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Effects of dispersion forces in the instability of polymer films*

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Spontaneous rupture of some polymer films upon heating is commonplace. The very criterion for this instability is the system free energy possessing a negative curvature. Within the framework of full frequency-dependent theory of dispersion forces, we have derived the excess free energy of a typical system—polystyrene film deposited on the silicon substrate. The excess free energy, wavelengths and growth rates are calculate and a comparison is made between the accurate results and the approximate results. It is found that the stability of the film can be tuned by the variation of the thickness of the coating and the retardation effects can be significant sometimes.

Keywords: liquid thin film, interfacial instability, excess free energy
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1. Introduction

Interactions at interfaces determine to a large extent our life and the way we experience our environment. Intermolecular forces may dominate physical behaviour at interfaces and properties of thin films.[1] The stability of thin films is essential in many technological applications, such as in coating or in microelectronic devices and has already been investigated extensively, both theoretically[2−9] and experimentally.[10−17] Many articles have been published to deal with the influence of intermolecular interactions.

It has been found that the stability and the morphologies exhibited by thin, unstable, homopolymer films can be rationalized in terms of a thickness dependent effective interface energy, $F(L)$, which quantifies the energy gain or penalties incurred by changing the film thickness L. If the second derivative of $F(L)$ with respect to x, $F^{''}(L)$, is negative, the film is unstable. Otherwise, the film is either stable or metastable.[18,19] From the shape of the potential of an unstable film one can infer the upper and lower limits of stable thickness by means of Maxwell constructions and also semi-quantitatively estimate the shape of a stable droplet.[19] By using the mean field approach and simplifying to linear calculations, Vrij and Overbeek[20], Cahn[21], and Wensink and Jerome[22] have shown that instability would drive the system into exponentially growing surface capillary waves, among which the fastest growing mode had wavelength $\lambda_{\rm m} = (-8\pi^2\gamma/F''(L))^{1/2}$ and growth rate $\Gamma_{\rm m} = L^3(F''(L))^2/(12\mu\gamma)$, where γ and μ are the liquid surface tension and viscosity, respectively. The theory also predicts that the instability should lead to the formation of correlated bicontinuous structure in a two-dimensional (2D) system bearing a characteristic wave vector equal to $2\pi/\lambda_{\rm m}$ in the initial state that will, however, coarsen in later times as the enlarged amplitude of the surface waves renormalizes the free energy of the system,[20] as shown by many experimental and theoretical research results.[5−18]

The by far most widely studied interactions in thin film systems are the long range Lifshitz–van der Waals (LW) interaction and the short-range interactions. In its most simple form, the LW interaction can be written as $F_{\rm LW} = -A/12\pi L^2$, where A is the Hamaker constant which gives the net strength and

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direction of the substrate-film interaction. Because polystyrene (PS) is a weakly electron-donor monopolar material, the short-range repulsive interactions between the molecules of PS are therefore ruled out. For a typical system of the polystyrene supported by an oxidized silicon substrate (hereafter referred to as the Air/PS/SiO_2/Si system), the unretarded LW potential is made up of three different LW interactions and can be readily obtained by pairwise summation in the microscopic approach of London and Hamaker,[11]

$$F(L) = -\frac{A_{\mathrm{Air-PS-SiO_2}}}{12\pi L^2} + \frac{A_{\mathrm{Air-PS-SiO_2}} + A_{\mathrm{Air-PS-Si}}}{12\pi(L+D)^2}, \qquad (1)$$

where D represents the thickness of oxide layer. $A_{\mathrm{Air-PS-SiO_2}}$ and $A_{\mathrm{Air-PS-Si}}$ denote the Hamaker constants.

Whereas, the dispersion contributions to the LW force begins to decay more rapidly due to the retardation effects when the film thickness exceeds 5nm. It is somewhat surprising that the effects of retardation have hardly been given any consideration. For interactions between molecules, this is of little consequence. However, for interactions between macroscopic bodies, where the forces can still be significant at large separations, the retardation effects must be taken into account and the energy in the full form should be used to investigate the dispersion force effects on the instability of the polymer films.[23]

In this work, we first derive the excess free energy of the typical system—polystyrene film deposited on the silicon substrate, which has a variable silicon oxide coating within the framework of full frequency-dependent theory of dispersion forces. Then the excess free energy, wavelengths and growth rates are calculated. A comparison between the accurate results and the approximate results is made to check the strength of retarded effects.

2. Theory

Owing to the inherent many-body nature of the interactions between particles in the solid, the vapour, and the liquid film, their effects can be most conveniently treated by considering all phases as isotropic continuous media characterized by frequency dependent dielectric function. This is the approach taken by Dzyaloshinskii, Lifshitz and Pitaevskii (DLP) that includes the temperature and retardation effects.[24] They first calculated the excess free energy per unit area of a film of a given medium between two other media by utilizing the full frequency-dependent dielectric function. Since their work, the theory has been generalized and applied to diverse systems.[1] 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,

$$F = k_{\mathrm{B}}T {\sum_{n=0}^{\infty}}' \int_0^{\infty} \ln W(\boldsymbol{q}, \omega = \mathrm{i}\xi_n) \frac{\mathrm{d}q_x \mathrm{d}q_y}{(2\pi)^2}, \qquad (2)$$

where $\mathrm{i} = \sqrt{-1}$. The prime on the sum sign, $\sum'$, indicates that the $n = 0$ term is halved. The function $W(\boldsymbol{q}, \omega)$ determines the dispersion relation of the electromagnetic normal modes that satisfy the corresponding boundary conditions and field equation, q_x and q_y are the components of the wave vector parallel to the layer surfaces. k_{B} is the Boltzmann's constant, and $\xi_n = (2\pi k_{\mathrm{B}}T/\hbar)n$ are the frequencies whereat $W(\boldsymbol{q}, \omega)$ is evaluated, T is the temperature and $2\pi\hbar$ is the Planck's constant. 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 LW free energy per unit area of the polystyrene film of thickness in the layered geometry of Air/PS/SiO_x/Si system,

$$F(L) = \frac{k_{\mathrm{B}}T}{8\pi L^2} {\sum_{n=0}^{\infty}}' \int_{r_n}^{\infty} \mathrm{d}x\, x \ln[g(R)g(\bar{R})], \qquad (3)$$

where

$$g(R) = 1 - \left(\frac{R(x_{\mathrm{i}}, x_{\mathrm{w}})R(x_{\mathrm{h}}, x_{\mathrm{w}}) + R(x_{\mathrm{i}}, x_{\mathrm{w}})R(x_x, x_{\mathrm{h}})\mathrm{e}^{-2x_{\mathrm{h}}d/L}}{1 - R(x_{\mathrm{v}}, x_{\mathrm{h}})R(x_{\mathrm{w}}, x_{\mathrm{h}})\mathrm{e}^{-2x_{\mathrm{h}}d/L}} \right) \mathrm{e}^{-x},$$

$$R(x_j, x_k) = (x_j - x_k)/(x_j + x_k),$$

$$\bar{R}(x_j, x_k) = (x_j\varepsilon_k - x_k\varepsilon_j)/(x_j\varepsilon_k + x_k\varepsilon_j),$$

$$x_{\mathrm{w}} = x,$$

$$x_k = [x^2 + r_n^2(\varepsilon_k/\varepsilon_{\mathrm{w}})]^{1/2} \quad (k = \mathrm{v}, \mathrm{h}, \mathrm{i}),$$

and dielectric functions ε of the materials (v, h, w, i) (corresponding to silicon, silicon oxide, polystyrene and air) are evaluated in the sequence of imaginary frequencies $i\xi_n$. The lower limit of integration is $r_n = 2L(\varepsilon_w)^{1/2}\xi_n/c$. If the silicon is clean, i.e. the layer of silicon oxide is removed, Eq.(3) reduces to the following form:

$$F(L) = \frac{k_B T}{8\pi L^2} \sum_{n=0}^{\infty}{}' \int_{r_n}^{\infty} dx x \left[\ln\left(1 - \frac{(x-x_i)(x-x_v)}{(x+x_i)(x+x_v)} e^{-x}\right) + \ln\left(1 - \frac{(\varepsilon_v x - \varepsilon_w x_v)(\varepsilon_i x - \varepsilon_w x_i)}{(\varepsilon_v x + \varepsilon_w x_v)(\varepsilon_i x + \varepsilon_w x_i)} e^{-x}\right)\right]. \quad (4)$$

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

$$F(L) = \frac{k_B T}{8\pi L^2} \sum_{n=0}^{\infty}{}' \int_{0}^{\infty} dx x \left[\ln\left(1 - \frac{(\varepsilon_v - \varepsilon_w)(\varepsilon_i - \varepsilon_w x)}{(\varepsilon_v + \varepsilon_w)(\varepsilon_i + \varepsilon_w)} e^{-x}\right)\right]. \quad (5)$$

In principle, DLP theory is applicable to any medium at any temperature, independent of its molecular nature. Since the theory follows from the exact equations of the electromagnetic field, it automatically takes account of retardation effects. Equation (3) assumes implicitly that the medium is isotropic. We neglect the polarizability anisotropy of the materials in this work for it seems to be small in our model system.

The dielectric functions required in the integral (3), $\varepsilon(i\xi)$, is the analytic extension of the material dielectric function $\varepsilon(\omega)$ to imaginary frequencies. They can be generated from the fitting of the dielectric response of the material to a damped-oscillator model of the form

$$\varepsilon(\omega) = 1 + \sum_j \frac{f_j}{e_j^2 - i\hbar\omega g_j - (\hbar\omega)^2}, \quad (6)$$

where e_j, f_j and g_j are fitting parameters.

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.[25] Data for silicon based on a single band model was obtained from Sabisky and Anderson[26] and the dielectric function for silicon oxide was taken from Hough and White that were based on a double band model.[27] In order to achieve accurate results, we use the five-band model dielectric function for polystyrene and two-band model for fused quartz in our calculations.

3. Numerical results

The integral in Equation (3) was directly calculated numerically. In order to check that our numerical procedure give correct results, we calculated the free energy of the air/water/ice system. The free energy per unit area as a function of film thickness is shown in Fig.1. We readily find that our results agree well with that of Elbaum and Schick,[28] where a minimum was obtained in the surface free energy corresponding to a rather thick film of water of 3.6nm.

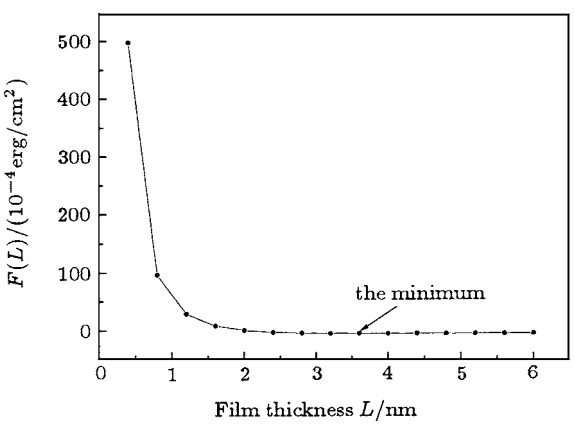


Fig.1. Free energy per unit area as a function of film thickness in air/water/ice system.

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. $F''(L)$ for different types of Si wafers is shown in Fig.2. When the thickness of silicon oxide are 2nm and 5nm, we can see that the sign of $F''(L)$ will change as the film thickness increases to 6nm and 15nm, respectively, whereas it is still negative when the film thickness becomes 100nm when the silicon oxide thickness is 106nm. These results show that the stability of the PS films can be modulated by the variation of the thickness of the oxide. The defects, thermal nucleation and spontaneous rupture all have a role in causing the instability of

the PS films, but the spinodal mechanism dominates when the thickness of films is small.

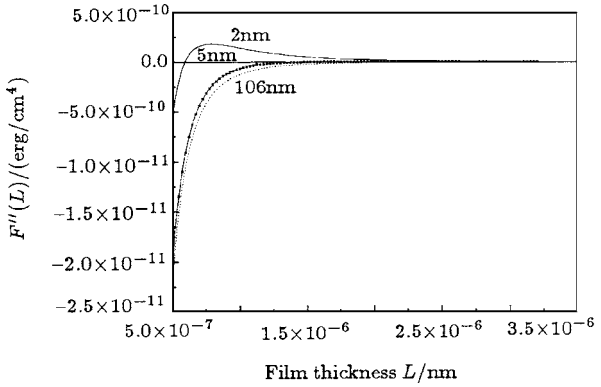


Fig.2. The second derivative of free energy per unit area of polystyrene on different types of Si wafers as a function of PS film thickness L.

In order to check the retardation effect, the values of the wavelengths and the growth rates are calculated by using both the full and approximate free energy form. The calculated results are showed in Figs.3 and 4. We can see that the full results deviate from the unretarded results at a smaller PS film thickness when the silicon oxide is small. These results show that the contributions 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 to the instability of polystyrene films sometimes.

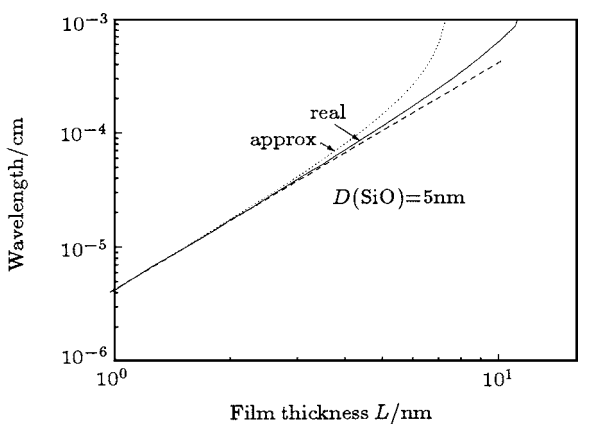


Fig.3. Values of the wavelength calculated by using the full and the approximate form of free energy.

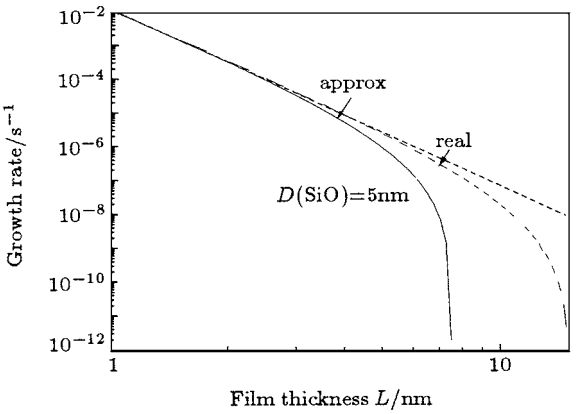


Fig.4. Values of the growth rate calculated by using the full and the approximate form of free energy.

4. Conclusions

We have investigated the retardation effects on the instability of PS films within the framework of the frequency-dependent theory of dispersion forces. The calculated results provide the LW contribution to the surface energy $F(L)$ of Air/PS/SiO_2/Si system with variable thickness of SiO_2. It is found that the stability of the film can be tuned by the properties and the variation of the thickness of the coating. Retardation effects always results in a positive, monotonic decrease in $F(L)$ with L, as $L \to \infty$. As the film thickness increases, the unretarded free energy will deviate from the full results because the retardation effects can be significant and the full free energy must be used to deal with the instability of the PS films.

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