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SHORT COMMUNICATION

A. El Ghzaoui
P. Ravel

Oscillating repulsive force between macroscopic surfaces as a consequence of the fluctuation of the density in the gap region

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A. El Ghzaoui (✉)
Centre de Recherche sur les Biopolymères Artificiels, Université Montpellier 1
Faculté de Pharmacie, 15 Avenue Charles Flahault, 34060 Montpellier, France

P. Ravel
ISTIV, Modélisation Numérique et Couplage, Avenue Georges Pompidou
83162 La Valette du Var, France

Abstract We try to explain the short-range repulsive force between surfaces as a consequence of a decrease in the configurational entropy of liquid molecules in the gap region as the width of the gap decreases. A simple model shows that the density has an oscillating variation when the surfaces are pushed towards each other. As a consequence, an oscillating repulsive force appears between the macroscopic surfaces, which is the result of a loss of configurational freedom of the liquid molecules because of their orientation in the gap.

In recent years, experimental techniques for directly measuring the forces between surfaces in liquids have been developed. Now, it is possible to accurately measure the forces between smooth solid surfaces, lipid bilayers or model biomembrane surfaces containing proteins and other biological molecules using the surface forces apparatus, the osmotic pressure technique or the atomic force microscope [1–6]. Since, more systems have been studied, it has become evident that the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory leaves many observations unexplained.

The stability of silica colloids is known to be irregular [7, 8] in the sense that it does not follow the predictions of the so-called DLVO theory [9, 10]. The reasons for this irregularity are not entirely clear, but it seems that the non-DLVO additional short-range force is probably an important factor. The measured force between two mica surfaces in KCl solutions shows an oscillatory short-range repulsive force. The period of these oscillations is about 0.25 nm, which corresponds to the size of a water molecule. There has been some debate over the mechanism that controls this force [11–17]. The most probable explanation may be attributed to the water molecules confined between the two surfaces. The water molecules appear to be arranged in layers, and as two surfaces approach, these layers are squeezed out sequentially. Such short-range-ordering molecules can occurs for all simple liquids. This is why this short-range repulsive force has also been measured in liquids other than water [18].

In the present study, we developed a new approach to explain the origin of this repulsive short-range force. Our approach is based on the variation of the entropy of the system due to the fluctuation of the number of liquid molecules in the system. This fluctuation induces a fluctuation of the liquid density between the two surfaces coming in close approach.

Let us consider an isolated thermodynamic system constituted of $2N$ molecules in a volume, V (Fig. 1). If we divide this system into two compartments, noted 1 and 2, of volume $V_1 = V_2 = V/2$, then the probability of finding $2N$ molecules in only one compartment is given by $1/2^{2N}$; therefore, the total number of configurations of the system will defined as $\Omega_0 = 2^{2N}$. On the other hand, the number of configurations which realise the most probable macroscopic state, $N_1 = N_2 = N$, where N_1 and N_2 represent the number of molecules in each compartment, is given by the following expression:

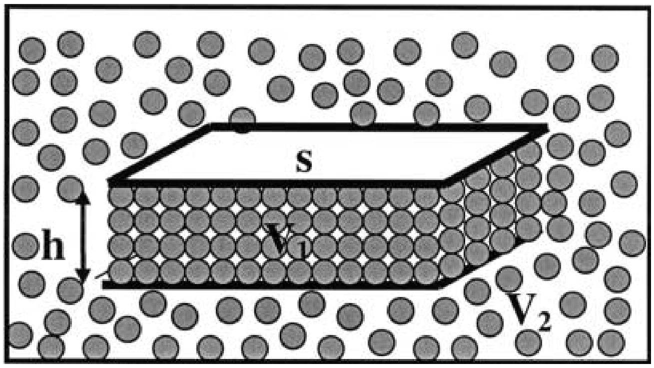

Fig. 1 Schematic view of the thermodynamic system, in which V is the total volume of the system, V_1 and V_2 are the volumes between the inner and outer surfaces, h is the width of the gap and s is the area of the surface

$$\Omega = \frac{2N!}{N!N!}.$$

We can write

$$\ln\frac{\Omega_a}{\Omega_0} = \ln 2N! - 2\ln N! - 2N\ln 2. \tag{1}$$

Using the following approximation, $\ln N! = N\ln N - N + \frac{1}{2}2N\pi$, Eq. (1) may be written

$$\frac{\Omega_a}{\Omega_0} = \frac{1}{\sqrt{\pi N}}. \tag{2}$$

If at given time, we assume that there are $N+n$ molecules in compartment 1 and $N-n$ in compartment 2, we introduce the fluctuation concept in the thermodynamic system. In this case the number of configurations which realise the most probable macroscopic state will be defined as $\Omega_n = \frac{2N!}{(N-n)!(N+n)!}$. The comparison between ln Ω_n and ln Ω_a gives

$$\ln\Omega_n = \ln\Omega_a = \frac{n^2}{N}, \tag{3}$$

$$\Omega_n = \Omega_0 \exp\left(-\frac{n^2}{N}\right). \tag{4}$$

Considering Eq. (4), one can notice that the maximum probability corresponds to the case where $n=0$.

The fluctuation of the molecules between the two compartments induces a fluctuation of the entropy of the system, ΔS,

$$\Delta S = k\Delta\ln\,\Omega = k(\ln\,\Omega_n - \ln\Omega_a) = -k\frac{n^2}{N}. \tag{5}$$

Equation (5) shows a negative variation of the entropy of the system which is inconsistent with the second law of thermodynamics. When the surfaces approach each other, the liquid molecules are progressively pushed away, out of the gap between the surfaces, and back into the solution. The variation of the entropy of the system becomes more and more negative as the distance between the surfaces decreases; in order to restore the equilibrium, the system reacts against the approach of the surfaces by the short-range repulsive force. This is a simple argument, essentially on the level of the principle of Le Chatelier. This repulsive force is often oscillatory because of the variation of the density of the liquid molecules between the surfaces. This variation can be easily determined. The number of liquid molecules N in the volume V_1 may be defined as

$$N = E\left(\frac{sh}{16\sqrt{2}}\right), \tag{6}$$

where s is the area of the surface and h is the distance between the surfaces (Fig. 1). The density between the surfaces is given by

$$\rho = \frac{E\left(\frac{sh}{16\sqrt{2}}\right)\frac{16\pi}{3}}{sh}. \tag{7}$$

If we consider h to be low but to be equal to $10R$ or greater (R is the radius of the liquid molecule) and $s \gg h^2$, then

$$E\left(\frac{s}{c}h\right) = \approx E\left(\frac{s}{c}\right)E(h), \tag{8}$$

where $c = 16\sqrt{2}$. Then

$$\rho = \frac{E\left(\frac{sh}{16\sqrt{2}}\right)\frac{16\pi}{3}}{sh} \approx \frac{\pi}{3\sqrt{2}}\frac{E(h)}{h}. \tag{9}$$

This equation gives the variation of the density in the case of orange-pile packing. In the case of symmetrical packing, the density is given by the following equation:

$$\rho = \frac{E\left(\frac{sh}{8}\right)\frac{16\pi}{3}}{sh} \approx \frac{\pi}{6}\frac{\mathrm{E}(h)}{h}. \tag{10}$$

Figure 2 shows the variation of the density, which is defined as $\Delta\rho = \rho_0 - \rho$, where ρ_0 is the density between the two surfaces at equilibrium, i.e. the density of the liquid in the bulk phase.

One can note that the local density of the liquid oscillates with the distance normal to the two surfaces (the gap between the surfaces). The period of the oscillations is approximately equal to the molecular radius of the liquid molecules, and the period increases as the confining gap width is reduced. The local density may be a convenient quantitative measure of self-arrangement of confined liquid into parallel layers between the surfaces and may be related to the observed macroscopic properties.

During the squeezing process, i.e. decrease of the gap between the surfaces, the number of molecules in the confined region decreases as some molecules are pushed into the bulk region. Therefore, if the liquid molecules are assumed to be arranged into layers, decreasing the

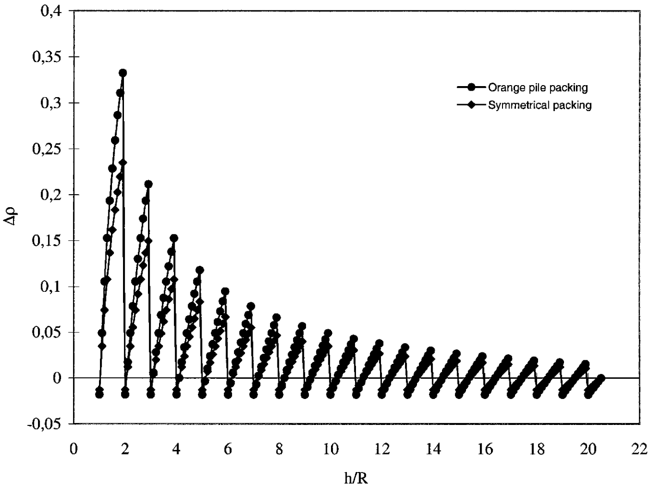

Fig. 2 Variation of the density in the gap region

width of the gap is accompanied by reduction of the number of layers in the confined film. Each period of the oscillations corresponds to the ejection of one layer. Each ejection of the liquid layer is followed by an organisation of the layers remaining in the gap. This organisation may depend on the degree of order of the liquid. This degree of order has been previously analysed in terms of order parameters [19]. The second-order moment of the orientation function, $P_2(\cos\theta)$, can be evaluated theoretically,

$$P_2(\cos\theta) = \left\langle \frac{(3\cos^2\theta - 1)}{2} \right\rangle,$$

where θ is the angle between the axis of the molecule and the stretching direction, or from spectroscopic measurements,

$$P_2(\cos\theta) = \left\langle \frac{(3\cos^2\theta - 1)}{2} \right\rangle = \frac{r-1}{r+2}\frac{r_0+2}{r_0-1},$$

where r is the dichroic ratio, defined as $r = A_\mathrm{p}/A_\mathrm{n}$, where A_p is the absorbance of given vibrations for the spectrum with the polarizer parallel to the stretching direction and A_n is the absorbance of given vibrations for the spectrum with the polarizer perpendicular to the stretching direction. r_0 is defined as $r_0 = 2\cot^2\alpha$, where α is the angle between the axis of the molecule and the dipole transition moment vector of the vibration being considered. It was found that the molecular bonds do not exhibit any orientational order in the bulk, $P_2(\cos\theta) \approx 0$, while in the confined region, between the surfaces, the molecules seem to lie preferentially parallel to the confining surfaces. The value of the order parameter also oscillates as the function of the gap between the surfaces, in the same way as the density. The maximal orientation corresponds to well-formed layers (for a given gap); the ejection of a liquid layer induces a decrease in the orientation of the liquid molecules.

Therefore, the variation of the density in a confined liquid as the gap decreases induces an organisation of the liquid molecules, which in turn gives rise to an oscillating repulsive force between the surfaces pushed towards each other. This is the result of a loss of configurational freedom because of the orientation of the liquid molecules in the gap and, as a consequence, because of the loss of entropy.

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