

Article ID: 1007-2985(2010)02-0055-05

Application of the Theory of Dispersion Forces to the Dewetting of Polymer Films*

WU Li-hua, ZHAO He-ping

(College of Physics Science and Information Engineering, Jishou University, Jishou 416000, Hunan China)

Abstract: The theory of Dzyaloshinskii, Lifshitz, and Pitaevskii (DLP) is applied to investigate the effects of dispersion forces in the dewetting of polymer films in the system of air, polymer, silicon oxide and silicon. The second derivate of the free energy, wavelength and growth rate are calculated. The results show that the coating can modulate the wettability of its substrate and the retarded effects can be significant sometimes. They should be taken into account to deal with the dewetting instability of the polymer films.

Key words: dispersion forces; dewetting; retarded effects; wavelength; growth rate

CLC number: O469

Document code: A

1 Introduction

Dewetting is a phenomenon in which thin liquid films on solid substrates break up into liquid droplets. Because of the widespread usage of organic films, much effort has been put into understanding dewetting phenomenon both experimentally and theoretically in recent years^[1-11]. Owing to the immense complexity of the involved mechanisms, there is yet no general agreement reached concerning the underlying physics of dewetting and structure formation at interface. On a theoretical basis, two mechanisms are possible, according to whether the film is unstable or metastable^[7]. With unstable films, rupturing occurs spontaneously via a spinodal mechanism. In metastable films, rupturing starts from nucleation of domain bubble, a process called heterogeneous nucleation. The distinction is thermodynamics in character, determined by the free energy per unit area of the film $F(L)$. The shape of $F(L)$, as a function of film thickness, L , contains crucial information about the stability of a thin film. The first and second derivatives of the potential yield the disjoining pressure and the spinodal parameter, with the latter containing information on the stability and initial evolution kinetics of a flat film. If $F''(L)$ is negative, the film is unstable; otherwise, the film is either stable or metastable. From the shape of the potential of an unstable film one can infer the upper and lower stable thickness by means of Maxwell constructions and also semi-quantitatively estimate the shape of a stable droplet. For apolar polymer films on a substrate, the most widely adopted form assumes the nonretarded Lifshitz-van der Waals (LW) interactions and it has almost exclusively been treated as nonretarded, meaning that they work instantaneously through the media separating the interaction surfaces, namely, $F(L) = -A/12\pi L^2$, where A is the Hamaker constants. However, this

* Received date: 2009-11-20

Foundation item: Supported by the NSF of Hunan Province (09JJ6011); Scientific Research Foundation of Hunan Provincial Education Department (08A055)

Biography: WU Li-hua (1974-), female, was born in Jishou city, lecturer of Jishou University; the major research area is condensed matter physics.

form of $F(L)$ is valid only for a very small film thickness less than 5 nm. Otherwise, retardation effects have to be considered^[12-15].

2 Theory

In this paper, we study a model system of air, polymer, silicon oxide, and silicon (hereafter referred to as the Air/PS/SiO/Si system), which turn out to account for the effects of dispersion forces in polymer dewetting. The second derivatives of the free energy, wavelength and growth rate are calculated to investigate the effects of the coating on the substrate and the retarded effects. Our studies focus on the calculation of the excess Helmholtz free energy of the polymer film of thickness L at the interface between two other media. Because of the inherent many-body nature of such interactions in condensed matter, the dispersion forces effects are most conveniently treated by considering all phase as isotropic continuous media characterized by frequency-dependent dielectric functions. This is the approach taken by Dzyaloshinskii, Lifshitz, and Pitaevskii (DLP) that includes the temperature and retardation effects^[16]. The main result is an expression for the excess free energy per unit area of a film of a given medium between two other media. The general scheme for calculating the LW free energy F in layered geometry is^[17-18]

$$F = k_B T \sum_{n=0}^{\infty} \int_0^{\infty} \ln W(\vec{q}, \omega = i\xi_n) \frac{dq_x dq_y}{(2\pi)^2}, \quad (1)$$

The function $W(\vec{q}, \omega)$ determines the dispersion relations of the electromagnetic normal modes that satisfy the corresponding boundary conditions and field equations. q_x and q_y are the components of the wave vector which are parallel to the surfaces. The prime on the sum indicates that the $n=0$ term is halved. $\xi_n = (2\pi k_B T / \hbar) n$, k_B , \hbar and T have their usual meaning. By assigning the energy of a harmonic oscillator to each allowed electromagnetic mode and solving Maxwell's equations with boundary conditions, we can get the excess free energy per unit area of the polystyrene film of thickness L in the layered geometry,

$$F(L) = \frac{k_B T}{8\pi L^2} \sum_{n=0}^{\infty} \int_{r_n}^{\infty} x \ln [g(R) g(\vec{R})] dx, \quad (2)$$

where: $g(R) = 1 - \left(\frac{R(x_i, x_w)R(x_h, x_w) + R(x_i, x_w)R(x_x, x_h)R(x_x, x_h)e^{-2x_h d/L}}{1 - R(x_v, x_h)R(x_w, x_h)e^{-2x_h d/L}} \right) e^{-x}$; $R(x_j, x_k) = \frac{x_j - x_k}{x_j + x_k}$;

$\vec{R}(x_j, x_k) = \frac{x_j \mathcal{E}_k - x_k \mathcal{E}_j}{x_k \mathcal{E}_k + x_j \mathcal{E}_j}$; $x_w = x$; $x_h = [x^2 + r_n^2 (\mathcal{E}_v / \mathcal{E}_w)]^{1/2}$ ($k = v, h, i$), and the material (v, h, w, i) (corresponding to silicon, silicon oxide, polystyrene and air) dielectric functions are evaluated at the sequence of imaginary frequencies $i\xi_n$. The lower limit of integration is $r_n = 2L(\mathcal{E}_v)^{1/2} \xi_n / c$. If the silicon is clean, i. e., the layer of silicon oxide is cancelled, equation (2) reduces to the following form,

$$F(L) = \frac{k_B T}{8\pi L^2} \sum_{n=0}^{\infty} \int_{r_n}^{\infty} x \left[\ln \left(1 - \frac{(x - x_i)(x - x_v)}{(x + x_i)(x + x_v)} e^{-x} \right) + \ln \left(1 - \frac{(\mathcal{E}_v x - \mathcal{E}_w x_v)(\mathcal{E}_x - \mathcal{E}_w x_i)}{(\mathcal{E}_x + \mathcal{E}_w x_v)(\mathcal{E}_x + \mathcal{E}_w x_i)} e^{-x} \right) \right] dx. \quad (3)$$

If the retardation effect is not included, an approximation to equation (3) can be written as

$$F(L) = \frac{k_B T}{8\pi L^2} \sum_{n=0}^{\infty} \int_0^{\infty} x \left[\ln \left(1 - \frac{(\mathcal{E}_v - \mathcal{E}_w)(\mathcal{E}_v - \mathcal{E}_w x)}{(\mathcal{E}_v + \mathcal{E}_w)(\mathcal{E}_v + \mathcal{E}_w x)} e^{-x} \right) \right] dx. \quad (4)$$

The dielectric functions required in the integral, $\mathcal{E}(i\xi)$, is the analytic continuation of the material dielectric function $\mathcal{E}(\omega)$ to imaginary frequencies. They can be easily generated from the fitting of the dielectric response of the material to a damped oscillator model of the form

$$\mathcal{E}(\omega) = 1 + \sum_j \frac{f_j}{e_j^2 - i\hbar\omega g_j - (\hbar\omega)^2}, \quad (5)$$

where e_j , f_j and g_j are fitting parameters.

In principle, DLP theory is applicable to any bodies at any temperature, independent of their molecular nature. Since the theory follows from the exact equations of the electromagnetic field, it automatically

takes account of retardation effects. Equation (2) assumes implicitly that the medium is isotropic. The LW result for materials with anisotropic polarizability functions had been worked out^[19]. We neglect anisotropy of the materials polarizability in this work for it seems to be small in our model system.

3 Results and Discussions

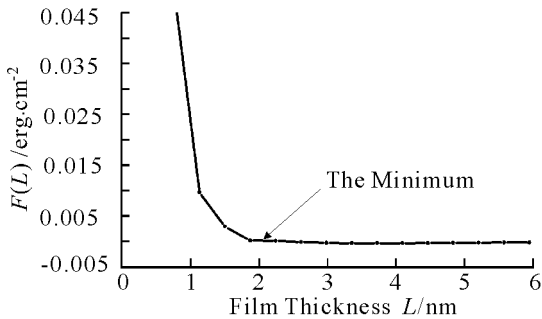


Fig. 1 The Free Energy per Unit Area as a Function of Film Thickness in Air/ Water/ Ice System

of film thickness L is shown in figure 1. We readily find that our results agree well with that of Michael Elbaum and M. Schick, which a minimum was obtained in the surface free energy corresponding to a rather thick film of water, $3.6 \text{ nm}^{[14]}$.

The effective interface potential of the system $F(L)$, or more precisely $F''(L)$, the second derivative of $F(L)$ with respect to the film thickness L , is related to the spontaneous rupture. It is readily shown that the spinodal instability can take place only if $F''(L)$ is negative. Whenever this is the case, the system is unstable. We show the free energy per unit area of polystyrene $F(L)$ and $F''(L)$ on different types of Si wafers in Figure 2 and Figure 3, respectively. It is found PS films on top of pure, clean Si substrate are stable, but they are unstable on infinitely thick oxide layers. When the thickness of silicon oxide are 2 nm, 5 nm, the sign of $F''(L)$ will change as the film thickness increases as large as 6 nm, 15 nm, respectively; whereas it is still negative when the film thickness becomes 100 nm when the silicon oxide thickness is 106 nm. These results show the stability of the PS films can be modulated by the variation of the oxide. From the Figure 2, we can see that excess free energy of air/PS/SiO system is almost the same as the air/PS/SiO/Si in which silicon oxide thickness is 106 nm. It can be inferred that the Si substrate has little influence on the total interaction in this case.

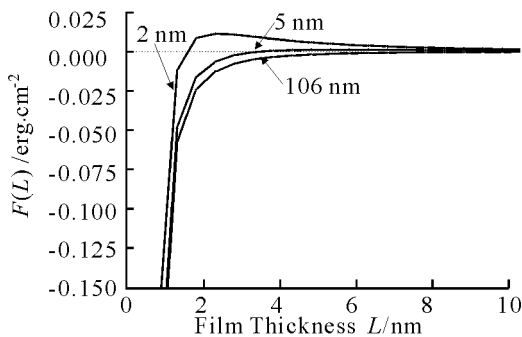


Fig. 2 The Free Energy per Unit Area of Polystyrene on Different Types of Si Wafers in Air/ PS/ SiO/ Si System

The dielectric functions come from several different sources. For ice, water and polystyrene, we have used the fits to the dielectric data determined by Parsegian and Weiss^[20]. Data for silicon based on a single band model was obtained from Sabisky and Anderson^[21] and the dielectric function for silicon oxide was taken from Hough and White that were based on a double band model^[18]. In order to check that our numerical procedure gave correct results, we calculated the free energy of air-water-ice system. The free energy per unit area as a function

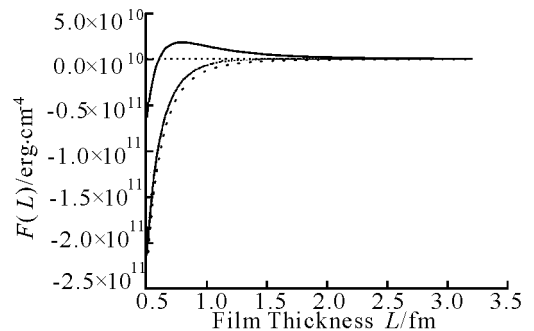


Fig. 3 The Second Derivative of the Free Energy Per Unit Area of Polystyrene on Different types of Si Wafers in Air/ PS/ SiO/ Si System

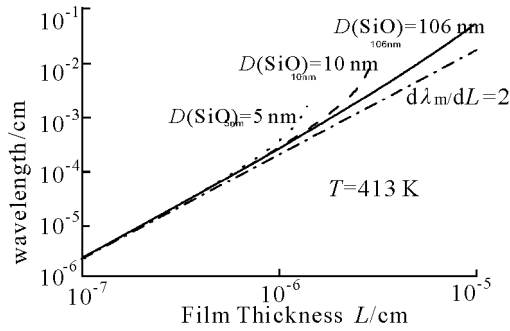


Fig. 4 The Wavelengths for Three Kinds of Si Wafers in Air/ PS/ SiO/ Si System

The long range LW interactions in our air/PS/SiO/Si system is made up of three interactions and can be readily obtained by pair wise summation in the microscopic approach of London and Hamaker^[15-16],

$$F(L) = \frac{A_{\text{SiO}}}{12\pi L^2} + \frac{A_{\text{SiO}} - A_{\text{Si}}}{12\pi(L + D)^2}, \quad (5)$$

where A_{SiO} and A_{Si} indicate the Hamaker constants of air/PS/SiO and air/PS/Si system respectively and D is the thickness of silicon oxide.

In order to check the retardation effects, a comparison is made for the values of the growth rates calculated by using the full (2) and approximate free energy form (5) in Figure 5. It is found that the full results deviate the non-retarded results at a smaller film thickness when the silicon oxide is small. Our study shows that the contribution of the layer of silicon oxide to the total interaction free energy must be important when its thickness is not large enough to screen the substrate and the retarded effect may be important in the instability of polystyrene films sometimes

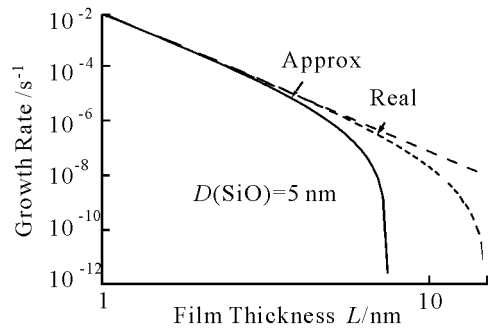


Fig. 5 The Values of the Growth Rates Calculated by Using the Full and the Approximate form of Free Energy in Air/ PS/ SiO/ Si System

4 Conclusions

In this work, we have applied the DPL theory to investigate the instability of PS films within the framework of the frequency-dependent theory of dispersion forces. It is found that the stability of the film can be tuned by the properties and the variation of the thickness of the coating. As the film thickness increases, we find that the retarded effects can be significant and the full results of free energy must be used to deal with the instability of the PS films. The film instability can only be induced by the defect or thermal nucleation if there is no coating on the substrate. As the coating thickness increases, the film becomes unstable. When the coating is as large as about, the film will become unstable, regardless of the substrate.

References:

- [1] REITER G. Unstable Thin Polymer Film: Rupture and Dewetting Processes [J]. Langmuir, 1993, 17: 5 560-5 567.
- [2] MITHIN V S. Dewetting of Solid Surface: Analogy with Spinodal Decomposition [J]. J. Colloid Interface Sci., 1993, 156: 491-498.
- [3] STANGE T G, EVANS D F, HENDRICKSON W A. Nucleation and Growth of Defects Leading to Dewetting of Thin

- Polymer Films [J]. Langmuir, 1997, 13: 4 459-4 464.
- [4] XIE R, KARIM A, DOUGLAS J F, et al. Spinodal Dewetting of Thin Polymer Films [J]. Phys. Rev. Lett., 1998, 81: 1 251-1 255.
- [5] REITER G, SHARMA A, CASOLI A, et al. Thin Film Instability Induced by Long-Range Forces [J]. Langmuir, 1999, 15: 2 551-2 558.
- [6] REITER G, KHANNA R, SHARMA A. Real-Time Determination of the Slippage Length in Auto-phobic Polymer Dewetting [J]. Phys. Rev. Lett., 2000, 85: 1 432-1 439.
- [7] SEEMANN R, HERMINGHAUS S, JACOBS K. Dewetting Patterns and Molecular Forces: A Reconciliation [J]. Phys. Rev. Lett., 2001, 86: 5 534-5 542.
- [8] DU B, XIE F, WANG Y J, et al. Dewetting of Polymer Films with Built-In Topographical Defects [J]. Langmuir, 2002, 18: 8 510-8 517.
- [9] TSUIA O K C, WANG Y J, ZHAO H, et al. Some Views About the Controversial Dewetting Morphology of Polystyrene Films [J]. Eur. Phys. J. E, 2003, 12: 417-422.
- [10] FETZER R, MUNCH A, WAGNER B, et al. Quantifying Hydrodynamic Slip: A Comprehensive Analysis of Dewetting Profiles [J]. Langmuir, 2007, 23: 10 559-10 566.
- [11] MARKUS RAUSCHER, RALF BLOSSEY, ANDREAS MUNCH, et al. Spinodal Dewetting of Thin Films with Large Interfacial Slip: Implications from the Dispersion Relation [J]. Langmuir, 2008, 24: 4 676-4 684.
- [12] P G. de Gennes. Toughness of Glassy Polymers: a Tentative Scheme [J]. Rev. Mod. Phys., 1991, 57: 519-523.
- [13] ELBAUM M, SCHICK M. Application of Theory of Dispersion to the Surface Melting of Ice [J]. Phys. Rev. Lett., 1991, 57: 1 713-1 717.
- [14] WILEN L A, WETTLAUFER J S, ELBAUM M, et al. Dispersion-Force Effects in Interfacial Premelting of Ice [J]. Phys. Rev. B, 1995, 52: 12 426-12 432.
- [15] ISRAELACHVILI J H. Intermolecular and Surface Forces [M]. New York: Academic Press, 1985.
- [16] DZYALOSHINSKII E, LIFSHITZ E M, PITAEVSKII L P. General Theory of Vander Waals' Forces [J]. Adv. Phys., 1961, 10: 165-188.
- [17] BAR-ZIV B R, SAFRAN S A. Surface Melting of Ice Induced by Hydrocarbon Films [J]. Langmuir, 1993, 9: 2 786-2 790.
- [18] HOUGH D B, WHITE L R. The Calculation of Hamaker Constants from Lifshitz Theory with Application to Wetting Phenomena [J]. Advances in Colloid and Interface Science, 1980, 14: 3-41.
- [19] DAL-CORSO A, TOSATTI E. Face-Dependent Hamaker Constants Surface Melting of Noncubic Crystals [J]. Phys. Rev. B, 1993, 47: 9 742-9 746.
- [20] PARSEGHIAN V A, WEISS G H. Spectroscopic Parameters for Computation of Van Der Waals Forces [J]. J. Colloid & Interface Sci., 1981, 81: 285-289.
- [21] SABISKY E S, ANDERSON C H. Verification of the Lifshitz Theory of the Van Der Waals Potential Using Liquid-Helium Films [J]. Phys. Rev. A, 1973, 7: 790-795.
- [22] VRIJ A, OVERBEEK J TH G. Rupture of Thin Liquid Films Due to Spontaneous Fluctuations in Thickness [J]. J. Am. Chem. Soc., 1968, 90: 3 074-3 077.
- [23] CAHN J W. Phase Separation by Spinodal Decomposition in Isotropic Systems [J]. J. Chem. Phys., 1965, 42: 93-99.
- [24] SHARMA A, KHANNA R. Instability of Thin Polymer Films on Coated Substrates: Rupture, Dewetting, and Drop Formation [J]. Macromolecules, 1996, 29: 93-99.
- [25] WENSINK K D F, JEROME B. Dewetting Induced by Density Fluctuations [J]. Langmuir, 2002, 18: 413-418.

应用色散力原理研究高分子薄膜的去湿润现象

吴利华, 赵鹤平

(吉首大学物理科学与信息工程学院, 湖南 吉首 416000)

摘 要: 应用 Dzyaloshinskii, Lifshitz, 和 Pitaevskii (DLP) 理论研究了“空气/高分子薄膜/SiO₂/Si”体系中色散力对薄膜表面去湿润的影响, 计算了自由能的二阶导数、波长和生长率。研究结果表明: 覆盖层可以改变基底的湿润性, 延迟效应在某些情况下起着很重要的作用, 在研究去湿润引起的高分子薄膜不稳定时必须考虑延迟效应。

关键词: 色散力; 去湿润; 延迟效应; 波长; 生长率

中图分类号: O469

文献标志码: A

(责任编辑 陈炳权)