# Combined Effect of Surface Tension, Gravity and van der Waals Force Induced by a Non-Contact Probe Tip on the Shape of Liquid Surface *

LIU Nan(刘楠)[1,2], BAI Yi-Long(白以龙)[1**], XIA Meng-Fen(夏蒙棼)[1,3], KE Fu-Jiu(柯孚久)[1,4]

[1] *State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080*
[2] *Graduate School of the Chinese Academy of Sciences, Beijing 100049*
[3] *Department of Physics, Peking University, Beijing 100871*
[4] *Department of Applied Physics, Beijing University of Aerospace and Aeronautics, Beijing 100083*

(Received 3 March 2005)

*Aiming at understanding how a liquid film on a substrate affects the atomic force microscopic image in experiments, we present an analytical representation of the shape of liquid surface under van der Waals interaction induced by a non-contact probe tip. The analytical expression shows good consistence with the corresponding numerical results. According to the expression, we find that the vertical scale of the liquid dome is mainly governed by a combination of van der Waals force, surface tension and probe tip radius, and is weekly related to gravity. However, its horizontal extension is determined by the capillary length.*

*PACS: 68.03.Hj, 68.03.Cd*

Since the invention of the first atomic force microscope (AFM), AFM has been widely used in various fields. Its main applications lie in the imaging of sample surface and the measurement of intermolecular interactions such as van der Waals force. However, AFM is often practically operated in ambient air, in which a liquid film is very often presented on the surface of substrate.[1−3] Due to the flowability of liquid, this film will no longer remain to be flat under its interaction with the probe tip. Hence, the measurement of the intermolecular interaction between the probe tip and the substrate can be significantly affected by the deformation of the intermediate liquid film, and then the image of the substrate becomes distorted.[4] When an AFM is used to measure the interaction of a solid particle with deformable liquid interface, i.e. the relationship between the force and the distance from the probe tip to the interface, it is necessary to understand the effects of various factors on the shape of liquid surface.

Almost all the previous investigations on shapes of liquid surface dealt with this problem by numerically solving the governing equation of deformed liquid surface.[5−8] Although there are some fittings of liquid surface shapes and the relationship of height of liquid surface with the distance between the probe tip and the undeformed surface, no analytical expressions have been reported. Without such expressions, one is unable to properly understand what physical factors and how they govern the deformation of liquid surface. Moreover, one cannot know how and when instability occurs, namely how and when stable liquid domes can no longer exist. In this Letter, we report an analytic expression of the shape of liquid surface, which reveals the combined effect of van der Waals force, surface tension, gravity and probe tip radius on the shape of liquid surface. This representation fits very well with the corresponding numerical results. This analytical formulation also enables us to characterize quantitatively the horizontal and vertical scales of liquid surface.

Following some previous investigations,[5,6] we model the probe tip as a sphere, as shown in Fig. 1, hence with no need to use additional approximations to the interactive force.[7,8] In our study, the total potential energy of the system, composed of the liquid surface energy $W_\gamma(y)$, gravitational potential coming from the mass of liquid raised above the undeformed state $W_g(y)$ and the energy related to the interaction between the probe tip and the liquid, $W_{vdW}(y)$, is a functional of the liquid surface shape $y(r)$. The van der Waals interaction considered here is nonretarded and unscreened attractively. Therefore, the potential between two unit volume elements takes the form $U(\xi) = -\dfrac{A}{\pi^2\xi^6}$, where $\xi$ is the distance between the two elements and $A$ is the Hamaker constant measuring the strength of the intermolecular interaction. Although the Hamaker constant is dependent on materials, its value is always in the range $10^{-21}$–$10^{-19}$ J,[9] hence in the following calculations, $A$ is taken to be $10^{-19}$ J.

By minimizing the total energy functional $W(y) = W_\gamma(y) + W_g(y) + W_{vdW}(y)$ with respect to the shape function $y(r)$, we can obtain the following governing equation for the shape of liquid surface $y(r)$:

* Supported by the National Natural Science Foundation of China under Grand No 10432050, and the Knowledge Innovation Project of Chinese Academy of Sciences (KJCX2-SW-L2).

** To whom correspondence should be addressed. Email: baiyl@lnm.imech.ac.cn

$$\gamma \frac{d}{dr}\Big[r\frac{y'}{(1+y'^2)^{1/2}}\Big] + \frac{4AR^3}{3\pi}\frac{r}{[(D-y)^2+r^2-R^2]^3} - \rho g r y = 0, \quad (1)$$

and the boundary conditions

$$y'(0) = 0, \quad (2)$$

$$\lim_{r\to\infty} y(r) = 0, \quad (3)$$

where $\rho$ is the liquid density, $g$ is the gravitational acceleration, $\gamma$ is the surface tension coefficient of the liquid, $R$ is the radius of probe tip, and $D$ is the distance between the centre of the sphere probe tip and the undeformed liquid surface, as shown in Fig. 1. This governing equation is consistent with the one proposed by Forcada for a liquid film on a substrate.[5] The three terms in Eq. (1) can be seen as the balance of the following forces: surface tension (the first term), van der Waals force (the second term) and gravity (the third term), specifically the van der Waals force can raise the liquid surface while the other two counteract the effect of the van der Waals force.

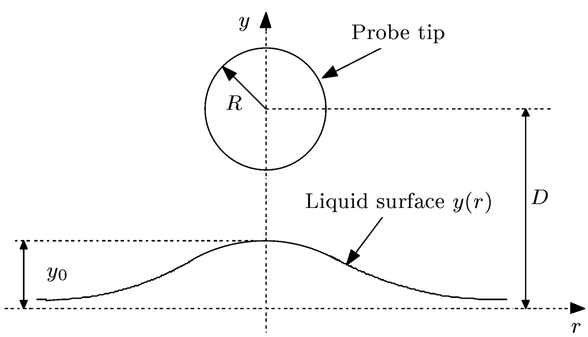


**Fig. 1.** Shape of liquid surface under the van der Waals interaction induced by a spherical probe tip.

For the liquid surface far from the probe tip, roughly speaking $r \gg R$, the van der Waals force can be omitted due to its short effective range. Meanwhile, the slope of liquid surface is far smaller than unit. Invoking these approximations, we can obtain the following simplified governing equation for $r \gg R$:

$$y'' + \frac{1}{r}y' - \frac{\rho g}{\gamma}y = 0. \quad (4)$$

According to the boundary condition of Eq. (3), the shape of liquid surface far from the probe tip reads

$$y(r) = -CK_0\Big(\frac{r}{\lambda}\Big), \quad (5)$$

where $K_0$ is the modified Bessel function of the second class,[10] $C$ is an unknown constant, and $\lambda = \sqrt{\dfrac{\gamma}{\rho g}}$, about 2.7 mm for water, is the capillary length representing the relative strength of surface tension to gravity. From the asymptotic behaviour of Eq. (5),[10] we can find that $\lambda$ characterizes the horizontal scale of the liquid surface.

To determine the vertical scale, we need to know how to describe the liquid surface near the probe tip. In this region, since the liquid surface is quite flat according to Eq. (2), we take $y(r)$ to be $y_0$, i.e. the height of the liquid surface at $r = 0$, as the first-order approximation in the term related to the van der Waals force as expressed in Eq. (1). In addition, from numerical solutions, we know that gravity is not significant and the slope of the liquid surface is also far smaller than unit in the region near the probe. Thus the shape of deformed liquid surface in this region is governed by

$$y'' + \frac{y'}{r} + \frac{4AR^3}{3\pi\gamma}\frac{1}{[(D-y_0)^2+r^2-R^2]^3} = 0. \quad (6)$$

Actually, the relative importance of gravity over surface tension can be estimated by $\rho g y/(\gamma y'/r) \sim \rho g y_0/(\gamma y_0/r^2) \sim \rho g r^2/\gamma \sim r^2/\lambda^2 \ll 1$ in the near-probe-tip region ($r \ll \lambda$).

The integration of Eq. (6) under the axisymmetric boundary condition (2) gives the profile of liquid surface near the probe tip:

$$y(r) = y_0 - \frac{AR^3}{6\pi\gamma} \cdot \frac{\ln\Big[1+\dfrac{r^2}{(D-y_0)^2-R^2}\Big] - \dfrac{1}{1+\dfrac{r^2}{(D-y_0)^2-R^2}} + 1}{[(D-y_0)^2-R^2]^2}. \quad (7)$$

Employing the matching principle proposed by Prandtl and described in Ref. [11] to solutions (7) and (5) in the near and far regions, respectively, i.e. equating the inner limit of Eq. (5) with the outer limit of Eq. (7), and manipulating tedious mathematics, we obtain the maximum height of the liquid surface $y_0 = y\ (r = 0)$:

$$y_0 = \frac{l_A^2 R^3}{3\pi}\frac{\Big[\dfrac{1}{2} + \ln\dfrac{2\lambda}{\sqrt{(D-y_0)^2-R^2}} - E_u\Big]}{[(D-y_0)^2-R^2]^2}, \quad (8)$$

and the whole representation of the shape of liquid surface from the near region to the far region

$$y(r) = -\Bigg\{\ln\frac{\sqrt{(D-y_0)^2-R^2+r^2}}{r} - \frac{1}{2}\frac{1}{\Big[1+\dfrac{r^2}{(D-y_0)^2-R^2}\Big]} - K_0\Big(\frac{r}{\lambda}\Big)\Bigg\} \cdot \Big[\frac{1}{2} + \ln\frac{2\lambda}{\sqrt{(D-y_0)^2-R^2}} - E_u\Big]^{-1} y_0, \quad (9)$$

where $E_u \approx 0.57721$ is Euler's constant. Clearly, the effect of gravity on the height of liquid surface is involved only in a logarithm function as expressed by Eq. (8), hence it is relatively less significant. Noticeably, $l_A = \sqrt{\dfrac{A}{\gamma}}$, about 1.2 nm for water, characterizes the relative strength between the van der Waals force and surface tension. Then, how does the vertical scale of the surface profile depend on the two length scales $l_A$ and $R$? Provided that the gap between the probe tip and the liquid surface, $D - y_0 - R$, is of the order of the maximum height $y_0$ but much less than the probe tip radius $R$, we realize that $y_0$ should be of the order $\sqrt[3]{l_A^2 R}$ according to Eq. (8), namely $\sqrt[3]{l_A^2 R}$ is the vertical scale of the liquid surface. This is several nanometres under the concerned condition.

We obtain the numerical results by the shooting methods, in which the Runge–Kutta–Fehlberg method with an adaptive stepsize control[12] is used to integrate the governing equation. Besides the Hamaker constant, other physical parameters used are $\rho = 1 \times 10^3\,\mathrm{kg/m^3}$, $g = 9.8\,\mathrm{m/s^2}$, $\gamma = 0.0728\,\mathrm{N/m}$ and $R = 0.1\,\mu\mathrm{m}$, and different values of distance $D$ are taken.

The comparisons of the above analytical and numerical results are shown in Figs. 2–4. It is obvious that the asymptotic solutions and the numerical ones are in very close consistency. Only the probe tip is very close to the liquid surface ($D = 1.066R$ in the concerned case), i.e. the liquid surface will jump to the probe tip, the maximum height of the surface $y_0$ given by the asymptotic solution shows a 10% difference compared to the numerical one (see the left part in Fig. 4). However, as shown in Figs. 3(a) and 3(b), the dimensionless shapes of liquid surface, normalized by its corresponding maximum height and obtained numerically and asymptotically, show a good agreement, even though the probe tip is close to the liquid surface ($D = 1.066R$), as shown in Fig. 3(b). This implies that the dimensionless height $y/y_0$ does not depend on the Hamaker constant, similarly to the previous numerical results.[8] However, according to the above analysis, we can see that this can be strictly valid only if the probe tip is far from the surface, i.e. $y_0$ is negligibly small on the right-hand side of Eqs. (8) and (9), which leads to the zeroth approximation,

$$y_0 = \frac{l_A^2 R^3}{3\pi} \frac{\left[\dfrac{1}{2} + \ln\dfrac{2\lambda}{\sqrt{D^2 - R^2}} - E_u\right]}{[D^2 - R^2]^2} \tag{10}$$

and

$$\frac{y(r)}{y_0} = -\left\{ \ln\frac{\sqrt{D^2 - R^2 + r^2}}{r} \right.$$

$$\left. - \frac{1}{2}\frac{1}{\left[1 + \dfrac{r^2}{D^2 - R^2}\right]} - K_0\left(\frac{r}{\lambda}\right) \right\} \cdot \left[\frac{1}{2} + \ln\frac{2\lambda}{\sqrt{D^2 - R^2}} - E_u\right]^{-1}. \tag{11}$$

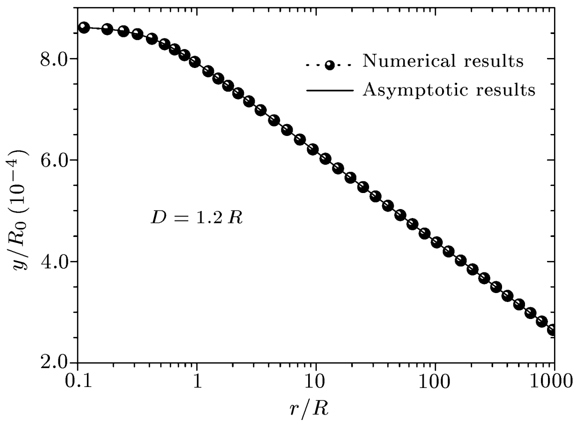


**Fig. 2.** Comparison of the shape of liquid surface between the numerical results and the asymptotic solutions.

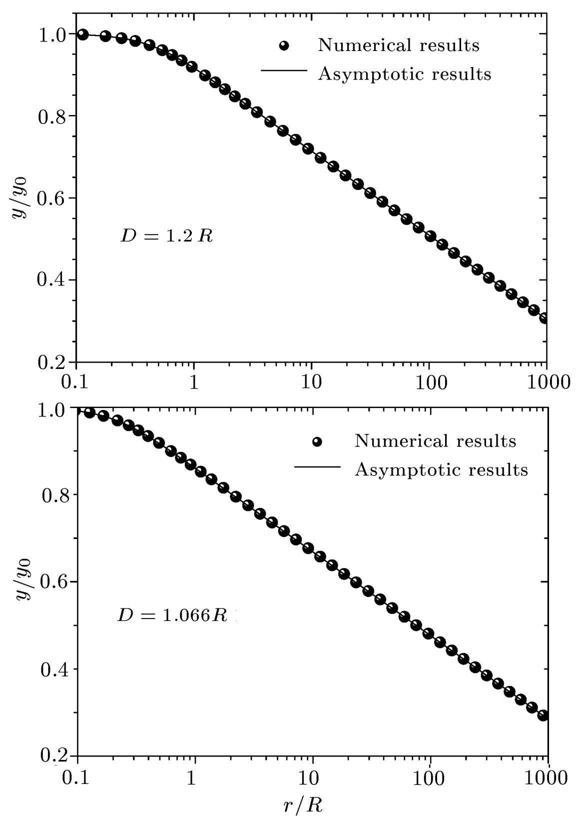


**Fig. 3.** Comparison of dimensionless shape of liquid surface normalized by $y_0$ between the numerical results and the asymptotic solutions.

From Fig. 4, we can also find that the errors of asymptotic solution become larger with the decreasing distance $D$, and the relative error is always less than 10%. It is more important that the growth rate of the maximum height with the decreasing distance becomes larger, and eventually singular. This indicates that the liquid surface approaches to a critical state to instability, i.e. the liquid surface will jump up to the probe tip.

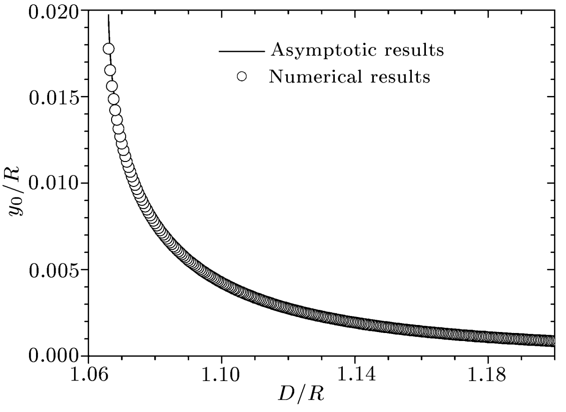


**Fig. 4.** Comparison of dimensionless maximum height $y_0/R$ versus dimensionless distance $D/R$ between the numerical results and the asymptotic solutions.

Finally, since the van der Waals force is omitted in the region far from the probe tip, the above asymptotic analytical results are valid only when the radius of the probe tip is far less than the capillary length. Considering that the radius of the probe tip commonly used in AFMs is often less than 1 $\mu$m while the corresponding capillary length is usually about millimeters, the above analytical results are meaningful in nanotechnology. Moreover, although higher order approximations can be more accurate, simple expressions such as the present ones are not available and then physical implications become unclear.

In summary, van der Waals force can raise the liquid surface while the surface tension and the gravity can counteract the effect of the van der Waals force. By using the perturbation theory, we have obtained two asymptotic analytical expressions, which are in good agreement with the corresponding numerical results and with the previous investigations. Based on the obtained formulae, we have clearly shown that the horizontal scale of the deformation of liquid surface is governed by the surface tension and the gravity via the capillary length $\lambda = \sqrt{\dfrac{\gamma}{\rho g}}$. More importantly, the vertical scale is mainly characterized by a combination of the van der Waals force, the surface tension and the probe tip radius $\sqrt[3]{l_A^2 R} = \sqrt[3]{AR/\gamma}$, while gravity appears in logarithm and then is relatively less important. We have clarified when the normalized shape of liquid surface becomes independent of the Hamaker constant.

## References


[1] Freund J et al 1999 *Microsc. Res. Tech.* **44** 327

[2] Colchero J et al 1998 *Langmuir* **14** 2230

[3] Sui L et al 2005 *Chin. Phys. Lett.* **22** 1010

[4] Cappella B and Dietler G 1999 *Surf. Sci. Rep.* **34** 1

[5] Forcada M L et al 1991 *J. Chem. Phys.* **95** 706

[6] Chan D Y C et al 2001 *J. Colloid Interface Sci.* **236** 141

[7] Cortat F P A and Miklavcic S J 2003*Phys. Rev.* E **68** 052601

[8] Cortat F P A and Miklavcic S J 2004 *Langmuir* **20** 3208

[9] Israelachvili J N 1985 *Intermolecular and Surface Forces* (San Diego: Academic)

[10] Courant and Hilbert 1953 *Methods of Mathematical Physics* (New York: Interscience)

[11] Nayfeh A H 1981 *Introduction to Perturbation Techniques* (New York: Wiley)

[12] Press W H 1992 *Numerical Recipes in Fortran 77: the Art of Scientific Computing* 2nd edn (New York: Cambridge University Press)