PHYSICAL REVIEW E **67**, 056311 (2003)

Tolman's nonlinearity of capillary waves

Anton V. Dolgikh, Dmitry L. Dorofeev, and Boris A. Zon*
Voronezh State University, Voronezh 394693, Russia

(Received 6 August 2002; published 22 May 2003)

A nonlinear theory of nanometer capillary waves is developed that takes curvature dependence of the surface tension coefficient (Tolman's nonlinearity) into account. Estimations are given that indicate the importance of Tolman's nonlinearity for thermocapillary waves.

DOI: 10.1103/PhysRevE.67.056311 PACS number(s): 68.03.Cd, 68.03.Kn

I. INTRODUCTION

The ordinary theory of capillary waves on the surface of a liquid is based on the assumption that the surface tension is a constant, independent of the surface curvature [1]. However, as it is well known, this assumption becomes incorrect for large curvatures. Taking into account only two leading terms, the dependence of the surface tension coefficient on the curvature radius R can be taken in the form [2]

$$\alpha=\alpha(\infty)\left(1-\frac{2\delta}{R}\right), \tag{1}$$

where δ is the Tolman length and $\alpha(\infty)$ is the surface tension of the flat surface $(R\to\infty)$. Thus, the change in the surface tension becomes essential when R lies in the range of several δ. Estimation of the Tolman length was carried out in a number of theoretical and experimental works (see, for example, Refs. [3–6] and references therein). It can be both negative and positive, and its absolute value is about the width of the monomolecular liquid-vapor interfacial layer and lies in the nanometer range.

In the present work, we consider the influence of dependence (1) on the characteristics of capillary waves. This dependence is most pronounced when R amounts to several nanometers.

The proposed approach is built on the frame of the model of continuous liquid, the molecular microstructure of the medium is neglected. Therefore, the wavelength is assumed to be sufficiently large in comparison with the intermolecular distance. It is also assumed that the wave period is larger than the characteristic relaxation time (the time of settled life of a molecule in the well of an intermolecular potential [7]). For shorter periods, the medium could not be treated as a liquid but rather as a solid one and, correspondingly, the capillary waves must be substituted by the Rayleigh ones, as treated by Frenkel [7].

Obtained results may be of interest for the theory of thermocapillary waves, widely investigated in the past years, both experimentally [8–10] and by molecular dynamics simulations [11,12]. It was assumed in Ref. [8] that an enhancement of the effective surface tension for the shortest thermocapillary waves may explain some unexpected experimental results obtained for an x-ray reflection on the methanol surface. Thus, in our work we discuss a specific mechanism that may lead to such a change in the effective surface tension, and we call it Tolman's nonlinearity.

This nonlinearity may also be essential for some applications in nanotechnology, for example, in creating wavelike periodic microstructures on a surface [13] and in the problem of electrohydrostatic instability [14].

II. MAIN FORMALISM

It is assumed that the velocity field in a liquid possesses the property of potentiality,

$$\Delta\Phi=0, \tag{2}$$

where Φ is velocity potential.

The axis z is directed vertically up, and the uperturbed liquid occupies the region $z<0$. Capillary waves propagate along axis x. Since the wave surface $\zeta(x,t)$ is not spherical, we must generalize Eq. (1) for nonspherical surfaces. For this purpose, we substitute the factor $-1/R$ in Eq. (1) by the mean curvature of the surface. With assumption $\partial\zeta/\partial x\ll 1$, it yields

$$-\frac{1}{R}\to\frac{1}{2}\,\frac{\partial^2\zeta}{\partial x^2}. \tag{3}$$

Then the Laplace equation, determining pressure under the curved surface of the liquid $(z=\zeta(x,t))$, in account of Eqs. (1) and (3), takes the form

$$\rho\frac{\partial\Phi}{\partial t}=\alpha(\infty)\left[\frac{\partial^2\zeta}{\partial x^2}+\delta\left(\frac{\partial^2\zeta}{\partial x^2}\right)^2\right], \tag{4}$$

where ρ is the density of the liquid.

Expressing the velocity of the liquid in terms of potential Φ, we get a condition that connects Eqs. (2) and (4):

$$\frac{\partial\zeta}{\partial t}=\frac{\partial\Phi}{\partial z}\Big|_{z=\zeta(x,t)}. \tag{5}$$

Following the standard procedure [1], we assume here that amplitude A of the wave is small in comparison with its length λ, i.e.,

$$\varepsilon=A/\lambda\ll 1. \tag{6}$$

---

*Email address: zon@niif.vsu.ru

This allows us to substitute condition $z=\zeta(x,t)$ in Eqs. (4) and (5) by $z=0$. Instead of x we introduce $\xi=x-ut$, where u is the velocity of a capillary wave. This gives us the Laplace equations with nonlinear boundary condition:

$$\frac{\partial^2\Phi}{\partial z^2}+\frac{\partial^2\Phi}{\partial \xi^2}=0;\quad \left[-u\frac{\partial\zeta}{\partial\xi}=\frac{\partial\Phi}{\partial z}\right]_{z=0}; \tag{7}$$

$$\left[u^3\rho\frac{\partial\Phi}{\partial\xi}=\alpha(\infty)u\frac{\partial^2\Phi}{\partial\xi\partial z}-\alpha(\infty)\,\delta\left(\frac{\partial^2\Phi}{\partial\xi\partial z}\right)^2\right]_{z=0}.$$

As a second boundary condition (over ξ), we take the periodic one

$$\Phi(\xi+\lambda)=\Phi(\xi). \tag{8}$$

Boundary condition (8) allows us to seek the potential in the form

$$\Phi(\xi,z)=\sum_{n=1}^{\infty}c_n e^{nkz}\cos(nk\xi)+\sum_{n=1}^{\infty}s_n e^{nkz}\sin(nk\xi). \tag{9}$$

Taken in this form the potential satisfies Eq. (2); $k=2\pi/\lambda$ is the wave number.

Substituting this expansion into Eq. (7) gives

$$\sum_{p=1}^{\infty}(\rho u^3 p-\alpha(\infty)up^2k)[c_p\sin(pk\xi)-s_p\cos(pk\xi)]$$

$$=\alpha(\infty)\,\delta\sum_{m,n=1}^{\infty}m^2n^2k^3[c_mc_n\sin(mk\xi)\sin(nk\xi)$$

$$-2c_ms_n\sin(mk\xi)\cos(nk\xi)+s_ms_n\cos(nk\xi)\cos(mk\xi)]. \tag{10}$$

Obviously, the ratio between s_1 and c_1 depends only on the choice of initial ξ. For simplicity, we set

$$s_1=c_1$$

and introduce dimensionless values

$$\tilde{c}_n=c_n/c_1,\quad \tilde{s}_n=s_n/c_1,\quad \tilde{c}_1=\tilde{s}_1=1,$$

$$\tilde{u}=u/u_0,\quad u_0=(\alpha(\infty)k/\rho)^{1/2},$$

and the nonlinearity parameter

$$\gamma=\delta k^2c_1/u.$$

Then Eq. (10) becomes

$$\sum_{p=1}^{\infty}p(\tilde{u}^2-p)[\tilde{c}_p\sin(pk\xi)-\tilde{s}_p\cos(pk\xi)]$$

$$=\gamma\sum_{m,n=1}^{\infty}m^2n^2[\tilde{c}_m\tilde{c}_n\sin(mk\xi)\sin(nk\xi)-2\tilde{c}_m\tilde{s}_n\sin(mk\xi)\cos(nk\xi)+\tilde{s}_m\tilde{s}_n\cos(nk\xi)\cos(mk\xi)]$$

$$=\frac{\gamma}{2}\sum_{m,n=1}^{\infty}n^2m^2[(\tilde{c}_m\tilde{c}_n+\tilde{s}_n\tilde{s}_n)\cos(m-n)k\xi+(\tilde{s}_n\tilde{s}_n-\tilde{c}_m\tilde{c}_n)\cos(m+n)k\xi-2\tilde{c}_m\tilde{c}_n(\sin(m-n)k\xi+\sin(m+n)k\xi].$$

Equalizing the coefficients at corresponding harmonics in the left-hand and right-hand sides yields

$$-p(\tilde{u}^2-p)\tilde{s}_p=\frac{\gamma}{2}\sum_{n=1}^{\infty}n^2\{[(n+p)^2\tilde{c}_{n+p}+(n-p)^2$$

$$\times(\tilde{c}_{n-p}-\tilde{c}_{p-n})]\tilde{c}_n+[(n+p)^2\tilde{s}_{n+p}$$

$$+(n-p)^2(\tilde{s}_{n-p}+\tilde{s}_{p-n})]\tilde{s}_n\},$$

$$-p(\tilde{u}^2-p)\tilde{c}_p=\gamma\sum_{n=1}^{\infty}n^2[(n+p)^2\tilde{c}_{n+p}$$

$$+(n-p)^2(\tilde{c}_{p-n}-\tilde{c}_{n-p})]\tilde{s}_n.$$

Zero approximation $\tilde{c}_p=\tilde{s}_p=0\ \ \forall p\geqslant 2$ gives $\tilde{u}=1$, i.e., $u=u_0$, which coincides with a familiar relation for capillary waves with constant surface tension [1].

First approximation: $\tilde{c}_p=\tilde{s}_p=0\ \ \forall p\geqslant 3$,

$$1-\tilde{u}^2=4\gamma(\tilde{c}_2+\tilde{s}_2),\quad 2(2-\tilde{u}^2)\tilde{s}_2=0,$$

$$1-\tilde{u}^2=4\gamma(\tilde{c}_2-\tilde{s}_2),\quad 2(2-\tilde{u}^2)\tilde{c}_2=\gamma$$

gives the solution

$$\tilde{c}_2=\frac{\gamma}{2},\quad \tilde{s}_2=0,\quad \tilde{u}\approx 1-\gamma^2.$$

Returning to dimensional values,

$$c_1=s_1,\quad c_2\approx\frac{\gamma}{2}c_1\quad s_2=0,\quad u\approx(1-\gamma^2)u_0. \tag{11}$$

The surface profile $\zeta(\xi)$ can be represented in the form of the expansion similar to Eq. (9):

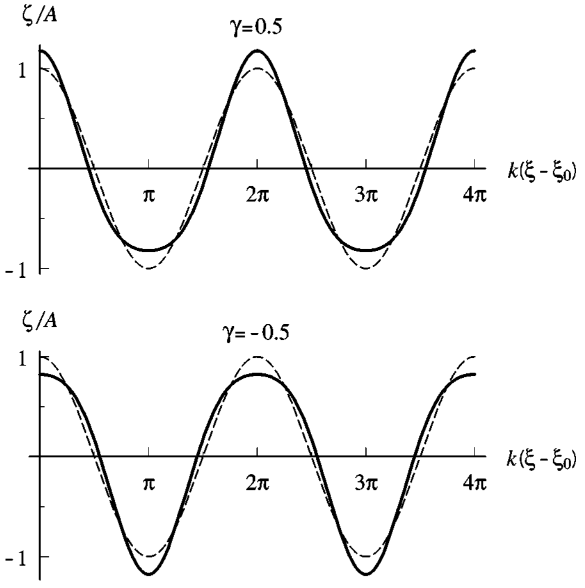

FIG. 1. Wave forms with nonlinearity parameter $\gamma=\pm 0.5$. The dashed line presents the first harmonic.

$$\zeta(\xi,t)=\sum_{n=1}^{\infty} a_n \cos(nk\xi)+\sum_{n=1}^{\infty} b_n \sin(nk\xi).$$

Then the second relation in Eq. (7) gives

$$a_n=s_n/u, \quad b_n=-c_n/u,$$

and, taking into account relations (11),

$$\zeta(\xi,t)=\sqrt{2}a_1 \cos(k\xi+\pi/4)-(\gamma a_1/2)\sin(2k\xi).$$

Finally, we rewrite this expression for an arbitrary initial phase

$$\zeta(\xi,t)=A\left(\cos[k(\xi-\xi_0)]+\frac{\gamma}{2\sqrt{2}}\cos[2k(\xi-\xi_0)]\right)$$

and express the parameter γ in terms of wave amplitude A and length λ,

$$\gamma=\frac{\delta k^2 A}{\sqrt{2}}=\frac{(2\pi)^2}{\sqrt{2}}\frac{\delta A}{\lambda^2}. \tag{12}$$

Note that factor $(2\pi)^2/\sqrt{2}\approx 27.9$ is rather large, hence nonlinear effects may be significant even for wavelengths λ much larger than the Tolman length δ.

III. RESULTS AND DISCUSSIONS

Figure 1 demonstrates wave forms $\zeta(\xi)$ for different values of γ. The nonlinearity, considered here, leads to a deformation of the original sinusoidal wave form and produces a crest-trough asymmetry: for $\gamma>0$, crests become narrower, and troughs wider; while for $\gamma<0$, the deformation is opposite. The wave velocity u changes according to Eq. (11), as presented in Fig. 2. Note that the velocity decreases both for positive and negative δ. Such a deformation of the wave form and the change in velocity are similar to the well-known Stokes wave [1]. However, in the case of Stokes waves, the cause of nonlinearity is finite amplitude of the wave in comparison with its wavelength, i.e., finiteness of parameter ε, defined in Eq. (6). On the contrary, the cause of, considered here, Tolman's nonlinearity is the finiteness of the curvature radius in comparison with the Tolman length, i.e., finiteness of parameter γ, defined in Eq. (12). Note that $\varepsilon \ll 1$ does not necessarily imply $\gamma \ll 1$, because γ depends not only on A/λ but also on δ/λ and multiplied by a rather large factor. Thus, for nanometer capillary wave, the described Tolman's nonlinearity, associated with γ, can be at least equally important as the familiar Stokes' nonlinearity, associated with ε.

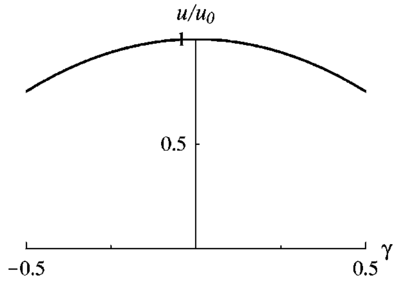

FIG. 2. Velocity of capillary wave as a function of γ.

In particular, Tolman's nonlinearity can be essential for thermally induced capillary waves on the surface of the liquid. Below, we estimate the characteristic value of γ for these waves using the method described in Refs. [15,16].

Let us assume the surface of the liquid to be a square in the x-y plane with side L, and require $\zeta=0$ at the boundary. Thermally induced fluctuations of surface at an arbitrary moment of time can be represented in the form of an expansion over harmonics of capillary waves:

$$\zeta(\mathbf{r})=\sum_{n,m} A_{nm}\sin\left(\frac{\pi}{L}nx\right)\sin\left(\frac{\pi}{L}my\right),$$

where $n,m=1,\ldots,N$, $N=L/l$, l is an empirical constant approximately equal to a characteristic intermolecular distance. For estimation we will neglect dependence (1) of surface tension α on the curvature. Then, the work W necessary for creating this fluctuation is proportional to the excess of surface area ΔS:

$$W=\alpha\,\Delta S=\int\int dx\,dy\,[(1+\zeta_x^2+\zeta_y^2)^{1/2}-1]$$

$$\approx\frac{\alpha}{2}\int\int dx\,dy\,(\zeta_x^2+\zeta_y^2)=\frac{\alpha\pi^2}{8}\sum_{n,m}(n^2+m^2)A_{nm}^2,$$

and the probability of fluctuation is proportional to Boltzmann's factor $\exp(-W/k_BT)$. In complete agreement with the equipartition theorem, this gives following amplitude variances:

$$\langle A_{nm}^2\rangle = \frac{4k_BT}{\alpha\pi^2(n^2+m^2)}.$$

In order to estimate the nonlinearity parameter γ, note that it presents a characteristic value of the mean curvature $(\zeta_{xx}+\zeta_{yy})/2$ multiplied by the Tolman length, hence

$$\langle \gamma^2\rangle \sim \delta^2 \langle \overline{(\zeta_{xx}+\zeta_{yy})^2}\rangle, \tag{13}$$

where the overline denotes averaging over x,y:

$$\overline{(\zeta_{xx}+\zeta_{yy})^2} = \frac{1}{4}\left(\frac{\pi}{L}\right)^4 \sum_{n,m} (n^2+m^2)^2 A_{nm}^2,$$

which yields

$$\langle \gamma^2\rangle \sim \frac{\delta^2}{4}\left(\frac{\pi}{L}\right)^4 \sum_{n,m} (n^2+m^2)^2 \langle A_{nm}^2\rangle$$

$$= \frac{\pi^2\delta^2 k_BT}{\alpha L^4}\sum_{n,m} n^2+m^2 \approx \frac{\pi^2\delta^2 k_BT}{\alpha L^4}\,\frac{2N^4}{3}.$$

Expressing α in terms of intermolecular potential depth ϵ, $\alpha \sim \epsilon/l^2$ [6], finally we get

$$\langle \gamma^2\rangle \sim \frac{k_BT}{\epsilon}\left(\frac{\delta}{l}\right)^2.$$

Then taking, for example, $k_BT/\epsilon \sim 0.5$, $\delta/l \sim 1$ obtain $\langle \gamma^2\rangle \sim 0.5$.

Obviously, these expressions give only a rough estimation, since the main contribution to $\langle \gamma^2\rangle$ is associated with wavelengths $\sim l$, for which the description in terms of capillary waves becomes inadequate, as mentioned in the Introduction. Nevertheless, this estimation suggests a significant role of the considered nonlinearity in the dynamics of thermocapillary waves. In particular, it means that an effective value of surface tension α_{eff} for thermocapillary waves can significantly differ from $\alpha(\infty)$. Indeed, using Eqs. (1), (3), and (13), an average change of surface tension for the whole ensemble of capillary waves can be estimated as

$$\Delta\alpha/\alpha(\infty) \sim \sqrt{\langle \gamma^2\rangle}, \tag{14}$$

and thus can approach values as large as 0.7.

In its turn, this change in α_{eff} will lead to a corresponding change in the mean-square amplitude of thermocapillary surface fluctuations [8]:

$$\sigma_c = \langle \zeta^2\rangle \approx \frac{k_BT}{2\pi\alpha_{eff}}\ln\left[\frac{\lambda_{max}}{\lambda_{min}}\right], \tag{15}$$

where λ_{max} and λ_{min} are some ''cutoff'' values for the wavelengths (see discussion on their proper choice in Ref. [16]). In combination with intrinsic interfacial width σ_p, which is of the order of the molecular radius, σ_c provides the total roughness of the liquid surface,

$$\sigma_t^2 = \sigma_c^2 + \sigma_p^2. \tag{16}$$

The values of σ_t can be extracted from experimental data on x-ray reflection by liquid surfaces [8–10]. The available accuracy is about 1–3 %, which is much better than it is needed in order to find the above change in the effective surface tension. Thus, the above theoretical analysis is, in principle, accessible for an experimental test by measuring the value of σ_t^2 and comparing it with theoretical values. However, in practice, we usually cannot clearly reveal the effect of the considered nonlinearity, since it is partially obscured by the well-known problems of the proper choice of λ_{min} and σ_p in Eqs. (15) and (16). Nevertheless, the discrepancy between experimental and theoretical estimations obtained for methanol in Ref. [8] seems rather characteristic. The corresponding values for methanol are the following: the experimental value of $\sigma_t = 4.80 \pm 0.06$ Å; the theoretical value for σ_c, calculated with $\alpha_{eff} = \alpha(\infty)$, is $\sigma_c = 4.74 \pm 0.08$ Å; then Eq. (16) gives for $\sigma_p \approx 0.7$ Å, which is considerably smaller than the theoretically expected value near the molecular radius $r_M = 2.52$ Å. The authors of Ref. [8] suggested that such a discrepancy can be explained by a larger value of α_{eff} in comparison with $\alpha(\infty)$, in complete accordance with our consideration above. On the other hand, similar experimental and theoretical estimations for water and carbon tetrachloride carried out in the same work do not demonstrate any pronounced discrepancies. It is assumed in Ref. [8] that a strong dimensional dependence of the surface tension and, hence, a large difference between α_{eff} and $\alpha(\infty)$ is a characteristic just for methanol, due to distinct anisotropy of its molecule, and is not so important for water and carbon tetrachloride with their more isotropic molecules. This last assumption is also indirectly confirmed by experimental results presented in Ref. [17], which give a relatively larger value of the Tolman length for methanol, $\delta/l \sim 2.7 \ldots 3.5$, than for water, $\delta/l \sim 1.7 \ldots 2.8$.

Thus, the above consideration shows that taking into account Tolman's nonlinearity can be useful in the analysis of nanometer capillary wave dynamics, in particular, the thermocapillary ones.

ACKNOWLEDGMENTS

The research was carried out under the support of the CRDF and the Ministry of Education of Russian Federation (Grant No. VZ - 010 - 0).

---

[1] G. B. Whitham, *Linear and Nonlinear Waves* (Wiley, New York, 1974).

[2] R.C. Tolman, J. Chem. Phys. **17**, 333 (1949).

[3] V.I. Kalikmanov, Phys. Rev. E **55**, 3068 (1997).

[4] D.I. Zhukhovitskii, J. Chem. Phys. **110**, 7770 (1999).

[5] A.E. van Giessen and E.M. Blokhuis, J. Chem. Phys. **116**, 302 (2002).

[6] A. V. Dolgikh, D. L. Dorofeev, and B. A. Zon, Khim. Fiz. (to

be published).

[7] Ya. I. Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946).

[8] A. Braslau *et al.*, Phys. Rev. A **38**, 2457 (1988).

[9] H. Tostmann *et al.*, Phys. Rev. B **61**, 7284 (2000).

[10] R.K. Heilmann, M. Fukuto, and P.S. Pershan, Phys. Rev. B **63**, 205405 (2001).

[11] Martin-D. Lacasse, G.S. Grest, and A.J. Levine, Phys. Rev. Lett. **80**, 309 (1998).

[12] S.W. Sides, G.S. Grest, and Martin-D. Lacasse, Phys. Rev. E **60**, 6708 (1999).

[13] C. Fradin, A. Braslau, and D. Luzet, Nature (London) **403**, 871 (2000).

[14] B.A. Zon, Phys. Lett. A **292**, 203 (2001).

[15] F.P. Buff and R.A. Lovett, Phys. Rev. Lett. **15**, 621 (1965).

[16] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).

[17] S.V. Stepanov, V.M. Byakov, and O.P. Stepanova, Russ. J. Phys. Chem. **74**, S65 (2000).