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Surface instability of viscoelastic thin films

S. A. Safran and J. Klein

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel 76100

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Abstract. — The surfaces of thin, liquid films can be unstable due to thinning van der Waals interactions, leading to the formation of holes in the initially uniform film. These instabilities can be greatly retarded in viscoelastic materials (and completely inhibited in elastic materials) even when the finite frequency shear modulus, $E$, is small compared to the infinite frequency modulus, $G$. This occurs when $E/G \gg (a/h_0)^2 \ll 1$ where $a$ is a molecular size and $h_0$ is the film thickness. We relate the growth rate of the instability to the dynamic viscosity, $\eta(\omega)$, with examples for the cases of a polymer brush, an elastic fluid (gel), and a transient polymer network, described by reptation dynamics.

1. Introduction.

While the production of thin films is important in many applications, a crucial consideration is whether the films remain flat and uniform at ambient temperatures in thermal equilibrium. The ultimate stability of such films depends of course on the equilibrium contact angle of the film material. Non-zero contact angles imply that the initially uniform film, formed perhaps by a non-equilibrium process such as spin-coating or molecular beam epitaxy, will eventually break up into disconnected islands. The kinetics of this process usually involves the formation of holes [1] in the otherwise uniform film; the holes grow and an island structure results [2, 3]. How quickly these holes nucleate is directly related to the metastability of the initially uniform film.

In polycrystalline solid films, a natural source of surface instabilities leading to eventual hole formation and dewetting are the intersections between grain boundaries [1, 4] while in liquid films, there exists an intrinsic mechanism for hole formation via the flow induced by a thinning van der Waals interaction. The spontaneous rupture of thin liquid films under this force has already been discussed for the case of simple, viscous liquids [5-7]. Recent experiments have focused on thin films [8] of polymers, where both hole formation and growth have been observed. At long times, the holes arrange themselves into characteristic patterns which may be related to a «spinodal» type of instability of the hole rim [9]. Thus far, the polymeric films have been discussed using a simple hydrodynamic model where the viscosity of the film is a constant. In this paper, we reexamine the spontaneous rupture of initially-uniform, thin liquid films using a linear viscoelastic model for the dynamics. When the interactions with the substrate are such that the equilibrium state is a disconnected set of islands or droplets — i.e., partial wetting — hole formation is a necessary intermediate state; we focus on the dynamics of the initial instability at the surface. For viscoelastic materials with a
single time which characterizes the crossover from elastic to viscoelastic response we show that even a small shear elastic restoring force can greatly retard the surface instability leading to hole formation; in elastic materials, where this crossover time becomes infinitely long the instability can be completely inhibited by the equilibrium shear modulus, even if it is small. We illustrate this with an estimate of the timescale for surface induced thinning of a polymer «brush» [10] (i.e., a monolayer of polymer grafted onto a solid surface). For materials with no equilibrium elastic shear modulus, but with a time dependent response to shear stress, the surface instability is similar to that of the Newtonian fluid, if the viscosity is replaced by the viscosity at the «frequency» scale of the instability; these results in a self-consistent equation for the growth-rate of the process. This equation is examined for a polymeric system where reptation dynamics [11] are assumed and it is shown that the characteristic time scales for hole formation can be large. The theory is motivated by recent experiments [12] which indicated that the addition of long-chain and surfactant-like polymers can inhibit hole formation in polymeric thin films, although the theory does not directly address these experiments in multicomponent systems.


The standard discussion of surface instabilities in thin, liquid films [6, 7] focuses on the effect of the van der Waals energy of a solid, with a normal in the z direction, covered by a thin film of local height \( h(x, y, t) \) where \( t \) is the time. Films that tend to thin are described by a van der Waals free energy per unit area, \( U(h) \) given by \([5, 6]\)

\[
U(h) = -\frac{A}{12\pi h^2}
\]  

(1)

where \( A \) is related to the difference between the Hamaker constants of the liquid and a molecule of the liquid interacting with the solid; \( A > 0 \) for thinning films which show surface instabilities which give rise to holes. This energy can be related to a (negative) disjoining pressure, \( \phi = -\frac{dF}{d\Omega} \) where \( F = \Omega U/h \) is the total free energy and \( \Omega \) is the volume. Noting that \( dF/d\Omega = (\partial F/\partial \Omega)_h + (\partial F/\partial h)(\partial h/\partial \Omega) \) we find:

\[
\phi = \frac{A}{6\pi h^3}.
\]  

(2)

The tendency of the van der Waals interaction to thin the film and thus enhance any surface fluctuations competes with the surface tension, \( \gamma \), which tends to flatten a nearly-flat surface. Large wavevector fluctuations are stable while small wavevector fluctuations, where the surface tension force is negligible, are unstable and holes are nucleated at a characteristic lengthscale determined by this competition.

The dynamics of this process are described by the Navier-Stokes equation and a linear stability analysis of the flat, incompressible film, with initial thickness, \( h_0 \). The linear stability analysis is appropriate for surface disturbances \( |h(x, y, t) - h_0| \ll h_0 \), but a non-linear analysis [7] indicates that the linear approximation gives a reasonable description of the process, at least for small initial perturbations. Since the flat film has zero velocity, the linearized, Navier-Stokes equation can be written:

\[
\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla p - \nabla \phi + \nabla \cdot \mathbf{\tau}
\]  

(3)

where \( \rho \) is the density, \( \mathbf{v} = (u, v, w) \) is the velocity, \( p \) is the pressure, \( \phi \) is the negative disjoining pressure, and \( \mathbf{\tau} \) is the stress tensor. For an incompressible, isotropic, viscoelastic
material, the stress tensor is related \([13, 14]\) to the strain tensor \(\varepsilon\) and to the rate of strain (velocity gradient) tensor \(\dot{\varepsilon}\) \((\text{e.g., } \dot{\varepsilon}_{zz} = \partial w / \partial z)\) where the dot signifies the time derivative, by:

\[
\tau_{ij} = E \varepsilon_{ij} + \eta_\infty \dot{\varepsilon}_{ij} + \sum_n \int_{-\infty}^{t} C_n e^{-\mu_n(t-T)} \dot{\varepsilon}_{ij}(T) \, dT.
\]

Here, \(E\) is the equilibrium shear modulus, \(\eta_\infty\) is the high frequency viscosity, corresponding to typical molecular motions, and \(\mu_n\) are the rates associated with the discrete spectrum of relaxation times. For Newtonian fluids, \(E = C_n = 0\) and the term \(\nabla \cdot \tau\) becomes \(\nabla^2 V\).

For non-Newtonian fluids, a simple relation exists for the Laplace transforms \([15]\) of the stress and the velocity gradient tensor:

\[
\tau_{ij}(\omega) = \eta(\omega) \dot{\varepsilon}_{ij}(\omega)
\]

where

\[
\eta(\omega) = \frac{E}{\omega} + \eta_\infty + \sum_n \frac{C_n}{\mu_n + \omega}
\]

In these equations, the Laplace variable \(\omega\) can be complex, in general. Equation (3) can be Laplace transformed to read:

\[
\rho \omega V(\omega) = -\nabla \Pi(\omega) + \eta(\omega) \nabla^2 V(\omega)
\]

where \(\Pi = p + \phi\). Similarly, the incompressibility condition can be written:

\[
w_z(\omega) = -(u_x(\omega) + v_y(\omega))
\]

where the subscripts signify derivatives. The Laplace transforms of the normal and tangential stress boundary conditions at the liquid surface characterized by a surface tension \(\gamma\), can be respectively written as:

\[
-p(\omega) + 2 \eta(\omega)(w_z)_n = \gamma \nabla^2 h(x, y; \omega)
\]

\[
u_x(\omega) + w_y(\omega) = v_x(\omega) + w_y(\omega) = 0.
\]

The stability analysis is performed by solving these equations in the lubrication approximation (for a rigorous treatment see Ref. [7]) where it is assumed that the length scale for fluctuations in the velocities, pressures and film height in the \(x\) and \(y\) directions is much larger than the film thickness, \(h_0\); the wavevector \(q\) associated with the instability is small compared with \(1/h_0\). We also assume that the deviations from a flat film, \(H(x, y; \omega) = [h(x, y; \omega) - h_0]\) are small. The growth rate of the instability is shown to be related to the value of \(\omega\) that satisfies these equations and the results derived below indicate that
\( \omega \) scales as \( q^4 \) so that to a first approximation, terms in \( \omega \) in equation (7) can be neglected. Consistent with this approximation is the neglect of spatial gradients of the velocity in the \( x \) and \( y \) directions in this equation and one finds:

\[
\eta(\omega) u_{zz}(\omega) = \Pi_x(\omega) \tag{11}
\]

\[
\eta(\omega) v_{zz}(\omega) = \Pi_y(\omega). \tag{12}
\]

Solving for \( u \) and \( v \) with the boundary conditions of no slip at \( z = 0 \) and equation (10) with the \( x \) and \( y \) derivatives again neglected (i.e., \( u_z(\omega) = 0 \) and \( v_z(\omega) = 0 \) at \( z = h_0 \), where we use [16] a linearization about \( h_0 \), we find:

\[
u(\omega) = \frac{1}{2 \eta(\omega)} \Pi_x(\omega)(z^2 - 2zh_0) \tag{13a}
\]

\[
v(\omega) = \frac{1}{2 \eta(\omega)} \Pi_y(\omega)(z^2 - 2zh_0). \tag{13b}
\]

To this order, the tangential stress boundary condition implies

\[-p = \gamma V^2h. \tag{14}\]

Thus, \( p \) and by equation (2) \( \Pi \) are independent [17] of \( z \). Finally, the incompressibility relation, equation (8) and the no-slip boundary condition determine \( w \) as

\[
w(\omega) = \frac{1}{2 \eta(\omega)} (\Pi_{xx} + \Pi_{yy}) \left( z^2 h_0 - \frac{z^3}{3} \right) \tag{15}\]

where we have again [16] linearized about \( h_0 \), and used \( \Pi = \phi(h) - \gamma V^2h \) where all the variables are the Laplace transforms (i.e., \( \Pi(\omega) \)).

The equation of motion for the surface is given from the kinematic boundary condition which relates the \( z \) component of the velocity at the surface \( z = h(x, y; t) \), \( V_z \), to the total time derivative of \( h \):

\[
\frac{\partial h}{\partial t} + (V_x \cdot \nabla) h = V_z \cdot \dot{z}. \tag{16}\]

Keeping terms linear in \( h(x, y; t) \) and Laplace transforming this equation yields

\[
\omega h(x, y; \omega) = w_z(\omega) \tag{17}\]

where the subscripted \( w_z(\omega) \) is the \( z \) direction velocity \( w(\omega) \) evaluated at \( z = h_0 \). Linearizing the expression for \( \phi \) in equation (2) about \( h_0 \) and using equation (15) we thus find:

\[
\omega H(x, y; \omega) = -\frac{h_0^3}{3 \eta(\omega)} \left[ \gamma \nabla^2 (\nabla^2 H(x, y; \omega)) + \frac{A}{2 \pi h_0^4} \nabla^2 H(x, y; \omega) \right]. \tag{18}\]

Consider a single Fourier mode of a fluctuation in the height with wavevector \( q \) with \( H(x, y; \omega) = H_q(\omega) \exp(iq \cdot r) \); we find an equation for the allowed value of \( \omega \):

\[
\omega = -\frac{\gamma h_0^3}{3 \eta(\omega)} q^2 [q^2 - q_c^2] \tag{19}\]

where

\[
q_c^2 = \frac{A}{2 \pi h_0^4 \gamma} \tag{20}\]
This result has the same form as the growth rate derived [6, 7] for hole formation in non-viscoelastic fluids, with the proviso that the viscosity $\eta$, which is constant in those systems, is replaced by the Laplace transform, $\eta(\omega)$ (Eq. (6)), evaluated self-consistently at the frequency, $\omega$, of the instability. The present derivation shows that this substitution is consistent with the lubrication approximation and indicates how corrections may be included. Positive values of $\omega$ indicate [15] that the surface fluctuation is unstable and will grow, leading to hole formation, while $\omega < 0$ indicates stability of the flat, uniform film to surface height fluctuations. Instability is obtained only for wavevectors $q < q_c$ where the van der Waals interaction dominates the surface tension term.

For an elastic materials with an equilibrium shear modulus, (i.e., $E \neq 0$ and $C_n = 0$ in Eq. (6)), the growth rate is given by:

$$\omega = -\alpha q^2 \left[ q^2 - \frac{3E}{\gamma h_0^3 q^2} \right]$$  \hspace{1cm} (21)

where

$$\alpha = \frac{\gamma h_0^3}{3 \eta_{\infty}}$$  \hspace{1cm} (22)

We see that at small enough values of $q$, $\omega < 0$ and the system is stable. For larger values of $q$ the system may be unstable, while as $q \to \infty$, the surface tension guarantees $\omega < 0$ and stability.

For a viscoelastic materials with a single, characteristic relaxation time $\tau_r = 1/\omega_r$, which separates the short-time elastic response (with a modulus, $E$) from the long-time viscous behavior, one can write equation (6) in the form:

$$\eta(\omega) = \eta_{\infty} + \frac{E}{\omega + \omega_r}$$  \hspace{1cm} (23)

From equation (19) one sees that there will be two surface modes, a stable one with $\omega < 0$ and unstable one. These solutions are given by:

$$\omega = -\frac{1}{2} a(q) \pm \frac{1}{2} \sqrt{a(q)^2 + 4b(q)}$$  \hspace{1cm} (24)

where

$$a(q) = \omega_r + \alpha q^2 [q^2 - q_c^2]$$  \hspace{1cm} (25)

and

$$b(q) = \frac{E}{\eta_{\infty}} + \alpha q^2 [q^2 - q_c^2] \omega_r.$$  \hspace{1cm} (26)

The physical meaning of these solutions is discussed below.


We first recapitulate the known results for a Newtonian fluid ($E = 0$, $C_n = 0$ in Eq. (6)) and write

$$\eta_{\infty} = G \tau$$  \hspace{1cm} (27)

where $G$ is a modulus (typically an energy of order $kT$ per unit molecular volume) and
\( \tau \) a characteristic molecular time scale. Equation (19) indicates that the growth rate is maximal at \( q_m^2 = q_c^2/2 \) and the fastest growing mode, \( \omega_m \) is given by

\[
\omega_m \tau = \beta_A
\]  
(28)

where

\[
\beta_A = \gamma h_0^3 q_c^4/12 G
\]  
(29)

and the subscript \( A \) denotes that \( \beta \) is related to the Hamaker constant by equation (20). We note that for most systems, one can set all the energy scales (in \( \gamma, G \) and \( A \)) to order \( kT \). Assuming a single microscopic length, \( a \), we find that \( \beta_A \sim (a/h_0)^3 \) to within a constant of order unity. For films greater than several molecular thickness, we thus expect \( \beta \ll 1 \). Thus, even the \textit{fastest} growing mode usually satisfies \( \omega_m \tau = \beta_A \sim (a/h_0)^3 \ll 1 \).

We next consider elastic materials. Equation (21) indicates that the maximal growth rate occurs as above at \( q_m^2 = q_c^2/2 \) and the value of the \( \omega_m \) is given by:

\[
\omega_m \tau = \beta_A - \beta_E
\]  
(30)

where \( \beta_E = E/G \) is the ratio of the shear elastic modulus to the viscosity modulus. We immediately see that if \( \beta_E > \beta_A \), \( \omega_m \) is always negative and the thin film is stable to surface undulations [18]. Since \( \beta_A \sim (a/h_0)^3 \) can be very small for a film whose thickness is much greater than a molecular size, even a very small equilibrium shear modulus — a small degree of network formation — can reduce the growth rate of the instability and even stabilize the film against holes. We note that thin polymeric films can show surface effects which can lead to vitrification and possibly network-like behavior [19].

A more realistic, but still phenomenological description of polymeric materials considers their viscoelastic response, with a characteristic frequency \( \omega_r \) (which may be molecular weight dependent as shown below) which separates the short-time elastic response \( (\omega > \omega_r) \) from the long-time viscous behavior. Using equation (24) we find that the growth rate of the fastest growing \textit{unstable} surface mode is:

\[
\omega_m \tau = \frac{1}{2} (\beta_A - \beta_E - \omega_r \tau) + \frac{1}{2} \sqrt{(\beta_A - \beta_E - \omega_r \tau)^2 + 4 \beta_A \omega_r \tau}.
\]  
(31)

In the limit that \( \beta_E > \beta_A \) which can be satisfied even for a very \textit{small} shear modulus since \( \beta_A \sim (a/h_0)^3 \ll 1 \), we find that:

\[
\omega_m \approx \omega_r \left( \frac{\beta_A}{\beta_E} \right).
\]  
(32)

For long characteristic times \( (\omega_r \tau \ll 1) \) compared to molecular relaxation times and for small ratios of \( \beta_A/\beta_E \), the growth rate can be very small indeed because (i) it is scaled by the (small) characteristic frequency of the viscoelastic material and (ii) because even a shear modulus, \( E \) which is small compared to that of a solid or the infinite frequency modulus of the polymer, results in a very small value of \( \beta_A/\beta_E \) for films much thicker than a molecular dimension. If the inverse growth rate is much slower than the experimental observation time, the system is effectively stable against surface undulations. Hole growth will not be observed and is inhibited for all practical purposes.

As a specific example, we consider a set of polymer chains end-attached to the surface of a solid substrate. For the case where there is no solvent, this is known as a polymer melt brush [10]. Hole formation is potentially possible when these ends are reversibly attached; we
focus on the surface instability of the brush. The shear modulus can be estimated by applying a lateral force to the top of the brush which shears the brushes by displacing each brush end at the surface by a distance, \( x \), in the direction of the force per unit area, \( F \). This results in the stretching of the brushes to a new length, \( L \), with a consequent elastic tension per chain, \( f \), along each chain. The value of \( x \) is such that the shearing force, \( F \) is exactly balanced by the component in the direction \( x \) of the elastic tension in the brush due to the stretched chains:

\[
F = \sigma f x L
\]

(33)

where the tension per chain is given by the derivative of the stretching free energy with respect to the chain length: \( f = 3 kT L / N b^2 \) for an ideal chain in a melt, where \( N \) is the degree of polymerization. This results in a modulus given by

\[
E = E_{\text{melt}} = \frac{3 kT \nu \sigma^2}{b^2}
\]

(34)

where \( \nu \) is the segmental volume, \( b \) is the monomer size, and \( \sigma \) is the number of chains per unit area of surface. This result has previously been derived by Fredrickson et al. [20] using a slightly different approach. For a brush in a good solvent, a similar argument [21] indicates that at low shear strains, \( E = E_{\text{sol}} = 3 kT \sigma^{3/2} \). The ratio \( E/G \) which enters in equation (30) is small, since the surface density (for a given melt brush height) is proportional to \( N^{-1} \) while \( G \) is independent of molecular weight and depends only on the entanglements between chains [20]. However, this small modulus is sufficient to stabilize the brush against surface undulations in the limit of large \( N \), since the film height, \( h_0 \), is proportional to \( N \) and in equation (30) \( \beta_\gamma \sim h_0^{-5} \). Thus, in equation (30), \( \beta_\gamma \sim N^{-2} \gg \beta_\delta \sim N^{-5} \) and the system is stable for asymptotically large \( N \). (For a brush in a good solvent the exponents are slightly different, but the conclusion is unchanged.)

Of course a melt brush with irreversibly grafted chains will never dewet and form holes. However, one can imagine that a melt with reversibly attached chains can be modeled as a viscoelastic material with no equilibrium shear modulus (i.e., at infinite time) but with a finite relaxation time which characterizes the crossover from the intermediate time shear modulus, \( E \), to the very short time modulus, \( G \), as discussed above. Hole formation for the case where the grafting locations are free to equilibrate on the substrate (but with a long relaxation time) may be governed by equation (32). For long chains, the ratio \( \beta_\delta \beta_\gamma \sim 1/N^3 \) and when this small factor is multiplied by a small value of \( \omega_n \), the system can be effectively stable with hole formation inhibited over any reasonable laboratory time scale.

Another system with a finite shear modulus is a physical gel (where the crosslinks are not permanent so hole formation can potentially occur). Again, the system will be elastic at times shorter than \( \omega_\gamma \) and viscous at longer time scales. The growth rate will again be given by equation (32) and even a value of \( E/G \ll 1 \) may still result in a very small value of the fastest growing surface mode, \( \omega_m \), since \( \beta_\delta \beta_\gamma \ll 1 \); for small enough values of the characteristic frequency \( \omega_n \), the system may appear to be stable to hole formation, while in fact it is unstable, but with an extremely slow growth rate.

We now consider a simple, non-crosslinked polymeric system with no equilibrium shear modulus, but with very long relaxation times. For this case, the longest relaxation times [11] are associated with the reptation of the polymer chains. The reptation modes of the chains have characteristic times which scale with the disengagement time for chain relaxation [11],

\[
\tau_d \sim \tau_0 N^3/N_c
\]

(35)

where \( \tau_0 \) is a (microscopic) segmental jump time, (of order \( \tau \)), \( N \) is the degree of
polymerization and $N_a$ is an « entanglement » degree of polymerization which depends on the particular polymer and concentration but is typically of order 200 in a melt. Because of the factor of $N^3$, these times are much longer than the microscopic time scales and can lead to a dramatic slowing down of the surface undulation instability and thus of hole formation and growth. In the reptation model, the complex viscosity can be written [11] 

$$\eta(\omega) = G^0 \tau_d f \left( \frac{\pi}{2} \sqrt{\omega \tau_d} \right)$$

(36a)

where 

$$f(x) = \frac{3}{\chi^2} \left[ 1 - \frac{\tanh x}{x} \right]$$

(36b)

and $G^0$ is a modulus that is independent of molecular weight but depends on concentration. In the limit where $\beta_A \ll 1$ and $(G^0 \tau_d)/(G_r) \gg 1$, the small $\omega$ limit of equation (36) yields $\omega_m \tau_d = g \beta_A$ where $g = G/G^0$. Thus, the maximum growth rate, $\omega_m$, is small not only because the film is relatively thick ($\beta_A \ll 1$), but because the characteristic time scale, $\tau_d$ is very long, scaling [22] with $N^3$. For long enough chains, this again may stabilize the surface instability on laboratory time scales.

In this context, it is interesting to note recent experiments in which thin films of a polymer melt were investigated. In one study [23], which we call the thick case, films of polystyrene with $N = 10^4$ and of thickness ca 500 nm were heated up to 70 °C above their glass transition temperature for periods of two weeks and longer, and remained quite stable (i.e., uniform and unbroken). In more recent work [8], which we refer to as the thin case, polystyrene films with $N \approx 300$ and of thickness 50-100 nm, heated to the same temperature, were observed to commence dewetting (holes began to form and grow) within ten minutes. While no systematic study has been carried out to date (in the work quoted, both the film thickness, $h_0$, and the longest ($N$-dependent) relaxation times were varied), the striking differences in film stability on increase of $h_0$ and $N$ are qualitatively in accord with our discussion. Our predictions for the fastest growing mode, $\omega_m$ indicate that the ratios of the times required for hole formation for the thick and thin cases can be enormous; the time required increases by a factor of $10^8$ for an increase in both the film thickness and the molecular weight by one order of magnitude. For the 50 nm film with $N \approx 300$ (taking $a \approx 10$ Å, $\tau \approx 10^{-12}$ s) the growth rate is estimated to be $\sim 500$ s while the 500 nm film with $N \approx 10^4$, the estimated growth rate is $10^{14}$ s and the system is effectively stable on laboratory time scales.

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References

[15] Note that here we use the Laplace and not the Fourier transform of the time dependent stress tensor;
    the quantity \( \omega \) which determines stability is thus real, and the time dependence is \( e^{\omega t} \).
[16] Since \( II_r(\omega) \) and \( II_z(\omega) \) already have terms linear in \( H(x, y; \omega) = h(x, y; \omega) - h_0 \), we evaluate
    the boundary conditions at \( z = h_0 \).
[17] This is consistent with the third Navier-Stokes equation, the analogue of equation (12) for
    \( w \). Using the incompressibility condition, equation (8), to solve for \( w \) indicates that
    \( w \) is proportional to \( q^2 \). Thus to first order terms in \( q \) in the Navier-Stokes equations, we can set
    \( w_n = 0 \) implying that \( II_z = 0 \).
[18] This can also be seen from the full dispersion relationship of equation (19). Similar restabilization
    has been considered in the context of jet breakup in references [13, 14]. While the present,
    dynamic argument yields the growth rate of unstable modes, an estimate of the modulus needed
    to prevent instability can also be obtained from energetic considerations.
[21] It is of interest that at this level, the modulus of a polymer brush in a good solvent is significantly
    larger than that of a melt brush, \( (E_{sol}/E_{melt}) = 1/(b \sqrt{\sigma}) = s/b \gg 1 \), where \( s = \sigma^{-1/2} \) is the mean
    interanchor spacing (\( s \gg b \)) and the segmental volume is taken as \( \nu = b^3 \).
[22] Experimentally, it is found that the longest relaxation times in entangled polymer systems scale as
    \( N^{13} \), but this does not change the present discussion (see FERRY J. D., Viscoelastic Properties