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patrick.kekicheff@ics-cnrs.unistra.fr)**MECHANISM OF NANOBUBBLE FORMATION
IN WATER ON A HYDROPHOBIC SURFACE**

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A possibility for nuclei of a new phase to emerge in the form of nanobubbles in water contacting with a hydrophobic surface (the “vapor–liquid” phase transition) at temperatures significantly lower than the ordinary phase transition temperature is discussed. A new mechanism has been proposed to explain this temperature reduction; namely, the repulsive forces significantly increase the chemical potential of the molecules in the liquid phase near the hydrophobic surface in comparison with that in the gas phase. The corresponding estimates show that, at the normal atmospheric pressure, the phase transition temperature can be shifted by about 50 K.

Key words: nanobubble, hydrophobic surface, phase transition phase transition shift, Laplace pressure, near-wall potential.

Water contacting with hydrophobic surfaces is known to demonstrate absolutely different effects than those, when it contacts with hydrophilic ones. Hydrophobic surfaces are characterized by a specific strong long-range interaction between them, provided that there is an aqueous solution in between. This interaction is characterized as attractive at large distances (more than 10 nm), with the force maximum being of the order of 10 nN. At distances shorter than about 1 nm, the interaction forces have a well-pronounced repulsive character, with the force maximum being equal to approximately 20 nN. The mechanism of those interactions has been actively discussed for the last three decades. However, for today, there is no theory that could satisfactorily explain certain experimental facts [1–5].

A bright illustration of this situation is the existence of nanobubbles on a hydrophobic surface contacting with water. Nanobubbles 5–100 nm in height and 0.1–0.8 μm in diameter arise spontaneously between the surface of an air-saturated polar solvent (e.g., water) and a hydrophobic surface. Nanobubbles can be detected making use of atomic force microscopy (AFM) or other techniques; e.g., neutron reflectometry. Puzzling is their appearance at a tem-

perature of 20 °C and a pressure of 10⁵ Pa, which does not correspond to the condition of “liquid–vapor” phase coexistence in unconfined systems, namely,

$$\mu_g(T, p) = \mu_l(T, p), \quad (1)$$

where $\mu_g(T, p)$ is the chemical potential of the gas phase at the temperature T and the pressure p , and $\mu_l(T, p)$ is the chemical potential of the liquid phase. We can explain this phenomenon by the presence of a hydrophobic surface. In this case, the potential of external repulsive forces acts on the water molecules in the near-wall layer. As a result, the internal energy per molecule increases. Let us rewrite formula (1) in the form

$$\begin{aligned} u_g(T, p) - Ts_g(T, p) + pv_g(T, p) = \\ = u_l(T, p) - Ts_l(T, p) + pv_l(T, p), \end{aligned} \quad (2)$$

where $u(T, p)$ is the internal energy, $s(T, p)$ the entropy, and $v(T, p)$ the volume per molecule in the gas (the subscript g) and liquid (the subscript l) phases. From expression (2), one can see that the pressure of hydrophobic forces increases the chemical potential of water near the surface more strongly than the chemical potential of saturated water vapor. As a result, the temperature of the “liquid–gas” phase transition decreases (see Fig. 1).

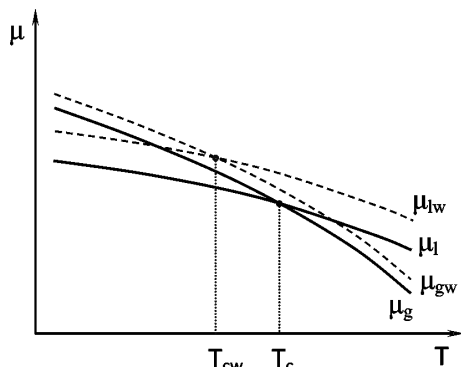


Fig. 1. Temperature dependences of the gas and liquid chemical potentials in the bulk (μ_g and μ_l , respectively) and near a hydrophobic wall (μ_{gw} and μ_{lw} , respectively). $p = \text{const}$, T_k is the ordinary temperature of phase equilibrium, and T_{kc} is the temperature of phase equilibrium near the wall

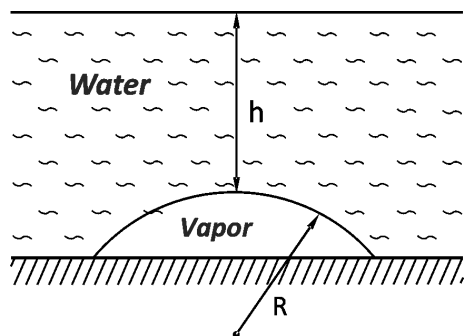


Fig. 2. Water-vapor bubble on the surface of a hydrophobic substrate embedded into water

Really, the energy components u_g and u_l of the chemical potentials in Eq. (2) are the quantities that obtain a direct contribution to the internal energy from the interaction potential of hydrophobic forces, as well as a contribution associated with structural effects. Immediate (direct) contributions in the gas and liquid phases are identical. On the other hand, the structural contribution to the gas phase is very insignificant. For estimations, let us consider the saturated vapor at the temperature $t = 17.2$ °C. The specific vapor volume in this case equals $63.3 \text{ m}^3/\text{kg}$ (at a pressure of 0.02 atm), which corresponds to an average distance of 12.4 nm between molecules. It is clear that the “compression” of this gas by external forces of the near-wall repulsive potential do not give rise to an additional growth in the internal energy of water vapor. But, in the case of the liquid

phase, a different situation is observed. The average distance between molecules amounts to 3 Å at this temperature, and even the slightest “compression” of the system with the help of external repulsive forces substantially increases the internal energy.

Let us evaluate the temperature shift for the “liquid–vapor” phase transition. It is easy to see from the figure that this problem is similar to the problem of boiling point shift when another component is added to the liquid [6]. The final result looks like

$$T_{kc} - T_k = -T_k \frac{\Delta u}{\lambda}, \tag{3}$$

where Δu is the average change of the internal energy of water in the near-wall layer, and λ is the latent heat of evaporation per molecule. Let us carry out some estimating calculations. In the case concerned, $\lambda = 7.4 \times 10^{-20} \text{ J}$. For Δu , in the case of water, we may take a value of the order of 10^{-20} J , which corresponds to the interaction of water molecules with one another. Then, we obtain $T_{kc} - T_k = -50 \text{ K}$. Hence, one can see that, near the surfaces of hydrophobic walls, the conditions required for the “water–water vapor” phase equilibrium to take place can be realized at temperatures considerably shifted from the ordinary boiling temperature toward lower values.

Note that a bubble of water vapor formed in the near-wall layer is strongly unstable with respect to an increase of its dimensions. Really, for the bubble to be stable under the given conditions, the following relation must be satisfied:

$$\Delta P_l = \frac{2\sigma}{R} = P_{\text{atm}}. \tag{4}$$

Here, ΔP_l is the Laplace pressure, σ the surface tension, R the curvature radius of the bubble surface, and P_{atm} the atmospheric pressure (see Fig. 2). In order to derive formula (4), we use the condition of mechanical equilibrium, according to which

$$P_{\text{atm}} + \rho gh - \Delta P_l = P_v, \tag{5}$$

where ρ is the water density, g the free fall acceleration, and P_v the pressure of saturated vapor in the bubble. In our case, $t = 17.2$ °C and $P_v = 0.02 \text{ atm}$. If the installation has ordinary dimensions ($h = 10^{-1} \text{ m}$), the terms ρgh and P_v in relation (5) can be neglected, and we arrive at formula (4).

Hence, a bubble formed in the fluctuation way on a hydrophobic substrate has very small dimensions

and is unstable, because ΔP_l is large. Therefore, at the initial moment of bubble formation, the strong inequality

$$P_{\text{atm}} + \rho gh - P_v \ll \Delta P_l, \quad (6)$$

rather than equality (5), is obeyed. In time, the bubble starts to increase, so that ΔP_l decreases until the bubble curvature radius reaches its equilibrium value determined by relation (4).

Let us make some evaluations. At the temperature $t = 20^\circ\text{C}$, the surface tension $\sigma = 72 \times 10^{-3} \text{ J/m}^2$. Then, from Eq. (4), we obtain $R = 1.4 \mu\text{m} \sim 10^3 \text{ nm}$. Note that the modern experimental data [2] give the value of curvature radius within rather wide limits, which correspond to the interval of external pressure from 7 to 30 atm.

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МЕХАНІЗМ ВИНИКНЕННЯ НАНОБУЛЬБАШОК
У ВОДІ НА ГІДРОФОВНІЙ ПОВЕРХНІ

Р е з ю м е

Обговорена можливість виникнення зародків нової фази при фазовому переході "рідина-пара" у воді, яка знаходиться в контактi з гiдрoфoбною поверхнею у виглядi так званих нанобульбашок, при температурах, суттєво нижчих, нiж температура звичайного фазового переходу. Запропоновано новий механiзм для пояснення цього зниження температури, який полягає в тому, що гiдрoфoбнi пристiнковi вiдштовхувальнi сили помiтно збiльшують значення хiмiчного потенцiалу молекул рiдкої фази порiвняно з молекулами газової фази. Проведенi в рамках цiєї теорiї оцiнки показують, що за нормального атмосферного тиску температура може змiщуватися на величину порядку 50 К.