynamic effects within the layer and inertial effects (these are negligible at the time scales of interest) and write the equation of motion for the fluctuating charge density in the standard manner as [9]

$$\frac{\partial \sigma_i(\vec{\rho})}{\partial t} + \left(v_i \frac{\partial}{\partial x} \sigma_i(\vec{\rho}) \right) = \Gamma \nabla^2 \frac{\delta f_s}{\delta \sigma(\vec{\rho})} + \theta_i(\vec{\rho}, t), \quad (9)$$

where the index $i = 1, 2$ accounts for the two layers. The two terms on the left-hand side of Eq. (9) represent the viscous motion of the layer charges under the action of the convective velocity of the shear flow. The velocity $v_1 = \dot{\gamma}D/2$, while $v_2 = -\dot{\gamma}D/2$. The first term on the right-hand side is the diffusive term; the in-plane Laplacian $[\nabla^2 = (\partial/\partial x^2 + \partial/\partial y^2)]$ arises from the conservation of charged molecules within the layer. The second term on the right-hand side represents the fluctuation forces in the system (Langevin-type term) which give rise to the Brownian motion of the layer charges in the plane. The fluctuation forces are independent in the two layers and are assumed to have only short ranged correlations:

$$\langle \theta_i(\vec{\rho}, t)\theta_j(\vec{\rho}\,', t')\rangle = -2k_B T \nabla^2 \Gamma \delta(\vec{\rho} - \vec{\rho}\,')\delta(t - t')\delta_{ij}\,. \tag{10}$$

All cross correlations between the different layers vanish since the noise is assumed to arise from very short ranged thermal fluctuations.

These linear equations are solved by Fourier transforming in both space and time; the steady-state fluctuations are obtained by using the expression for the equal time correlation function for the layer charge fluctuations in the expression for the shear stress:

$$\langle \sigma_1(\vec{q}, t)\sigma_2(-\vec{q}, t)\rangle \sim \int_{-\infty}^{\infty} d\omega \langle \sigma_1(\vec{q}, \omega)\sigma_2(-\vec{q}, -\omega)\rangle\,. \tag{11}$$

This relation is due to the fact that in steady state, the correlation function is only a function of differences in the time. Since experimental shear rates are macroscopic (on the order of inverse seconds) while the molecular relaxation rates are much larger ($\sim 10^8$ sec^{-1}), the shear generally acts as a small perturbation on the system. We therefore linearize the solutions of the equations of motion in the shear rate, or velocity v, and find

$$\sigma_1(\vec{q}, \omega) = \frac{-(a + i\omega)\theta_1(\vec{q}, \omega) + b\theta_2(\vec{q}, \omega) - iq_x v \theta_1(\vec{q}, \omega)}{b^2 - a^2 - \omega(2ia - \omega)}\,, \tag{12}$$

with a similar equation for σ_2 where $v \to -v$, $\sigma_1 \leftrightarrow \sigma_2$, and $\theta_1 \leftrightarrow \theta_2$. In Eq. (12), $a = \Gamma_0 q^2 A(q)$ and $b = \Gamma_0 q^2 B(q)$, where $\Gamma_0 = \Gamma k_B T$.

In the expression for the shear stress [Eq. (8)] we must keep terms linear in q_x so that the integral over the wave vector does not vanish by symmetry. The only terms that will contribute to the cross correlation function that are linear in q_x give

$$\sigma_{xz} = \frac{v\Gamma_0}{A_0} \sum_{\vec{q}} q_x^2 q^2 B^2(\vec{q}) \times \int_{-\infty}^{\infty} d\omega \frac{\langle [|\theta_1(\vec{q}, \omega)|^2 + |\theta_2(\vec{q}, \omega)|^2]\rangle}{(b^2 - a^2 + \omega^2)^2 + 4a^2\omega^2}\,. \tag{13}$$

Using the expression for the correlation functions of the fluctuating force, we get a contribution to the shear stress that scales similar to $k_B T \Gamma$. Performing the integral over ω to get the equal time correlation function under shear, using $v = \dot{\gamma} D/2$, and converting the sum over wave vectors to an integral, we find

$$\sigma_{xz} \sim \frac{k_B T D \dot{\gamma}}{\Gamma_0} \int dq \frac{q B^2(\vec{q})}{A(\vec{q})[A^2(\vec{q}) - B^2(\vec{q})]}\,, \tag{14}$$

where the proportional sign indicates that a numerical coefficient of order unity has been omitted.

The integrals over the wave vector can be simplified in the large and small distance limits. The scaling of these limits is determined by the relative magnitudes of the interlayer spacing D and the charge dependent length $\lambda = 1/(2\pi\ell\sigma_0)$, over which the charge fluctuations are significant. Note that λ can be large with respect to molecular sizes if the charge density is very small. Thus, small D compared with λ does not have to involve molecularly close surfaces. With these definitions, we can rewrite the shear stress as

$$\sigma_{xz} \sim \frac{D\sigma_0\dot{\gamma}}{\Gamma\lambda^2} \int dx \frac{x^2 e^{-2xd}}{(1 + x)[(1 + x)^2 - e^{-2xd}]}\,, \tag{15}$$

where $d = D/\lambda$. For large values of d, one can neglect the exponential in the denominator. Furthermore, the exponential in the numerator indicates that only small values of x will contribute (since d is large). The denominator may be approximated by unity and the integral scales similar to $(\lambda/D)^3$.

To obtain more physical insight, it is instructive to note that the kinetic coefficient Γ has dimensions of the inverse of a time multiplied by an energy. We thus write $\Gamma^{-1} = \tau_s k_B T$ which defines the surface diffusion time τ_s for the layer charges. The shear stress now takes the following simple form:

$$\sigma_{xz} \sim k_B T(\dot{\gamma}\tau_s)\left(\frac{1}{D^2\ell}\right). \tag{16}$$

This has the correct dimensions of an energy per unit volume where the volume is set by $D^2\ell$. In addition, the shear stress depends linearly on the relaxation time of the layer charges, τ_s. If that time becomes very short, the charges relax to equilibrium very quickly and the energy to displace the two charge correlated layers becomes very small. For times less than τ_s, however, the motion generated by the shear displaces the regions of correlated charge fluctuations with respect to their optimal positions in the two layers, i.e., with respect to equilibrium, and therefore costs free energy, resulting in a finite shear stress. The dimensionless product of τ_s and the shear rate $\dot{\gamma}$ determine how fast or slow the rearrangement occurs as the system is sheared.

It is important to compare the magnitude of the charge fluctuation-induced shear stress with that of the background liquid separating the two layers. Simple hydrodynamics yields $\sigma_{xz} \sim \eta\dot{\gamma}$, where η is the viscosity. The viscosity has the dimensions of a liquid molecular relaxation time τ_l, multiplied by a typical energy density: $\eta \sim k_B T \tau_l / a^3$, where a is the molecular size. Thus the background liquid contributes a shear stress:

$$\sigma_{xz} \sim k_B T(\dot{\gamma}\tau_l)\left(\frac{1}{a^3}\right). \tag{17}$$

The ratio ν of the electrostatic to background liquid shear stresses, i.e., the ratio of Eq. (16) to Eq. (17), scales similar to

$$\nu \sim \frac{\tau_s a^2}{\tau_l D^2}\,, \tag{18}$$

where we have assumed that the Bjerrum length and the molecular size are comparable. Although for large spacings $D \gg a$, the relaxation time of the layer charges which can be impeded by the entanglement of their hydrophobic tails in the case of membranes and by lattice effects in the case of solid, charged surfaces, may be much larger than the liquid relaxation time τ_l. In this case, it is possible that the electrostatic contribution to the shear stress will exceed that of the background liquid and give a measurable effect. This effect may be particularly large near the liquid-gel transition of charged lipids or surfactants where one expects the surface relaxation time to get very large [10].

The separation of time scales for the layer charges and background fluid can give rise to an interesting situation in which the layer charge distribution can remain "frozen-in" while the background fluid remains in equilibrium. This occurs when the shear rate is high enough that the layer charges cannot reequilibrate (at least for short times after the shear is applied), $\dot{\gamma}\tau_s \gg 1$, but the background liquid can satisfy, $\dot{\gamma}\tau_l \ll 1$. In this case, the shear stress of the background liquid is $\dot{\gamma}\eta$ while the shear stress for the layer charges is determined by the modulus k_BT/D^3 for the case $D \gg \lambda$. Their ratio ν scales similar to $(a^3/D^3)(\dot{\gamma}\tau_l)^{-1}$. This may indeed be quite large even if D is on the order of ten molecular spacings, depending on the smallness of the product of the shear rate and liquid relaxation time.

In the limit where the surfaces or membranes are closer than the Gouy-Chapman length, $D \ll \lambda$, one can again estimate the scaling of the integral in Eq. (15). In this case, the integral is dominated by large values of x up to a value $x \sim 1/d$, where $d = D/\lambda$ is small. The integral then gives a dominant contribution which scales as $\log(D/\lambda)$ and the shear stress scales such as

$$\sigma_{xz} \sim k_BT(\dot{\gamma}\tau_s)\left(\frac{1}{\lambda^2\ell}\right)\left(\frac{D}{\lambda}\right)\log\left(\frac{D}{\lambda}\right). \tag{19}$$

One can again form the ratio of the electrostatic contribution to the liquid contribution to the shear stress, and in the limit $D \ll \lambda$ one finds (dropping the logarithm)

$$\nu \sim \frac{\tau_s D a^2}{\tau_l \lambda^3}, \tag{20}$$

where we have assumed that the molecular scale and the Bjerrum length are comparable. Again, while the length scale factors may indicate that the electrostatic contribution is small, this will not be the case when the surface relaxation time of the membrane molecules or surface charges is much longer than the liquid, molecular relaxation time τ_l when the electrostatic contribution may dominate.

Finally, we briefly consider the effects of the "free" counterions in solution to the shear stress. In contrast to the layer charges whose dynamics may be much slower than those of the molecules of the background fluid, the fundamental relaxation time of the counterions τ_c should be comparable to that of the fluid molecules. The shear stress has the form of $k_BT(\dot{\gamma}\tau_c)/L^3$, where the length L is maximally D^3 and minimally ℓ^3. Since $\tau_c \sim \tau_l$, we do not expect that the contribution of the counterions can ever become larger than that of the background fluid. This is in contrast to the electrostatic contribution of the layer charges whose slower dynamics can result in a large effect. This assumption must be checked by including the coupling between the counterion and layer charge fluctuations.

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[1] Phil Attard, Roland Kjellander, and D. John Mitchell, J. Chem. Phys. **89**, 1664 (1988); Chem. Phys. Lett. **139**, 219 (1987); Phil Attard, D. John Mitchell, and Barry W. Ninham, J. Chem. Phys. **88**, 4987 (1988); V. Bloomfield, Biopolymers **31**, 1471 (1991); R. Podgornick, D. Rau, and V.A. Parsegian, Biophys. J. **66**, 962 (1994); F. Oosawa, Biopolymers **6**, 134 (1968); J. Ray and G.S. Manning, Langmuir **10**, 2450 (1994); J.L. Barrat and J.F. Joanny, Adv. Chem. Phys. **94**, 1 (1996); M.J. Stevens and K. Kremer, J. Chem. Phys. **103**, 1669 (1995); N. Gronbech-Jense, R.J. Mashl, R.F. Bruinsma, and W.M. Gelbart, Phys. Rev. Lett. **78**, 2477 (1997); B.-Y. Ha and A.J. Liu, Phys. Rev. Lett. **79**, 1289 (1997).

[2] P.A. Pincus and S.A. Safran, Europhys. Lett. **42**, 103 (1998).

[3] L. Guldbrand *et al.*, J. Chem. Phys. **80**, 2221 (1984); B. Svensson, B. Jonsson, and C. Woodward, J. Phys. Chem. **94**, 2105 (1990); S. Marcelja, Biophys. J. **61**, 1117 (1992), and references therein.

[4] S. Panyukov and Y. Rabin [Phys. Rev. E **58**, 7053 (1997)] discuss the case of irreversibly, randomly charged objects.

[5] Samuel A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Reading, MA, 1994).

[6] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Oxford University, New York, 1988).

[7] S. Alexander, P.M. Chaikin, P. Grant, G.J. Morales, P. Pincus, and D. Hone, J. Chem. Phys. **80**, 5776 (1984).

[8] See footnote 10 of Ref. [2].

[9] P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University, Cambridge, England, 1995), p. 466.

[10] A. Haibel, G. Nimtz, R. Pelster, and R. Jaggi, Phys. Rev. E **57**, 4838 (1998).