Vol 14 No 9, September 2005
1009-1963/2005/14(09)/1774-05

Chinese Physics

© 2005 Chin. Phys. Soc.
and IOP Publishing Ltd

Effect of temperature on the morphology of nanobubbles at mica/water interface*

Zhang Xue-Hua(张雪花)[a)b)†], Li Gang(李 刚)[a)], Wu Zhi-Hua(吴志华)[a)], Zhang Xiao-Dong(张晓东)[a)], and Hu Jun(胡 钧)[a)c)]

[a)] *Nanobiology Laboratory, Bio-X Life Science Research Center, Shanghai Jiaotong University, Shanghai 200030, China*
[b)] *Department of Macromolecular Science and The Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China*
[c)] *Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China*

(Received 3 February 2005; revised manuscript received 16 May 2005)

The great implication of nanobubbles at a solid/water interface has drawn wide attention of the scientific community and industries. However, the fundamental properties of nanobubbles remain unknown as yet. In this paper, the temperature effects on the morphology of nanobubbles at the mica/water interface are explored through the combination of AFM direct image with the temperature control. The results demonstrate that the apparent height of nanobubbles in AFM images is kept almost constant with the increase of temperature, whilst the lateral size of nanobubbles changes significantly. As the temperature increases from 28°C to 42°C, the lateral size of nanobubbles increases, reaching a maximum at about 37°C, and then decreases at a higher temperature. The possible explanation for the size change of nanobubbles with temperature is suggested.

Keywords: nanobubbles, temperature, morphology, AFM
PACC: 0779, 6810G

1. Introduction

The interface between solid and aqueous solution has aroused wide interest because it is ubiquitous in biological, chemical and colloidal systems.[1] Recently the existence of a gas layer on the nanometre scale between some kinds of solid surface and water has been put forward and supported by various results from neutron reflection (NR), surface force apparatus (SFA), ellipsometry and atomic force microscopy (AFM).[2−12] Especially, the studies by use of AFM have provided both the topographical characteristics and the mechanical and mobile properties of these nanobubbles on substrates in a wide range.[5−11] The great implication of the aggregated gas at the interface has been noticed in various fields concerning the surface interaction, hydrodynamics and nanotechnology.[13−20] Meanwhile, such processes as the stability of emulsion without surfactant, the micro boiling behaviours, the mineral floatation, and the rupture of wetting film, have been explained in relation to the presence of interfacial nanobubbles.[21−25]

At present the formation of nanobubbles has been examined in some experiments. The degassing has proven to play an essential role of dissolving gas in the formation of nanobubbles and the tiny holes in cryofixation silicon substrate.[26,27] This may serve as another strong support to the existence of interfacial nanobubbles. The studies have also reported that the physical and chemical characteristics of the substrate are important for the formation and the number of nanobubbles.[8] Importantly, some methods have been established to intentionally produce a large number of nanobubbles especially when the exchange procedures are employed, which has paved the way for the systematic exploration of nanobubbles.[8,26]

However, many fundamental properties of nanobubbles remain unknown up to now except the stability of nanobubbles.[2,6,8] In this paper we report the temperature effect on the morphology of nanobubbles at mica/water interface. To our knowledge, the

*Project supported by the National Natural Science Foundation of China (Grant Nos 20403010 and 10335070) and the Science and Technology Commission of Shanghai Municipality (Grant Nos 0352nm116 and 0452nm007).
†Corresponding author. E-mail: xuehuazhang28@hotmail.com

temperature effect on the morphology of nanobubbles has not been reported. It can be predicted that such studies would make a contribution to the understanding of nanobubble-related interfacial behaviours, particularly related to the influence of dissolving gas.[28] The results in this paper demonstrate that the water temperature could influence the size of nanobubbles significantly. Surprisingly, the lateral size reaches a maximum at about 37°C and decreases at a higher temperature.

2. Experiments

The MultiMode Nanoscope IIIa AFM (Digital Instruments Veeco Metrology Group, NY USA) and a liquid cell with an o-ring were used. Before each experiment the liquid cell and the probe were cleaned thoroughly. A normal NP probe (Digital Instruments Veeco Metrology Group, NY USA) was used and the spring constant of the cantilever was 0.32N/m. The control of the temperature in the liquid cell was realized through the thermal accessory for MultiMode AFM (Digital Instruments Veeco Metrology Group, NY USA). The heating accessory consists of a sample heater and electronic heater controller.[29] A single-probe thermal coupler (Cole-Parmer®Instrument Company, Illinois USA) was used to measure the water temperature in the liquid cell.

The formation of nanobubbles was realized by the exchange of ethanol with water, as introduced in our previous reports.[5,26] The water used was purified with a Mill-Q system (Millipore Corporation, Boston USA). Ethanol and other alcohols were purchased from the Chinese Chemical Reagent Company. The mica was obtained from the S&J Trading Company (NY, USA). The mica was freshly cleaved in air and used as the substrate. After injecting water into the liquid cell to displace the ethanol, we took images of nanobubbles in 5 regions in a tapping mode. Then the AFM tip was withdrawn and the setting temperature on the heater controller was raised to heat the water in the liquid cell. After the temperature reached equilibrium, the tip was approached and nanobubbles were imaged again. Such processes to increase temperature were conducted until the water in the liquid cell increased up to 42°C.

The averaged relative values of the morphologic parameters at different temperatures were compared, for it is hard, experimentally, to obtain in situ images of nanobubbles after the processes of changing temperature. Here the morphologic parameters included the apparent height and the lateral size of nanobubbles. (The height threshold for the statistic by using off-line software was 2.5–3nm.) Since the initial morphology of nanobubbles sometimes varied in a large range from several nanometres to tens of nanometres, the relative values, which were given out by dividing the morphologic parameters by the lateral size of nanobubbles at the initial temperature, were averaged in order to eliminate the variance from time to time. (The AFM tip may affect the apparent size of nanobubbles.[5,12] But the tip effects may be excluded in our experiments for the same tip was used at different temperatures in an experimental group.)

3. Results and discussion

After the exchange of ethanol with water, nanobubbles could be produced as reported in our previous papers.[26] On mica surface nanobubbles could be observed in a tapping mode, but not in a contact mode under the experimental condition (Appendix A). We found that besides ethanol other alcohols completely miscible with water, e.g. methanol, 1-propanol, 2-propanol and tert-butanol, can also be displaced to form nanobubbles at mica/water interface.

Figure 1 shows the typical images of nanobubbles when the water temperature is increased after the formation of nanobubbles. It can be seen that nanobubbles at 37°C are obviously larger than those at 32°C and 42°C. The changes of the apparent height and lateral size of nanobubbles with temperature are shown in Fig.2. The apparent height of nanobubbles almost remains constant throughout the range of temperature, whilst the lateral size of nanobubbles changes significantly. As the temperature increases from 28°C to 42°C, the lateral size of nanobubbles increases before reaching a maximum at about 37°C and decreases at a higher temperature. The lateral size of nanobubbles at about 37°C is 2.5 times larger than that at 28°C. It shows that the nanobubble size increasing with temperature is mainly due to the enlargement of the lateral size rather than the increase of the height of nanobubbles. (The effects of temperature on the apparent contact angle and the density of nanobubbles are shown in Appendix B).

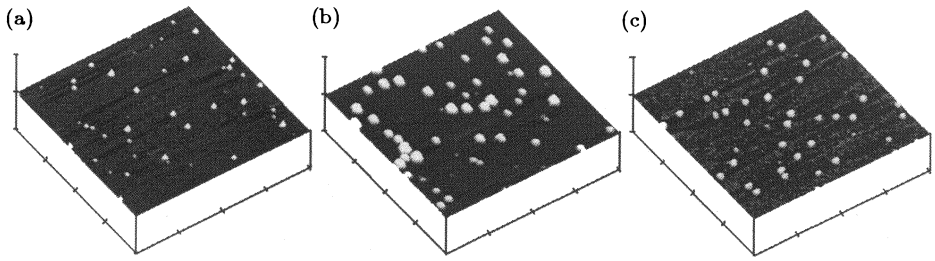


Fig.1. AFM height images of nanobubbles in water at different temperatures. The water temperatures are (a) 32°C, (b) 37°C, and (c) 42°C. The scan size of all images is 2μm by 2μm. The sizes of nanobubbles are different at different temperatures. Nanobubbles at 37°C are obviously the largest of the three images.

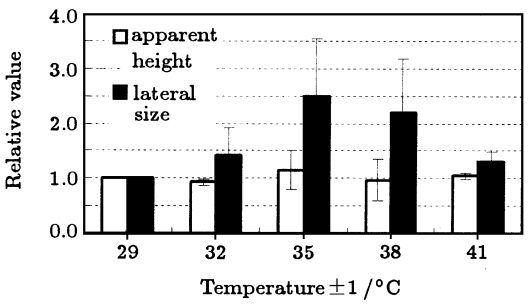


Fig.2. Effect of temperature on the morphology of nanobubbles. The relative values on the vertical axis are calculated by dividing the apparent height by the lateral size of nanobubbles at the initial temperature.

What causes the size of nanobubbles to change with the increase of temperature is quite interesting. At first thought, one may surmise that the evaporation could lead to the expanding of the nanobubbles, thus, to the increase in size. However, the decrease in size after 37°C can help exclude this possibility. Another consideration may be given to the water–vapour surface tension, which changes to some extent with the temperature and possibly causes the variation of nanobubble size in AFM images. However, the difference between the water and vapour surface tensions in a range of the experimental temperatures (28°C–42°C) is too small to have a significant influence.[29] We suppose that the main reason for the change of nanobubble size might be due to the temperature dependence of the gas solubility in water. It is known that the solubility of non-polar gas in water is a nonmonotonic function of temperature, which, passes through a solubility minimum near a temperature of about 310–350K.[30–32] Possibly the size of nanobubbles grew as gas dedissolves from the water with the temperature increasing and coincidentally reaches the maximum at the temperature where the gas solubility is minimum. That is to say, the slight change of gas solubility in water might make a great contribution to the significant increase or decrease in size. It is also interesting to explore the evaporation effect at a higher temperature, and the solubility effects of the gas inside nanobubbles in a gas environment under control. Because of the instrumental limitation, we cannot perform these experiments currently.

Based on our explanation, the dependence of hydrophobic hydration of gas molecules on temperature could cause the change of gas solubility with temperature, resulting in the change of nanobubble size. It has been proposed that the size of nanobubbles would determine the range of hydrophobic force between macroscopically extended surfaces according to present views.[3] Therefore the size of nanobubbles might bridge the hydrophobic effect from molecular level to macroscopic length scale. We expect that our results might help explain the experimental result that the range and magnitude of the hydrophobic interaction would change with temperature.[33]

4. Conclusion

The effects of temperature on the morphology of nanobubbles at mica/water interface have been studied through the combination of AFM direct image with the temperature control. The results show that as the temperature increases from 28°C to 42°C, the apparent height of nanobubbles almost remains constant whilst the lateral size of nanobubbles changes significantly. The lateral size of nanobubbles increases before reaching a maximum at about 37°C and decreases at a higher temperature. Although the temperature effect on the morphology of nanobubbles is carried out only at mica/water interface in this study, we believe that this conclusion may benefit the understanding of other surface behaviours relevant to nanobubbles.

Appendix A The influence of AFM image mode on the observation of nanobubbles

After the formation of nanobubbles, the AFM image mode can influence the observation of nanobubbles at mica/water interface. Under our experimental condition nanobubbles could be observed in a tapping mode, but not in a contact mode, as shown in the supporting Fig.A-1. This is different from the nanobubbles on gold surface, which can be observed in a contact mode.[34] The smooth mica surface image in a contact mode may help eliminate the possibility that the features in a tapping mode image are caused by adsorbed particles.

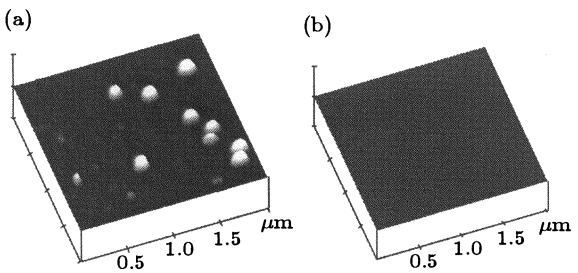


Fig.A-1. AFM height images of nanobubbles at mica/water interface observed in different modes. (a) tapping mode; (b) contact mode.

Appendix B The effects of temperature on the apparent contact angle and the density of nanobubbles

The temperature dependence of the apparent contact angles of the nanobubbles can be determined from the effects of temperature on the apparent height and the lateral size of nanobubbles. The following correlation must hold among the height H, the bubble radius R and the apparent contact angle θ of the bubble:[35,36]

$$H/R = \tan(\theta/2)$$

With the increase of temperature, the height H is constant. From the above equation, the radius R determines that the apparent contact angle θ decreases, and then increases when temperature is higher than 37°C. Here the possible deformation of nanobubbles under the influence of AFM tip is neglected.

The influence of temperature on the density of nanobubbles, i.e. the number per unit area, is shown in the supporting Fig.B-1. The density of nanobubbles increases and then decreases with the increase of temperature which is similar to the variation of nanobubble size with temperature. This might not result from the appearance and disappearance of nanobubbles with temperature, but from the fluctuation of nanobubbles that is larger than the threshold for the statistic by using off-line software.

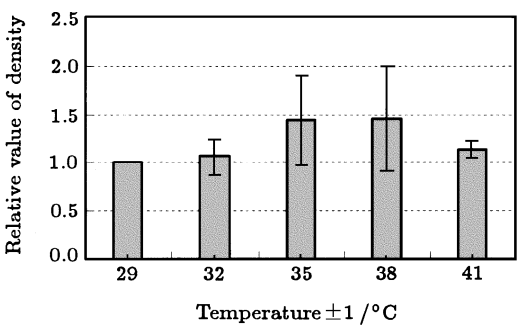


Fig.B-1. The effect of temperature on the density of nanobubbles. The relative values on the vertical axis are given out by dividing the density of nanobubbles by the lateral size of nanobubbles at the initial temperature.

References

[1] Ball P 2003 *Nature* **423** 25

[2] Steitz R, Gutberlet T, Hauss T, Klösgen B, Krastev R, Schemmel S, Simonsen A C and Findenegg G H 2003 *Langmuir* **19** 2409

[3] Tyrrell J W G and Attard P 2001 *Phys. Rev. Lett.* **87** 176104

[4] Castro L B R, Almeida A T and Petri D F S 2004 *Langmuir* **20** 7610

[5] Lou S T, Ouyang Z Q, Zhang Y, Li X J, Hu J, Li M Q and Yang F J 2000 *J. Vac. Sci. Technol.* B **18** 2573

[6] Tyrrell J W G and Attard P 2002 *Langmuir* **18** 160

[7] Ishida N, Inoue T, Miyara M and Higashitani K 2000 *Langmuir* **16** 6377

[8] Yang J W, Duan J M, Fornasiero D and Ralston J 2003 *J. Phys. Chem.* B **107** 6139

[9] Simonsen A C, Hansen P L and Klösgen B 2004 *J. Colliod Interf. Sci.* **273** 291

[10] Otsuka I, Yaoita M, Higano M and Nagashima S 2003 *Surface Rev. Lett.* **10** 337

[11] Holmberg M, Kühle A, Garnæs J, Mørch K A and Boisen A 2003 *Langmuir* **19** 10510

[12] Lou S T, Gao J X, Xiao X D, Li X J, Li G L, Zhang Y, Li M Q, Sun J L and Hu J 2001 *Chin. Phys.* **10** S108

[13] Carambassis A, Jonker L C, Attard P and Rutland M W 1998 *Phys. Rev. Lett.* **80** 5357

[14] Attard P 2003 *Adv. Colloid Interfac.* **104** 75

[15] Zhang X H and Hu J 2004 *Progress in Chemistry* **16** 673

[16] Tretheway D C and Meinhart C D 2004 *Phys. Fluids* **16** 1509

[17] de Gennes P G 2002 *Langmuir* **18** 3413

[18] Granick S, Zhu Y and Lee H 2003 *Nature Materials* **2** 1

[19] Switkes M, Kunz R R, Rothschild M, Sinta R F, Yeung M and Baek S Y 2003 *J. Vac. Sci. Tehcnol.* B **21** 2794

[20] Paxton W F, Kistler K C, Olmeda C C, Sen A, Angelo S K St, Cao Y, Mallouk T E, Lammert P E and Crespi V H 2004 *J. Am. Chem. Soc.* **126** 13424

[21] Pashley R M 2003 *J. Phys. Chem.* B **107** 1714

[22] Maeda N, Rosenberg K J, Israelachvili J N and Pashley R M 2004 *Langmuir* **20** 3129

[23] Thomas O C, Cavicchi R E and Tarlov M J 2003 *Langmuir* **19** 6168

[24] Zbik M and Horn R G 2003 *Colloid. Surfaces* A **222** 323

[25] Stockelhuber K W, Radoev B, Wenger A and Schulze H J 2004 *Langmuir* **20** 164

[26] Zhang X H, Zhang X D, Lou S T, Zhang Z X, Sun J L and Hu J 2004 *Langmuir* **20** 3813

[27] Switkes M and Ruberti J W 2004 *Appl. Phys. Lett.* **84** 4759

[28] Ralston J, Fornasiero D and Mwashchuk N 2001 *Colloids Surf.* A **192** 39

[29] Digital Instruments 1998 *Thermal Accessory for Multi-Mode and Dimension Scanning Probe Microscopes* Support Note 252, Rev. B. (New York: Digital Instruments Veeco Metrology Group) http://www.veeco.com

[30] Dean J A 1973 *Lange's Handbook of Chemistry* (New York: McGraw-Hill) p1725

[31] Pollack G L 1991 *Science* **251** 1323

[32] Garde S, Garc´ia A E, Pratt L R and Hummer G 1999 *Biophys. Chem.* **78** 21

[33] Parker J L, Claesson P M and Attard P 1994 *J. Phys. Chem.* **98** 8468

[34] Holmberg M, Kühle A, Garnæs J, Mørch K A and Boisen A 2003 *Langmuir* **19** 10510

[35] Ishida N, Inoue T, Miyara M and Higashitani K 2000 *Langmuir* **16** 6377

[36] Yang J W, Duan J M, Fornasiero D and Ralston J 2003 *J. Phys. Chem.* B **107** 6139