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On the Unified Mechanism of the Action of Surface Forces of Different Natures

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Abstract—Based on simple considerations, it has been shown that surface forces of different natures—electrostatic, dispersion, structural, and hydrophobic ones—are governed by the osmotic pressure of components present in a system.

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INTRODUCTION

Recently, interest in surface phenomena has again increased due to the development of nanotechnologies and the involvement of new subjects, including biological and medical ones, into the area of colloid science. The development of modern experimental equipment is also of great importance, because it allows one to precisely measure surface forces and detect fine features of their short-range actions. As a result, researchers are today considering several dozen different surface forces [1, 2] that are used to describe the interactions between colloidal particles or condensed-phase surfaces. We face now a situation similar to the one that took place in physics in the early 20th century, when each phenomenon was characterized by its "own" forces. Then, it was shown that different forces are actually of the same nature at the molecular level and represent derivatives of electromagnetic forces acting between electrons and nuclei. Analysis of the published data on surface forces shows that, when introducing these or those forces, researchers leave the actual mechanism of their action out of the equation. Additional components of surface forces are introduced to explain "unexpected" experimental data. It is assumed that each component of the surface forces should have its own mechanism of action. However, an attentive consideration of the manifestations of surface forces shows that the same mechanism is behind their diversity. In all fairness, it should be noted that, in some cases, the mechanism has been revealed; however, it was considered to be a particular case of the action of surface forces.

In this work, it will be shown that the main surface forces–electrostatic, dispersion, structural, and hydrophobic ones–result from a unified mechanism. Now, let us explain this unity.

SURFACE FORCES AS DERIVATIVES OF OSMOTIC PRESSURE

Depletion Forces

We start our analysis with a colloidal system in which the surface forces seem to be a secondary factor. However, close consideration of this system will enable us to gain a deeper insight into the unity of the mechanism of action of surface forces. The matter concerns a dispersion of colloidal particles in a solution of macromolecules. For a long time, it could not be determined why this colloidal system loses its stability with an increase in the polymer concentration in the absence of any specific interactions. It has eventually been shown [3] that the loss of stability is determined by the action of so-called depletion forces. The depletion forces are, in turn, governed by the osmotic pressure of macromolecules. Figure 1 illustrates the mechanism of the emergence of depletion forces. When colloidal particles approach one another and the distance between their surfaces becomes smaller than the size of a polymer molecule (its radius of gyration R_g), the macromolecules become incapable of penetrating the region of overlapping shown in Fig. 1 because of geometric confinements. Eventually, a specific effect develops similar to that observed for semipermeable membranes: a kind of excess osmotic pressure arises in the solution relative to the solvent pressure in the region of overlapping. As a consequence, particles are attracted to each other due to the osmotic pressure of macromolecules. The forces related to the osmotic pressure are referred to as depletion forces, since they are caused by the formation of layers containing no polymer molecules (depleted layers). Force magnitude F for colloidal particles is determined by the following equation:

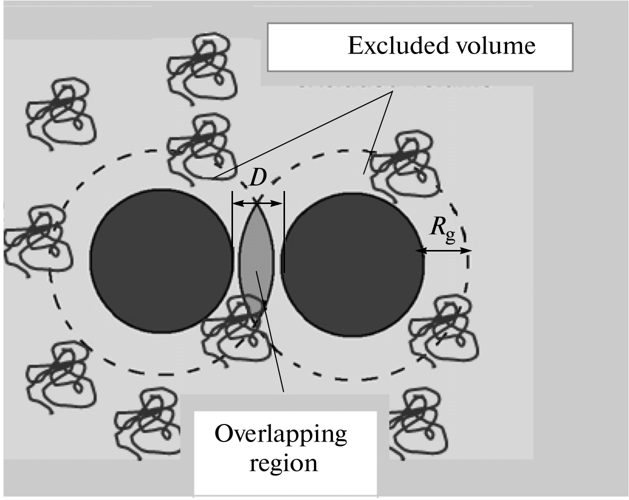

Fig. 1. Schematic representation of the mechanism of action of depletion forces in polymer solutions.

$$F = -\frac{\pi n_p}{4} k_B T (2R_g - D)(2d + 2R_g + D), \qquad (1)$$

where n_p is the concentration of polymer molecules, k_B is the Boltzmann constant, T is the temperature, d is the diameter of particles, and D is the minimal distance between their surfaces. In fact, Eq. (1) is a product of osmotic pressure $n_p k_B T$ and the geometric cross-sectional area of the region of overlapping. Formula (1) has been derived under the assumption that macromolecules are solid spheres with radius R_g. More realistic situations have been discussed in [4]; however, we are not going to focus on them, because our main goal is to qualitatively describe the surface forces from a unified point of view. It should only be noted that polymer molecules can, nevertheless, penetrate the interparticle region, although with a low probability. In this case, their concentration will be nonzero but significantly lower than the overall concentration, which also causes osmotic pressure to emerge, and force F will be nonzero in this case as well; however, it will have a more cumbersome form. We shall not discuss more complex situations, but confine ourselves to the simplest considerations in order to illustrate the unified nature of the mechanism of action of surface forces. For the same reason, we shall replace colloidal particles with two planar surfaces below.

Let us draw a brief conclusion from this section. The attractive forces that arise via the mechanism of boundary layer depletion result from the osmotic pressure of polymer molecules.

Electrostatic Forces

Electrostatic forces are most consistent with the notion that osmotic effects play a decisive role. The electrostatic interaction between colloidal particles (surfaces) is characterized by disjoining pressure Π_e [1, 2] related to the interionic electrostatic interaction. It has been shown [1] that, for a symmetric electrolyte ($z_+n_+ = z_-n_- = zn$),

$$\Pi_e = 2nk_B T[\mathrm{ch}(ze\varphi_m/k_B T) - 1], \qquad (2)$$

where n is the electrolyte concentration and φ_m is the value of the potential at the point of an extreme (see Fig. 2). The value of Π_e is the excess pressure [1] in the central part of the film with respect to the pressure in the bulk solution. Note that, at a low electrolyte concentration, Eq. (2) can be reduced to the following form [1]:

$$\Pi_e = k_B T[n_+(x_m) + n_-(x_m) - 2n], \qquad (3)$$

where $n_+(x_m)$ and $n_-(x_m)$ are the concentrations of cations and anions at the extreme point of the potential. It is easy to understand that the right-hand side of this expression is the osmotic pressure of ions. Langmuir was the first to formulate this interpretation of the interaction forces between charged colloidal particles [5]. Although it has been stated [1] that Eq. (2) cannot be reduced to osmotic pressure at arbitrary ion concentrations, we cannot agree with this statement. It has been clearly shown [1] that Eq. (2) is the excess pressure that develops between charged surfaces. It is the surface charge that retains the ions in the space between these surfaces. In other words, there is a perfect analogy with a semipermeable membrane. The excess pressure that arises in this situation is the osmotic pressure by definition. Hence, Eq. (2) expresses the osmotic pressure at any electrolyte con-

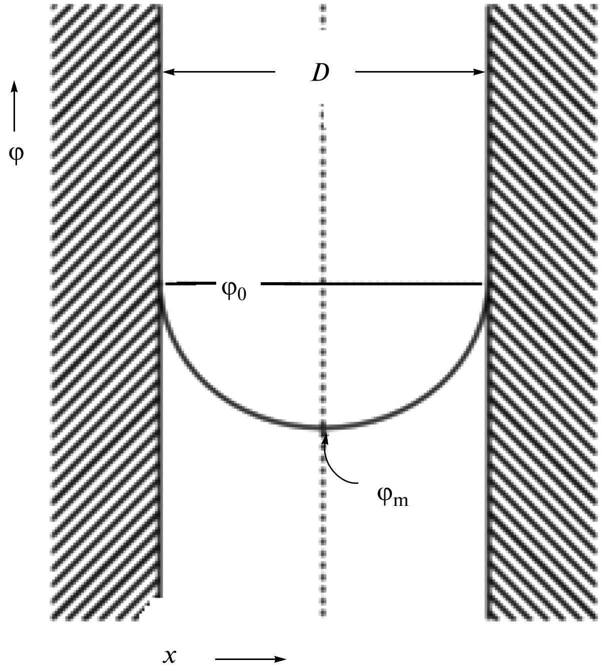

Fig. 2. Toward determination of the electrostatic component of surface forces.

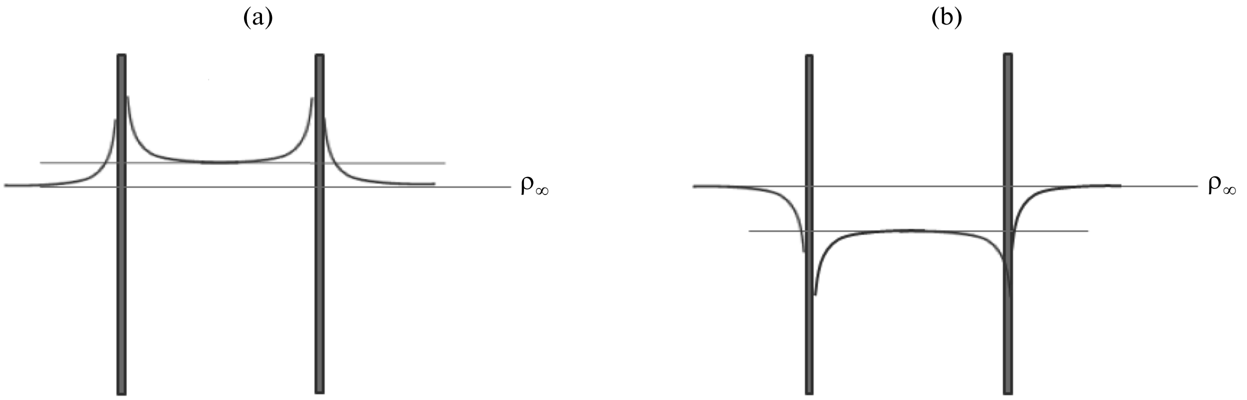

Fig. 3. Liquid density distributions near (a) hydrophilic and (b) hydrophobic plates; ρ_∞ is the bulk density of water.

centration. To conclude this section, it may be noted that the electrostatic component of surface forces results from osmotic pressure of ions.

Structural and Hydrophobic Forces

In this section, we shall demonstrate that structural and hydrophobic forces are also determined by osmotic pressure. These forces are of the same nature and differ only in their sign. Let us consider two hydrophilic and hydrophobic plates placed (to be more specific) into an aqueous medium (Fig. 3). The hydrophilicity and hydrophobicity of the plates are determined by the ratio between the potentials of the interaction of water molecules with a solid phase and an aqueous medium. If the intensity of the attractive interaction with a plate prevails over the interaction with water, the plate will be hydrophilic; if the interaction with the aqueous phase is stronger, the plate is considered to be hydrophobic. The density profiles of the liquid near the hydrophilic and hydrophobic plates are schematically represented in Figs. 3a and 3b, respectively. Let us use the data obtained for a liquid composed of solid spheres [6]. These data are accurate; therefore, we shall draw an analogy between the liquid of solid spheres and real systems. It has been shown [6] that the disjoining pressure (or hydration (structural) forces) is preset by the following equation:

$$\Pi_{\text{str}} = k_{\text{B}}T[\rho_D(0) - \rho_\infty(0)], \tag{4}$$

where $\rho_D(0)$ is the number density of the liquid in the plane of solid spheres closest to a plate on the side of liquid interlayer with thickness D and $\rho_\infty(0)$ is the density of the liquid in the plane of the solid spheres closest to the plate on the external side.

It is clear that this equation expresses the osmotic pressure in the interlayer. The fact that the solid spheres seem to be able to freely penetrate the interlayer and leave it does not play any significant role. Nevertheless, the slitlike gap represents a "semipermeable" membrane, since it restricts the motion of the spheres inside the interlayer. Were the motion unrestricted, the $\rho_D(0)$ and $\rho_\infty(0)$ values would be identical. Remember that the possibility of (restricted) penetration of polymer molecules into the interparticle space is also allowed in the case of depletion forces. The nature of the repulsion between hydrophilic colloidal particles and the attraction between hydrophobic particles can now be easily understood. In the case of hydrophilic particles, molecules are, on average, affected by forces (mean force potential) attracting them into the interplate space. On the contrary, for hydrophobic particles, the mean force potential repulses the liquid molecules from the gap. As a result, the average density of a liquid in the gap between the hydrophilic surfaces is increased relative to its bulk value, while the density of the liquid in the gap between the hydrophobic surfaces is reduced. This fact leads us to conclude that $\rho_D(0)$ will be higher than $\rho_\infty(0)$ for hydrophilic surfaces and lower for hydrophobic surfaces. Thus, there is an excess osmotic pressure (structural forces) in the interplate space (identically to the case of ions attracted to the surface) for hydrophilic plates, and there is an analogue of the depletion forces for the hydrophobic surfaces: the excess osmotic pressure of bulk water (penetration of its molecules into the interplate space is hindered) induces the hydrophobic attraction.

It may be inferred that both structural and hydrophobic forces are specific manifestations of the osmotic effect for hydrophilic and hydrophobic colloidal particles.

Dispersion Forces

Let us now discuss the most interesting case of dispersion forces. They are often considered [2] to be a result of the interaction (attraction) between instantaneous (fluctuating) molecular dipoles induced in condensed bodies (Fig. 4). Although this is an approxi-

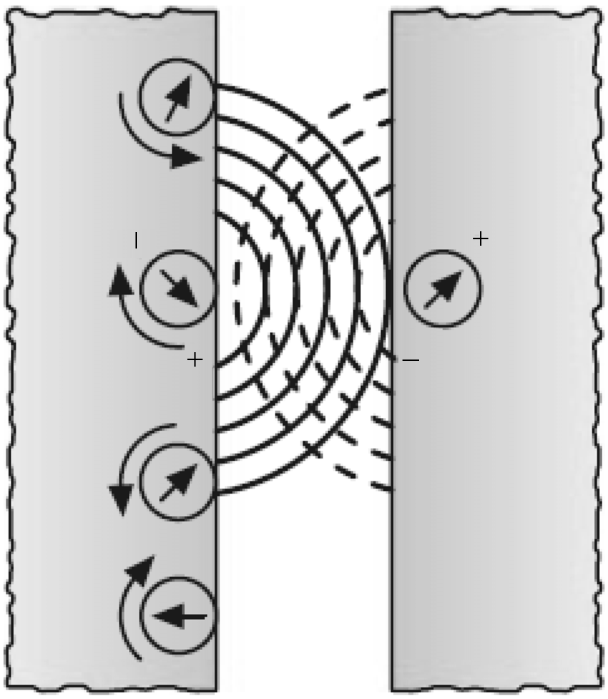

Fig. 4. Schematic representation of the mechanism for the development of dispersion forces via the interaction between instantaneous dipoles.

mate consideration, it yields qualitatively correct results. A more rigorous consideration of the dispersion forces is based [1, 2, 7, 8] on the calculation of the stress tensor of a fluctuating electromagnetic field. This approach is strongly formalized, so we are not going to discuss it. Note that this approach is commonly regarded to be a more exact consideration of the interaction between instantaneous dipoles induced by the fluctuations of an electromagnetic field. However, the dispersion attraction can also be interpreted in a different way.

Let us turn to Casimir's study [9], which has been generalized in [8]. Casimir's approach [9] is advantageous in working out a more obvious illustration of the essence of the dispersion interaction. Here, we shall use this approach to formulate an original interpretation of the dispersion attractive forces.

Two metal plates located at a short distance (Fig. 5) were considered in [9]. The energy of a fluctuating electromagnetic field (photons) was calculated in the presence and absence of the metal plates. In the presence of the plates, photons with a wavelength longer than the interplate distance cannot arise in the space between them, because it is believed that the electromagnetic field cannot penetrate into the metal plates. Taking into account this restriction, Casimir [9] has found that, in the presence of the plates, the energy of the fluctuating electromagnetic field decreases by the following value:

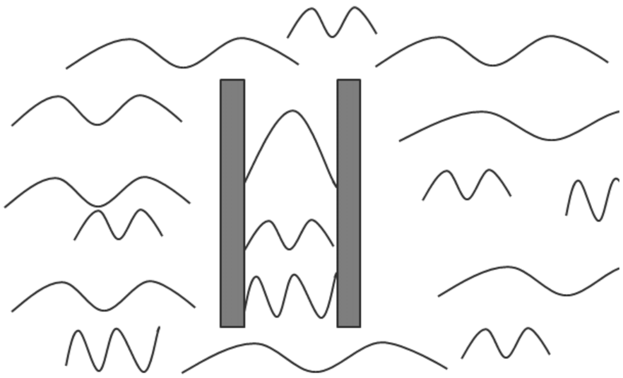

Fig. 5. Schematic representation of the mechanism for the development of dispersion forces via osmotic pressure of virtual photons.

$$U_{ss}(D) = \hbar c \frac{1}{2\pi^2}\left(\sum_n \int_0^\infty \sqrt{n^2\frac{\pi^2}{D^2} + k_\tau^2}\, k_\tau dk_\tau - \int_0^\infty\int_0^\infty \sqrt{k_x^2 + k_\tau^2}\, k_\tau dk_\tau \frac{D}{\pi} dk_x\right) \approx -\frac{\hbar c}{720}\frac{\pi^2}{D^3}, \qquad (5)$$

where c is the speed of light; $\hbar$ is the Planck constant; and k_x and k_τ are the components of the photon wave vector normal and tangential to the plate surface, respectively. A negative value of energy (5) shows that the plates attract one another. The summation instead of the integration in the first of the parenthetic terms is predetermined by the constraint on the wavelengths of the photons that can be generated in the interplate space. Note that the calculation of the energy does not clarify the nature of the forces responsible for the attraction between the plates.

Let us have a look at the situation illustrated in Fig. 5 from another point of view. Assume that photons with different wavelengths are always present in the space around the plates owing to quantum fluctuations. The interplate space does not contain photons with wavelengths longer than the interplate distance (i.e., some photons cannot get into the interplate space). In other words, two plates can be considered to be a semipermeable membrane that holds long-wave photons. As a result, the external side of the plates contains excess long-wave photons (increased photon concentration). This excess may be related to the osmotic pressure, which, identically to the case of depletion forces, makes the plates approach one another. Thus, it may be concluded that the dispersion attraction is generated by *the osmotic pressure of virtual photons*.

If we have dielectric rather than metal plates, the situation is identical to the case of depletion forces with polymers that can penetrate into the interparticle space. In this case, the osmotic pressure is induced by certain constraint of photons in the interplate space, so that their concentrations inside and outside the interplate gap will be different. This difference will determine the osmotic pressure magnitude. It is clear that this pressure is rather difficult to calculate, and we shall not do it. Furthermore, the answer is already known [1, 2].

CONCLUSIONS

All of the above-mentioned shows that the surface forces of different natures can eventually be reduced to osmotic pressure, which results in either attraction or repulsion between the surfaces of the condensed phases. Other forces used to describe the interaction between macroscopic bodies can also be easily reduced to the osmotic pressure [1, 2]. The short-range oscillating forces can easily be included into this scheme as well: the osmotic pressure in a thin gap may obviously depend on molecule sizes. Moreover, the surface forces are easy to calculate via the osmotic pressure. For different forces, the answer will undoubtedly be the same as that obtained using the existing approaches. So, we leave the choice of the method for determining the surface forces up to our readers. We believe the proposed interpretation of the surface forces of different natures to be worth presenting in *Colloid Journal*.

REFERENCES

1. Derjaguin, B.V., Churaev, N.V., and Muller, V.M., *Surface Forces*, New York: Consultants Bureau, 1987.
2. Izraelachvili, J., *Intermolecular and Surface Forces*, Burlington: Academic, 2011.
3. Napper, D., *Polymeric Stabilization of Colloidal Dispersion*s, London: Academic, 1983.
4. Lekkerkerker, H.N.W. and Tuinier, R., *Colloids and the Depletion Interaction*, Heidelberg: Springer, 2011.
5. Langmuir, I., *J. Chem. Phys.*, 1938, vol. 6, p. 873.
6. Henderson, D., *Fundamentals of Inhomogeneous Fluids*, New York: Marcel Dekker, 1991.
7. Pitaevskii, L.P. and Lifshitz, E.M., Statistical Physics: Theory of the Condensed State. Oxford: Butterworth-Heinemann, 1980.
8. Dzyaloshinskii, I.E., Lifshits, E.M., and Pitaevskii, L.P., *Usp. Fiz. Nauk*, 1961, vol. 73, p. 38.
9. Casimir, H., *Proc. K. Ned. Akad. Wet.*, 1948, vol. 51, p. 793.

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