

Interaction between a charged or neutral particle and a semi-infinite nonpolar dielectric liquid

Mikel L. Forcada, Néstor R. Arista,* and Alberto Gras-Martí

Departament de Física Aplicada, Universitat d'Alacant, Apartat 99, E-03080 Alacant, Spain

Herbert M. Urbassek

*Institut für Theoretische Physik der Technische Universität Braunschweig,
Mendelssohnstrasse 3, D-3300 Braunschweig, Germany*

Rafael Garcia-Molina

Departamento de Física, Universidad de Murcia, E-30071 Murcia, Spain

(Received 2 January 1991)

We analyze classically the static interaction between a charged or neutral atomic particle and a semi-infinite nonpolar dielectric liquid. The particle is always external to the liquid. A differential equation for the shape of the deformed liquid surface in the presence of the particle is derived taking into account the effects of particle-liquid interaction, surface tension of the liquid, and gravity. The equation is solved numerically, and the stability of equilibrium shapes is discussed. Analytical solutions for the differential equation are obtained in the limit of large particle-liquid distances. No equilibrium shapes are found for particle-surface distances below a certain threshold, and some liquid-independent relations hold at that threshold. We propose simple models that account for these features of the numerical solutions. The potential energy of the particle-liquid system is also calculated.

I. INTRODUCTION

The analysis of interactions among neutral or charged particles and liquid media is relevant in studies of aerosol physics,¹ of atmospheric processes,² biophysics,^{3,4} and surface science. In particular, we refer to studies of atom-surface interaction processes in liquid He,⁵⁻⁸ to the self-trapping of electrons in macroscopic dimples on the surface of liquid He,⁹ and more recently, to the atomic-force microscopy of liquid films.¹⁰ The basic study of the static interactions between particles and liquids is relevant to the understanding of such a variety of phenomena.

We analyze here the equilibrium shape for the surface which limits an incompressible semi-infinite nonpolar liquid, treated as a continuum, when a charged or neutral atomic (pointlike) particle is held fixed at a certain height above it. We also compute the potential energy of the interacting system. To our knowledge, a detailed analysis of this simple configuration seems to be absent in the literature. A few of these results have already been reported.¹¹

Gras-Martí and Ritchie¹² calculated the contribution of capillary-wave (rippion) excitations to the interaction energy of a static charged particle with a nonpolar dielectric liquid. This calculation was extended later¹³ for polar liquids. In the quantum many-body formalism used in these two papers, the self-energy of a charged particle interacting with the liquid is obtained as the zero-point energy of the coupled charge-rippion field system. A classical approach is used in the calculations reported in this paper, and the results of both theoretical schemes will be compared. A calculation of the surface shape implied by

the results of Gras-Martí and Ritchie¹² will be obtained.

This paper is organized as follows. The differential equation for the surface shape is derived and discussed in Sec. II. The basic equation is solved analytically in Sec. III for the limiting case of a distant particle-surface interaction, while Sec. IV discusses the exact numerical results. Sections V and VI present two simple models that retain the basic properties of numerical solutions. Full numerical and approximate calculations of the potential energy of the particle-liquid system are reported and discussed in Sec. VII. Conclusions are presented in Sec. VIII.

II. EQUATION FOR THE EQUILIBRIUM SURFACE OF THE LIQUID

We wish to determine the equilibrium shape of a nonpolar liquid surface when a charged or neutral atomic particle is held fixed at a height R above its original (nonperturbed) horizontal surface, Fig. 1. Because of the cylindrical symmetry, the radial distance from the symmetry axis, ρ , is the only variable. The equilibrium surface, which will be described by its height z at a distance ρ from the origin, is subject to three forces which must balance: gravity, the attraction between the particle and the constituents of the liquid, and surface tension. Minimization (see Appendix A) of the total potential energy of the system yields the following nonlinear differential equation:

$$\sigma \frac{1}{\rho} \frac{d}{d\rho} \left[\frac{\rho(dz/d\rho)}{[1+(dz/d\rho)^2]^{1/2}} \right] - nMgz(\rho) - nv(r(\rho)) = 0 \quad (1)$$

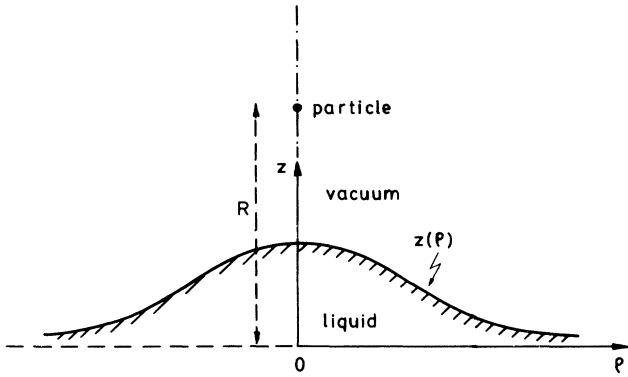


FIG. 1. Schematics of the deformation of the liquid surface due to the attractive interaction with a point particle.

which will be hereafter referred to as the *basic equation*. The liquid enters this equation via M , the mass of its constituents (atoms or molecules; both will be called *molecules* in the following), its number density n , and surface tension σ ; g is the gravity acceleration, and $v(r(\rho))$ is the interaction energy between the external particle and a molecule at the surface of the liquid, where $r(\rho) = \{\rho^2 + [R - z(\rho)]^2\}^{1/2}$ is the mutual distance.

For the nonretarded interaction of a *charged* particle (of charge Q) with the dipoles it induces in the molecules of the liquid, we use

$$v^{\text{charged}}(r) = -\frac{1}{2}\alpha Q^2 r^{-4}, \quad (2a)$$

where α is the polarizability of the liquid molecules. Equation (2a) is valid only to first order in α : the interaction energy for a more polarizable liquid has a more complicated form,¹³ due to the fact that molecules polarize one another.

For the nonretarded van der Waals interaction of a *neutral* atomic particle with the molecules of the liquid,

$$v^{\text{neutral}}(r) = -\Lambda r^{-6}, \quad (2b)$$

where Λ is the van der Waals coefficient for the atom-molecule interaction.

It has to be stressed that solutions of the basic equation (1) do not necessarily correspond to stable-equilibrium shapes (minima of the total energy of the system). The solutions can as well correspond to maxima of the total energy (unstable equilibrium) or saddle points. These possibilities will be analyzed later. Furthermore, if the particle is not held fixed above the liquid, the total potential energy decreases as the particle approaches the liquid, and the equilibrium state is then one of total immersion for the particle. This case falls outside the scope of this paper.

If we remove the particle (i.e., $R \rightarrow \infty$) the equilibrium configuration of the liquid surface has to be planar, $z(\rho) = 0$. This is indeed the solution of Eq. (1) in that case.

A boundary condition that may be used to solve Eq. (1) is

$$z(\rho \rightarrow \infty) = 0. \quad (3)$$

It seems physically reasonable to require z to be a smooth function for all ρ . For $z \neq R$, this implies that

$$\left. \frac{dz}{d\rho} \right|_{\rho=0} = 0, \quad (4)$$

which is a further boundary condition that shall be used to solve Eq. (1).

III. DISTANT INTERACTION: LINEARIZED EQUATION

It is convenient to start by considering the case when the particle is far from the liquid surface. This limiting case allows us to linearize and simplify the basic equation (1). The results obtained in this section should be directly comparable with existing treatments of particle-induced ripple-wave excitations^{5,6,12,13} which only consider small departures from flatness.

For a large R such that $z \ll R$, one may assume that the surface is nearly flat, namely $(dz/d\rho)^2 \ll 1$. The basic equation (1) reduces then to a linear inhomogeneous differential equation,

$$\sigma \left[\frac{d^2 z}{d\rho^2} + \frac{1}{\rho} \frac{dz}{d\rho} \right] - n[Mgz + v(\rho, R)] = 0. \quad (5)$$

This equation may be solved by the Fourier transform technique, to yield

$$z^{\text{lin}}(\rho) = -\frac{n}{\sigma} \int_0^\infty dk k J_0(k\rho) \frac{v(k, R)}{k^2 + 2/a^2}, \quad (6)$$

where

$$v(k, R) = \int_0^\infty d\rho' \rho' J_0(k\rho') v(\rho', R), \quad (7)$$

and $a = (2\sigma/Mng)^{1/2}$ is the capillary constant,¹⁴ a typical lateral dimension of the system.

For the charged-particle case the linearized profile of the liquid is

$$z_{\text{charged}}^{\text{lin}}(\rho) = \frac{n\alpha Q^2}{4\sigma R^2} \int_0^\infty du K_1(u) J_0\left(\frac{u\rho}{R}\right) \frac{u^2}{u^2 + 2R^2/a^2}, \quad (8a)$$

whereas for the neutral-particle case, the linear solution is

$$z_{\text{neutral}}^{\text{lin}}(\rho) = \frac{n\Lambda}{8\sigma R^4} \int_0^\infty du K_2(u) J_0\left(\frac{u\rho}{R}\right) \frac{u^3}{u^2 + 2R^2/a^2}. \quad (8b)$$

In the above equations, K_1 , K_2 , and J_0 are Bessel functions.¹⁵ The integrals in Eqs. (8a) and (8b) are dimensionless functions of R , ρ , and a .

In Appendix B we derive the solutions (8a) and (8b) in a way that is parallel to the treatment of Gras-Martí and Ritchie¹² for the interaction of a charged particle with the ripplon (capillary-gravity-wave) field.

Very good approximations to the maximum height $z(0)$ of the profiles given by Eqs. (8a) and (8b) may be ob-

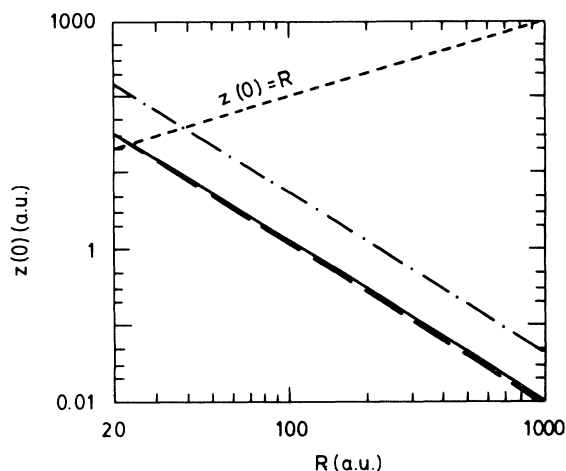


FIG. 2. Linearized results for liquid profile heights for a unit point charge and liquid He (---), Ne (—), and Ar (- · - ·). The straight line (---) is the $z(0)=R$ or “contact” line.

tained for values of R which are small compared to the capillary constant a (which is usually very large in atomic scale). Using small-argument approximations to the modified Bessel functions,¹⁵ one obtains

$$z_{\text{charged}}^{\text{lin}}(0) \simeq \frac{n\alpha Q^2}{4\sigma R^2} \ln\left(\frac{\sqrt{2}a}{e^{\gamma}R}\right) \quad (9a)$$

and

$$z_{\text{neutral}}^{\text{lin}}(0) \simeq \frac{n\Lambda}{4\sigma R^4} \left[\frac{1}{2} + \ln\left(\frac{\sqrt{2}a}{e^{\gamma}R}\right) \right]. \quad (9b)$$

In these equations, $\gamma \simeq 0.57721$ is Euler’s constant.

Figure 2 shows these linearized results for the interaction of a particle of unit charge with liquid He, Ne, and Ar, using the data given in Table I. We see in Fig. 2 that for distances long enough for the linear approximation [$z(0) \ll R$] to hold, the profile heights are extremely small, comparable to the size of a single atom. For more significant values of $z(0)$ (10 a.u.), the approximation $z(0) \ll R$ breaks down. One should then solve numerically the full, nonlinear equation (1).

IV. NUMERICAL SOLUTIONS FOR THE NONLINEAR BASIC EQUATION

The method applied to find solutions to the nonlinear basic differential equation (1) uses standard fourth-order Runge-Kutta formulas for second-order differential equations¹⁵ to solve the initial value problem specified by Eq. (1), condition (4) and by

$$z(0) = Z, \quad (10)$$

where Z , unknown *a priori*, is used as a *shooting* value in the following way: for a given particle-surface distance, the solution will show the correct asymptotic behavior for $\rho \rightarrow \infty$, Eq. (3) for a certain value of Z . Incorrect values of Z lead to solutions that either show a minimum at some positive value of $z(\rho)$ for a certain value of ρ , and blow up from that ρ on, or intersect the $z=0$ line to apparently sink towards minus infinity. The method is extremely sensitive to small variations in the value of the guess Z . In the test runs, the agreement between the numerical results for the linear differential Eq. (5) and the analytical results in Eqs. (8a) and (8b) was complete for large values of R .

The algorithm has then been applied to the complete, nonlinear basic equation (1). Figure 3 shows the linear and nonlinear results for $z(0)$ as a function of R , for a unit-charged particle in front of liquid He at 1.7 K (material parameters given in Table I). For decreasing distances R , the solutions depart clearly from the linear regime. The strikingly different behavior of the nonlinear results as compared to the linear results is commented on in the following.

We see in Fig. 3 that there is only one distance R for each $z(0)$. An interesting observation is that there is no profile $Z(\rho)$ which is a solution of the type described above for R below a certain critical value R^* . This distance is rather large, $R \simeq 73$ a.u. for a unit charge and liquid He at 1.7 K. More interestingly, for $R > R^*$, two different solutions are found for the liquid profile. The small or low- $z(\rho)$ solution is the one that approaches the linear behavior as R increases, whereas the high- $z(\rho)$ solution shows a completely different behavior: as R increases, the maximum height of the profile increases too.

A numerical energy variation analysis of the branches of the nonlinear curve depicted in Fig. 3 shows that only the low- $z(0)$ branch corresponds to an energy minimum, whereas the high- $z(0)$ corresponds to a saddle point.

If Z^* is the maximum height of the profile $z(0)$ for the

TABLE I. Values, in atomic units, of the material constants (Refs. 20 and 21), the capillary constant a , and the van der Waals coefficient (Refs. 5, 6, and 22).

	He (1.7 K)	Ne (25 K)	Ar (85 K)
Atomic polarizability α	1.37	2.63	10.9
Atomic mass M	7.30×10^3	3.68×10^4	7.28×10^4
Number density n	3.12×10^{-3}	5.34×10^{-3}	3.13×10^{-3}
Surface tension σ	2.25×10^{-7}	3.53×10^{-6}	8.48×10^{-6}
Capillary constant a	1.35×10^7	1.81×10^7	2.62×10^7
van der Waals coefficient ^a Λ	1.7	4.0	47

^aBetween like atoms.

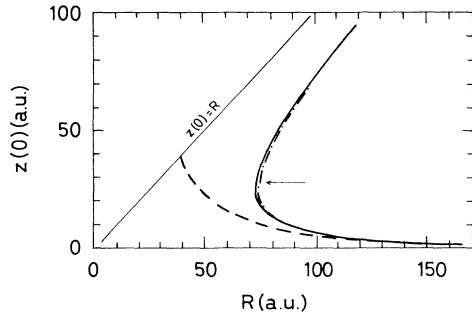


FIG. 3. Comparison of linear (---), nonlinear (—), and scaled-shape approximation (-·-·-) heights of the liquid profile induced by unit point charge in front of liquid He. The arrow indicates the maximum $z(0)$ above which solutions do not correspond to stable-equilibrium situations.

smallest particle-liquid distance for which a solution exists, R^* , we have found the following numerical results (in atomic units) for a unit-charged particle in front of liquid He, Ne, and Ar: He, $R^*=72.9$, $Z^*=24.1$; Ne, $R^*=44.2$, $Z^*=14.6$; Ar, $R^*=44.8$, $Z^*=14.8$. The data in Table I have been used in the calculations. This suggests an interesting liquid-independent relation,

$$R_{\text{charged}}^* \approx 3Z_{\text{charged}}^* \quad (11a)$$

Results (in atomic units) for a single atom in front of its corresponding liquid, obtained using the data in Table I, are the following: He, $R^*=15.85$, $Z^*=3.16$; Ne, $R^*=12.16$, $Z^*=2.47$; Ar, $R^*=15.05$, $Z^*=3.03$. The corresponding liquid-independent result for the neutral particle may be written

$$R_{\text{neutral}}^* \approx 5Z_{\text{neutral}}^* \quad (11b)$$

Sections V and VI deal with simple models that reproduce these liquid-independent results.

Figure 4 shows a comparison between a numerical solution of the nonlinear equation and its linearized counterpart for a distance R outside the range of applicability

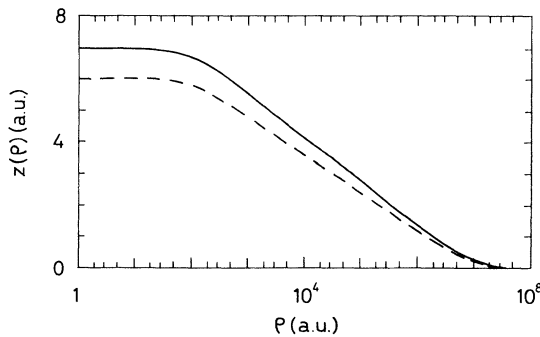


FIG. 4. Comparison between the profiles for a unit charge in front of liquid He, $R=96$ a.u., obtained using the linearized Eq. (4) (---) and the exact Eq. (1) (—).

of the linear approximation. Note that both profiles show a very flat top and have similar shapes.

V. THE SCALED-SHAPE APPROXIMATION

We have found a very simple, liquid-independent model that gives a very good approximation to the numerically computed profiles, including the simple relations (11a) and (11b). Numerically computed profiles show shapes that are almost liquid independent if ρ is measured in $a/\sqrt{2}$ units, and they simple scale vertically for all ρ when we change the height of the particle R . Thus the profiles may be approximately written in terms of a “universal” function as follows:

$$z^{\text{SSA}}(\rho) = z(0)F(\sqrt{2}\rho/a). \quad (12)$$

Here the superscript SSA stands for “scaled-shape approximation.” The function $F(x)$ should satisfy the following boundary conditions:

$$F(0) = 1 \quad (13)$$

and

$$\lim_{x \rightarrow \infty} F(x) = 0 \quad (14)$$

and it is different for each type of interaction (charged or neutral particle).

In addition, we will assume that surfaces are so smooth that $(dz/d\rho)^2 \ll 1$ (this allows us to write a simple expression for the surface-tension energy), and that the particle-liquid interaction may be approximated by the interaction of that particle with a planar surface located at a height $z(0)$ (see the flat top of profiles in Fig. 4). With these approximations, the total potential energy of the system (see Appendix A) may be written as a function of R and $z(0)$ only. For the charged-particle case,

$$E_{\text{charged}} \approx \pi \left[\sigma A_{\text{charged}} z(0)^2 - \frac{n\alpha Q^2}{2[R - z(0)]} \right], \quad (15a)$$

whereas for the neutral-particle case,

$$E_{\text{neutral}} \approx \pi \left[\sigma A_{\text{neutral}} z(0)^2 - \frac{n\Lambda}{6[R - z(0)]^3} \right]. \quad (15b)$$

A_{neutral} and A_{charged} are constants related to the corresponding scaling function F_{neutral} or F_{charged} by

$$A = \int_0^\infty dx \left[F^2(x) + \left(\frac{dF(x)}{dx} \right)^2 \right]. \quad (16)$$

Minimization of the energy expressions (15a) and (15b) with respect to $z(0)$, for a given value of R , yields an expression relating R and $z(0)$ for each case:

$$R_{\text{charged}} = z(0) + \left[\frac{n\alpha Q^2}{4\sigma A_{\text{charged}} z(0)} \right]^{1/2}, \quad (17a)$$

$$R_{\text{neutral}} = z(0) + \left[\frac{n\Lambda}{4\sigma A_{\text{neutral}} z(0)} \right]^{1/4}. \quad (17b)$$

Minimization of R in (17a) and (17b) with respect to $z(0)$ yields the liquid-independent equalities (11a) and (11b). The corresponding values of R^* are

$$R_{\text{charged}}^* = \frac{3}{2} \left[\frac{n\alpha Q^2}{2\sigma A_{\text{charged}}} \right]^{1/3}, \quad (18a)$$

$$R_{\text{neutral}}^* = \frac{5}{4} \left[\frac{n\Lambda}{\sigma A_{\text{neutral}}} \right]^{1/5}. \quad (18b)$$

The parameter A may either be used as an adjustable parameter to fit the numerical results or may be computed for each pair of numerical results $[R, z(0)]$ to check its small range of variation.

VI. THE FLAT-TOP MODEL

There is an even simpler approach to the computation of profile heights, based on two of the above approximations: the flat-top approximation and the small-slope $[(dz/d\rho)^2 \ll 1]$ approximation. Thus one may just substitute $z(0)$ for $z(\rho)$ in the last term of the right side of Eq. (1) [$z(\rho)$ only starts to depart appreciably from $z(0)$ when ρ is large enough for the potential to be very small] and take the linear form of the surface-tension term to write

$$\sigma \left[\frac{d^2z}{d\rho^2} + \frac{1}{\rho} \frac{dz}{d\rho} \right] - n[Mgz(\rho) + v(\rho, R - z(0))] = 0. \quad (19)$$

The solution of this equation is just Eq. (6), with $R - z(0)$ instead of R . The resulting implicit expression has to be solved iteratively. Or, one may use $R - z(0)$ as an independent variable to get the corresponding values of $z(0)$ and R . The agreement of this approximation with the numerical results is remarkable, especially near the minimum distance R^* , where the linear approximation is not applicable. A comparison between the results of this treatment and those of the scaled-shape approximation shows that the “constant” A in Eq. (16) depends logarithmically, i.e., very smoothly, on $R - z(0)$.

VII. POTENTIAL ENERGY OF THE PARTICLE-LIQUID SURFACE SYSTEM

The expressions for the total potential energy of a charged or neutral particle in front of a liquid surface are given by Eqs. (A2)–(A5) in Appendix A. As it has been shown in Sec. V, they may be approximated, using a scaled-shape approximation, by the simple expressions (15a) and (15b). The exact expressions have been numerically integrated during the process of solving the basic differential equation. Results for a charged particle in the long-distance limit reproduce the linearized result of Gras-Martí and Ritchie.¹² The *self-energy* of a charged particle in front of the surface [which excludes the contribution of the unperturbed planar surface, $E_{\text{planar}} = -\pi n\alpha Q^2/(2R)$] may be rewritten in the linear approximation as

$$\Delta E_{\text{charged}} = -\frac{\pi n^2 \alpha^2 Q^4}{16\sigma R^4} \int_0^\infty du \frac{u^3}{u^2 + 2R^2/a^2} K_1^2(u) \quad (20a)$$

[see Eq. (11) in Gras-Martí and Ritchie¹²].

Figure 5 shows a comparison of potential energies, for a unit charge in front of liquid He: the full numerical integration result, as well as the scaled-shape approximation, obtained from Eq. (15a), and the linear result, Eq. (20a), are shown, all plotted relative to the potential energy for the unperturbed plane. As expected, the nonlinear and linear results meet in the long-distance limit. These results may be used to estimate the range of R where the linear approximation is applicable (this approximation was also used by Gras-Martí and Ritchie¹² to compute the energy loss of a charged particle moving parallel to the surface of the liquid).

An expression for the neutral case may be obtained following closely the procedure of Gras-Martí and Ritchie¹² for the van der Waals potential:

$$\Delta E_{\text{neutral}} = -\frac{\pi n^2 \Lambda^2}{64\sigma R^8} \int_0^\infty du \frac{u^5}{u^2 + 2R^2/a^2} K_2^2(u). \quad (20b)$$

It may be added that, if one integrates (in the linear approximation) the corresponding form of the interaction energy, Eq. (A3), using the linear result for the profile, Eqs. (8a) and (8b), one obtains exactly twice the self-energy, Eqs. (20a) and (20b). This is consistent with the fact that the profile depends linearly on the perturbation and that the interaction energy also depends linearly on the profile and the perturbation.

Forces may be computed by differentiation of the total potential energy. The results for a neutral atom in front of a dielectric liquid, for instance, may be used to predict, at least qualitatively,¹⁶ the behavior of a liquid in the atomic-force microscope.^{10,17} In these experiments, the gradient of the force between a tip and a surface is measured by observing the static or dynamic behavior of a microfabricated cantilever that holds the tip.

It should also be noted that, according to a simple simulation of “frozen” liquids where molecular structure is explicitly taken into account, a single external atomic particle moving parallel to the surface hardly experiences any variation of the potential energy due to the effect of individual molecules in the liquid, even at the shortest equilibrium distances computed. In addition, if the molecules of the liquid are allowed to move, canonical averag-

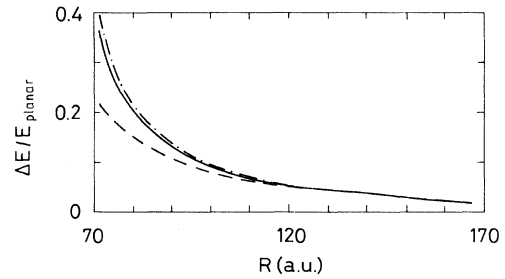


FIG. 5. Contribution of the profile of the liquid to the image potential of a unit point charge in front of liquid He (ΔE) relative to the contribution of the plane ($E_{\text{planar}} = -\pi n\alpha Q^2/2R$): full curve, numerical result; dashed curve, linear result (Ref. 12); dotted-dashed curve, scaled-shape approximation.

ing over the positions of the liquid molecules would lead to a zero balance of lateral forces. These considerations confirm the validity of the continuum approximation used throughout this paper.

VIII. CONCLUSIONS

We have computed classically the static interaction between a charged or a neutral particle and a semi-infinite incompressible, nonpolar, dielectric liquid, when the particle is held fixed above the surface. The results obtained in the long-distance regime for the charged-particle case agree with the previous quantum-mechanical treatment by Gras-Martí and Ritchie,¹² that was applied also to the case of a moving charge.

Some interesting results include (a) the existence of a threshold distance R^* , below which no equilibrium solutions are found; (b) the inadequacy of the linear treatment at near-threshold distances; and (c) the availability of simple models that reproduce the nonlinear results and may be used to estimate them easily for new cases of interest.

These results suggest that, at short particle-liquid distances, where the perturbation of the liquid is stronger, any dynamical treatment should go beyond the first-order or linear approximation.

The results for the case of the neutral particle are closely related to the observed behavior of liquid surfaces in atomic-force microscopy,¹⁰ and in fact, the extension of this treatment to study the interaction of a spherical tip with thin liquid films has already been published.¹⁶ Our results predict a strong effect of nonlinearity in the short-distance interaction of a helium atom with a liquid-helium surface. The possible influence of these nonlinear effects on the problem of scattering of He atoms on liquid-helium surfaces⁵⁻⁸ still has to be assessed.

ACKNOWLEDGMENTS

We thank F. Flores for suggesting part of these calculations. We also thank R. H. Ritchie for helpful comments and M. M. Jakas and M. Vičánek for valuable discussions. This project was partially funded by the Spanish DGICYT (Projects No. PS88-0066 and No. PS89-0065, partial support for M.L.F., and a sabbatical stay for N.R.A.). The collaboration of N.R.A. was also sponsored by the Generalitat Valenciana (Program PROPIO). An Acción Integrada of the MEC and the German DAAD made possible the participation of H.M.U.

APPENDIX A: DERIVATION OF EQ. (1)

The equilibrium equation, Eq. (1), describes the stationary points of the total potential energy of the system (D'Alembert's principle). Some of the stationary points will be minima, and thus will correspond to stable equilibrium. Leiderer, Ebner, and Shikin⁹ have minimized numerically the energy of a system that bears some resemblance to the one considered here (charge-containing dimples in the surface of liquid He under an electric field).

The total potential energy E of the particle-liquid system is a functional of the axisymmetrical surface profile $z(\rho)$. We are looking for solutions $z(\rho)$ satisfying

$$\delta E[z] = 0. \quad (\text{A1})$$

The total energy of the system is the sum of the interaction term, the surface-tension term, and the gravitational energy,

$$E = E_{\text{int}} + E_{\sigma} + E_g. \quad (\text{A2})$$

The attractive interaction between the particle that we place above the liquid surface and the molecules of the liquid can be described as a sum of pairwise interactions of the form $v(r)$, Eqs. (2a) and (2b). The interaction energy takes the form

$$E_{\text{int}} = 2\pi n \int_0^{\infty} d\rho \rho \int_{-\infty}^{z(\rho)} dt v(r), \quad (\text{A3})$$

where r is $[\rho^2 + (R - t)^2]^{1/2}$ and n is the number density of the liquid. The contribution from surface tension σ is

$$E_{\sigma} = 2\pi\sigma \int_0^{\infty} d\rho \rho [(1 + z'^2)^{1/2} - 1], \quad (\text{A4})$$

where the integral is the change of the surface area. The gravitational term (using the unperturbed surface as the origin of potential energies) is

$$E_g = \pi Mng \int_0^{\infty} d\rho \rho z^2(\rho), \quad (\text{A5})$$

where M is the mass of the liquid molecules.

Variation of the total energy¹⁸ with respect to $z(\rho)$ yields the differential equation (1). Our choice of origin for the potential energies (unperturbed surface, particle at infinity) guarantees that the equation satisfies the conditions $z = (dz/d\rho) = (d^2z/d\rho^2) = 0$ for $\rho \rightarrow \infty$. Due to the infinite volume of the system considered, there is no constraint of volume conservation.

APPENDIX B: ALTERNATIVE DERIVATION OF THE LINEAR SURFACE PROFILE, EQ. (6)

In Sec. III, the linearized version of the equilibrium profile is obtained from the linearized differential equation. Another possibility is to perform a direct minimization of the linearized form of the total potential energy in reciprocal space. For this purpose, we expand the surface profile in terms of Fourier components,

$$z(\rho) = \Omega^{-1/2} \sum_{\mathbf{k}} Z_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \boldsymbol{\rho}) \quad (\text{B1})$$

where Ω is a normalization area. We take the linear form of the interaction energy,

$$E_{\text{int}}^{\text{lin}} = n \int \int d^2\rho z(\rho) v(\rho, R), \quad (\text{B2})$$

and use Cole's¹⁹ linear expressions for the surface-tension and gravitational potential energy of the liquid limited by $z(\rho)$,

$$E_{\text{liq}}^{\text{lin}} = \frac{1}{2} \sum_{\mathbf{k}} (Mng + \sigma k^2) Z_{\mathbf{k}} Z_{-\mathbf{k}}. \quad (\text{B3})$$

Minimization of $E_{\text{int}}^{\text{lin}} + E_{\text{liq}}^{\text{lin}}$ with respect to $Z_{\mathbf{k}}$ yields

$$Z_k^{\text{eq}} = -2\pi n \Omega^{-1/2} \frac{v(k, R)}{Mng + \sigma k^2}, \quad (\text{B4})$$

where $v(k, R)$ has been defined in Eq. (7). Substituting

(B4) into (B1) and taking the limit $\Omega \rightarrow \infty$, one readily gets the linear profile, Eq. (6). The expressions for the self-energy, Eqs. (20a) and (20b), may be obtained by substituting Eq. (B4) into Eqs. (B2) and (B3) and taking $\Omega \rightarrow \infty$.

*Permanent address: División Colisiones Atómicas, Centro Atómico Bariloche, RA-8400 San Carlos de Bariloche, Argentina.

¹Aerosol Microphysics I: Particle Interactions, edited by W. H. Marlow (Springer-Verlag, New York, 1980).

²Yu. S. Sedunov, *Physics of Drop Formation in the Atmosphere* (Wiley, New York, 1974).

³V. A. Parsegian, *Nature* (London) **221**, 844 (1969).

⁴R. Gabler, *Electrical Interaction in Molecular Biophysics: An Introduction* (Academic, New York, 1978).

⁵P. M. Echenique and J. B. Pendry, *Phys. Rev. Lett.* **37**, 561 (1976).

⁶P. M. Echenique and J. B. Pendry, *J. Phys. C* **9**, 3183 (1976).

⁷D. R. Swanson and D. O. Edwards, *Phys. Rev. B* **37**, 1539 (1988).

⁸F. O. Goodman and N. García, *Phys. Rev. B* **33**, 4560 (1986).

⁹P. Leiderer, W. Ebner, and V. B. Shikin, *Surf. Sci.* **113**, 405 (1982).

¹⁰C. M. Mate, M. R. Lorenz, and V. J. Novotny, *J. Chem. Phys.* **90**, 7550 (1989).

¹¹M. L. Forcada, A. Gras-Martí, N. R. Arista, H. M. Urbassek, and R. García-Molina, in *Interaction of Charged Particles with Solids and Surfaces*, Vol. 271 of *NATO Advanced Study Institute, Series B: Physics*, edited by A. Gras-Martí *et al.*

(Plenum, New York, in press).

¹²A. Gras-Martí and R. H. Ritchie, *Phys. Rev. B* **31**, 2649 (1985).

¹³N. Barberán, R. García-Molina, and A. Gras-Martí, *Phys. Rev. B* **40**, 10 (1989); *Surf. Sci.* (to be published).

¹⁴L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, Oxford, 1987).

¹⁵*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun, (Dover, New York, 1985).

¹⁶M. L. Forcada, M. M. Jakas, and A. Gras-Martí, *J. Chem. Phys.* **95**, 706 (1991).

¹⁷G. Binnig, C. F. Quate, and C. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).

¹⁸R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, MA, 1964), Vol. II, Sec. 9.

¹⁹M. W. Cole, *Phys. Rev. B* **10**, 4239 (1970).

²⁰R. J. Donnelly, in *A Physicist's Desk Reference*, edited by H. L. Anderson (AIP, New York, 1989).

²¹*CRC Handbook of Chemistry and Physics*, 59th ed., edited by R. C. Weast (CRC, Boca Raton, FL, 1982).

²²J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1985).