Effect of an electric field on the surface tension of a liquid at low temperatures

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An external electric field changes the dispersion law of waves on the surface of a liquid. Besides the usual capillary term ($\propto k^3$, k is the wave number) and gravitational term ($\propto k$), a term quadratic in the wave vector appears in the expression for the square of the frequency in a homogeneous field. These excitations are associated with the variation of the coefficient of surface tension of the liquid at low temperatures. In the case of a large field tangent to the surface, the correction is proportional to $T^{8/3}$, unlike the $T^{7/3}$ correction in the absence of a field. © *1997 American Institute of Physics.* [S1063-7761(97)01804-0]

The temperature dependence of the coefficient of surface tension close to absolute zero is associated with low-energy excitations of the liquid–gas boundary (surface waves).[1] The usual classification separates capillary and gravitational waves. The properties of the former are mainly determined by surface-tension forces, which are substantial in the limit of small wavelengths. The gravitational forces, on the other hand, correspond to long wavelengths. This paper discusses the spectral variation effect associated with an external electric field constant in time. It is substantial in the region intermediate (in wavelength) between the capillary and gravitational regimes.

Let us find the dispersion relation for a surface wave propagating in the presence of external field $\mathbf{E}_0$ (for definiteness, let $\mathbf{E}_0$ be the field outside the liquid). The x axis is in the wave-propagation direction, while the z axis is upward, perpendicular to the surface of the unperturbed liquid. The surface displacement from the equilibrium position in this wave is described by a function of the form

$$z = \zeta(x,t) = \zeta e^{ikx - i\omega t}.$$

Assuming that the liquid is incompressible, the continuity condition of Ref. 2 is imposed on the velocity $\mathbf{v}$ and takes the form

$$\operatorname{div} \mathbf{v} = 0. \tag{1}$$

The Euler equation in the linear approximation (deviations from equilibrium are considered small) gives a second condition for the velocity:

$$\frac{\partial v_i}{\partial t} = \frac{1}{\rho} \frac{\partial \sigma_{ik}}{\partial x_k}, \tag{2}$$

where

$$\sigma_{ik} = -(\rho g z + P)\delta_{ik} - \frac{E^2}{8\pi}\left[\varepsilon - \rho\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T\right]\delta_{ik} + \frac{\varepsilon E_i E_k}{4\pi} \tag{3}$$

is the stress tensor.[3] Here P is the pressure corresponding to the same density ρ in the absence of a field, and ε is the permittivity of the liquid. The electric field itself obeys the following equations (all the velocities are much less than the velocity of light, and the liquid is assumed not to have any free charges):

$$\operatorname{div} \mathbf{E} = 0, \quad \operatorname{curl} \mathbf{E} = 0. \tag{4}$$

The corresponding field distribution, periodic along the x axis, has the form

$$\mathbf{E}^g = \mathbf{E}_0 + \mathbf{A}e^{ikx - kz}, \quad \mathbf{E}^l = \mathbf{E}_0^l + \mathbf{B}e^{ikx + kz},$$

where the superscripts l and g refer to the liquid and gas, respectively, with

$$A_x = -iA_z = -iA, \quad B_x = iB_z = iB, \quad A_y = B_y = 0.$$

The possibility of making the following transformation of the right-hand side of Eq. (2) by using Eq. (4) is essential for the subsequent treatment:

$$\frac{\partial v_i}{\partial t} = \frac{1}{\rho} \frac{\partial \sigma_{ik}}{\partial x_k} = \frac{1}{\rho} \frac{\partial}{\partial x_i}\left[-(\rho g z + P) + \frac{E^2}{8\pi}\rho\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T\right].$$

As a consequence, the motion of the liquid is irrotational; i.e., $\mathbf{v} = \boldsymbol{\nabla}\psi$. Using Eq. (1), we get

$$\psi = \dot{z}\frac{e^{kz}}{k} = -\zeta\frac{i\omega}{k}e^{ikx + kz - i\omega t}.$$

Euler's equation itself in terms of the potential ψ takes the form

$$\frac{\partial \psi}{\partial t} = -\left(gz + \frac{P}{\rho}\right) + \frac{E^2}{8\pi}\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T. \tag{5}$$

At the interface, the electric field satisfies[3]

$$\mathbf{E}_{\parallel}^g = \mathbf{E}_{\parallel}^l, \quad \mathbf{E}_{\perp}^g = \varepsilon \mathbf{E}_{\perp}^l.$$

We can use the surface $z = 0$ for the interface (we assume $k\zeta \ll 1$). After elementary transformations, we get

$$E_{0x} = E_{0x}^l, \quad E_{0y} = E_{0y}^l, \quad E_{0z} = \varepsilon E_{0z}^l,$$

$$A = k\zeta\frac{\varepsilon - 1}{\varepsilon + 1}(E_{0z} - iE_{0x}), \quad B = k\zeta\frac{\varepsilon - 1}{\varepsilon + 1}\left(\frac{E_{0z}}{\varepsilon} + iE_{0x}\right). \tag{6}$$

Using explicit expressions for σ_{ij}^g and σ_{ij}^l in the boundary conditions for the stress tensor,

$$\sigma_{ij}^g n_j = \sigma_{ij}^l n_j - \alpha\frac{\partial^2 \zeta}{\partial x^2}n_i$$

(here $\mathbf{n}$ is the unit vector normal to the interface, while α is the coefficient of surface tension), we get the equation for the pressure at the boundary:

$$P=\text{const}=-\alpha\frac{\partial^2\zeta}{\partial x^2}+\frac{E^{l2}\rho}{8\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T-\frac{\varepsilon-1}{8\pi}(\varepsilon E_\perp^{l2}+E_\parallel^{l2}).\quad(7)$$

Finally, substituting Eq. (7) into Eq. (5) and using Eq. (6), we find

$$\omega^2=gk+\frac{\alpha}{\rho}k^3+\frac{(\varepsilon-1)^2}{4\pi\rho\varepsilon(\varepsilon+1)}(\varepsilon E_\parallel^2\cos^2\theta-E_\perp^2)k^2.\quad(8)$$

Above, for brevity, we have omitted the subscript 0 in the field and have introduced into the treatment the angle θ between the wave vector $\mathbf{k}$ and the projection of field $\mathbf{E}$ onto the horizontal plane. It is clear that the dispersion relation for surface waves in a liquid in a magnetic field is obtained from Eq. (8) by replacing the permittivity by the permeability. In fact, in the particular cases of tangential and normal fields, our result coincides with that of Ref. 4.

The resulting formula is inapplicable for large vertical fields. The unperturbed surface of the liquid in this case cannot be regarded as a horizontal plane. For such a surface to be stable, the quantity ω^2 must be positive for all k, since otherwise the amplitudes of the waves with the corresponding wave vectors will grow without limit. It is easy to obtain the required limitation on the field:

$$(\varepsilon-1)^4E_\perp^4<64\pi^2\rho\alpha g\varepsilon^2(\varepsilon+1)^2.$$

For example, in water, the density is $\rho=1$ g/cm^3, $\varepsilon=81$, $\alpha=73$ dyne/cm, and the critical field is $E=2.5$ kV/mm. In the limit $\varepsilon\to\infty$, corresponding to a conductor, the stability condition goes over to the inequality $E_\perp^4<64\pi^2\rho\alpha g$ (Ya. I. Frenkel', 1935; see, for example, Ref. 3, section 5).

The generalization of the dispersion relationship to a weakly inhomogeneous external field is obvious. If the characteristic scale l over which E_0^2 varies is much larger than the corresponding scale of the wave (ζ or $1/k$), the only thing that changes in Eq. (8) is the coefficient g (which, of course, will no longer mean the acceleration of gravity, but will characterize the force acting on unit mass of the material in the combined electric and gravitational fields). For example, in the geometry of a charged jet surrounded by a cylindrical layer of liquid with radius r,

$$g=\frac{\varepsilon-1}{4\pi\varepsilon}\frac{E_0^2}{\rho r}.$$

Here E_0 is the field at the surface, gravitation is considered small, and the applicability condition is $\zeta\ll r$.

In a strong horizontal field, when the capillary and gravitational terms can be neglected, $\omega\propto k|\cos\theta|$, and the group velocity is independent of $\mathbf{k}$ and is always parallel to the field. The surface thus becomes effectively rigid in the direction of the field.

The correction $\delta\alpha$ to the coefficient of surface tension (relative to the value at $T=0$) equals the derivative of the "quasi-partial" (associated with the surface waves) potential Ω with respect to the surface area:

$$\delta\alpha=\left(\frac{\partial\Omega}{\partial S}\right)_T,$$

for an ideal two-dimensional Bose gas, it is determined by[5]

$$\delta\alpha=T\int\ln\left[1-\exp\left(-\frac{\hbar\omega}{T}\right)\right]\frac{d^2k}{4\pi^2}.$$

Assuming that the variation of the spectrum associated with the field is small, we get

$$\delta\alpha=-\frac{T}{8\pi^2}\int_0^{2\pi}d\theta\int_0^\infty\frac{k^2}{e^q-1}dq$$

$$\approx-\Gamma\left(\frac{7}{3}\right)\zeta\left(\frac{7}{3}\right)\frac{\rho^{2/3}T^{7/3}}{4\pi\alpha^{2/3}\hbar^{4/3}}$$

$$+\Gamma\left(\frac{5}{3}\right)\zeta\left(\frac{5}{3}\right)\frac{(\varepsilon-1)^2\rho^{1/3}(\varepsilon E_\parallel^2-2E_\perp^2)T^{5/3}}{48\pi^2\varepsilon(\varepsilon+1)\alpha^{4/3}\hbar^{2/3}}$$

$$\approx-0.1341\frac{\rho^{2/3}T^{7/3}}{\alpha^{2/3}\hbar^{4/3}}$$

$$+0.004\frac{(\varepsilon-1)^2\rho^{1/3}(\varepsilon E_\parallel^2-2E_\perp^2)T^{5/3}}{\varepsilon(\varepsilon+1)\alpha^{4/3}\hbar^{2/3}},$$

where $q=\hbar\omega/T$. In the opposite case of a strong tangential field, however,

$$\delta\alpha\approx\sqrt[3]{\frac{T^8}{\alpha\hbar^5}}\sqrt{\frac{\varepsilon+1}{\pi^3}}\frac{2\rho^{5/6}}{(\varepsilon-1)E}\int_0^\infty dr\int_0^\infty ds\ln[1$$

$$-\exp(-\sqrt{r^2+s^3})]\approx-0.59\frac{\rho^{5/6}T^{8/3}\sqrt{\varepsilon+1}}{\alpha^{1/3}\hbar^{5/3}(\varepsilon-1)E}.$$

We should point out that it is convenient to use waves propagating perpendicular to the field direction to experimentally measure the surface tension. Their dispersion relationship depends on the field only via the renormalized surface tension. Atkins's theory is actually applicable only to liquid helium and hydrogen. Since the former is only very weakly polarizable ($\varepsilon=1.047$), the effect under consideration apparently cannot be measured with present-day experimental technique. The susceptibility is much larger in hydrogen ($\varepsilon=1.231$), while a fairly low temperature can be attained. Thus, it is preferable to choose hydrogen for measuring the correction to the surface tension.

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[2] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Nauka, Moscow, 1988; Pergamon Press, Oxford, 1987).

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[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Nauka, Moscow, 1995; Pergamon Press, Oxford, 1980), part 1.