Cavitation in Adhesives

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The bubbles that usually appear in the bulk of an adhesive film during separation allow for a significant deformation of the adhesive material and are therefore an essential ingredient for a high dissipation. Recent observations have shown that they appear in the early stages of separation. The present model describes the early deformations induced in the film by the bubbles, and predicts how many will appear, depending on the separation velocity and on the number of weak points in the film. The trends we obtain are in agreement with observations.

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Adhesive materials have been replacing standard mechanical joints in industry for decades. They are also very present in day-to-day life. Repeatedly, new adhesive materials are designed, for instance with switchable properties for specific applications (Ref. [1] describes a transition in the adhesive properties of a structured material at a well-defined temperature).

But what is adhesion [2]? The quantity that best describes it is now considered to be the adhesion energy, i.e., the work needed to separate the objects: it depends principally on the sole dimensions and properties of the adhesive film itself. This point was by no means obvious because day-to-day experience shows that it is much easier to peel off an adhesive tape from a table (where the backing of the tape is a flexible object) than to debond two rigid objects from one another: the force needed to separate two objects strongly depends on their mechanical properties, and not only on the adhesive film.

The point became much clearer when it was possible to measure not only the energy needed for peeling a flexible tape (which is simply related to the peeling force) but also the energy required to separate two rigid bodies. Around 1985, Albrecht Zosel carried out the first experiments in the so-called probe-tack geometry: the pulling force needed to detach a flat, solid punch from an adhesive film is recorded during the entire separation process performed at constant velocity [3]. The traction curves obtained in such experiments are far from linear: usually, for good adhesives, the force increases sharply and reaches a peak value, then drops suddenly and stabilizes at a plateau value, before it eventually vanishes. The adhesion energy is the work done during the entire separation, whereas the force measured in the earlier experiments is in fact the peak value of the traction curve.

If the adhesion energy is to be important, it is essential that the adhesive film should undergo large deformations: for good adhesives, the typical displacement of the probe before the measured force vanishes is up to 10 times the original thickness of the film. Polymeric materials such as those used for making adhesive films are almost incompressible. Therefore, achieving such large deformations without triggering a comparatively easy interfacial fracture is a real challenge. Zosel observed that filaments known as "fibrils" can appear in the probe-tack geometry (and not just during a peel test, as was already known). The polymeric material in the fibrils is very much elongated during separation and the corresponding dissipation contributes to the adhesion energy.

In recent probe-tack experiments, where one of the solids is transparent, the film can be observed normally during the entire separation process. These experiments have shown that what were usually thought of as fibrils, when observed from the edge, are in fact small bubbles that grow and develop into large cavities [4]: they have shown unambiguously that, very early in the separation process, the bubbles stop growing laterally and only deform in the direction of traction. In other words, the polymer film soon turns into a two-dimensional foam and is then further stretched in the normal direction. The authors also clearly observe that the number of cavities saturates before the force reaches its plateau value, typically at the point where the force is maximum or soon afterwards.

This Letter aims at predicting the number of bubbles that appear in the film per unit surface area during separation. Our model is based on the assumption (inspired by the above observations) that the bubbles appear in the early stages of deformation and that their number is fixed thereafter. As we shall see, the effect of the rheology of the material can be described rather simply with this assumption, and the number of bubbles is amenable to calculation. For simplicity, we consider here a material whose shear properties follow Maxwell's model (shear modulus μ, relaxation time τ, viscosity $\eta \approx \mu\tau$). The same approach, however, can also be used in the case of more complex rheological behaviors. This work will soon be presented elsewhere in a more thorough manner [5]. It is based on scaling laws, and numerical coefficients are omitted (just as in an earlier work devoted to interfacial bubbles [6]).

Essentially, we describe two phenomena that can determine the number of bubbles: (i) a limited number of weak points (defects) in the adhesive material, where bubbles can nucleate, and (ii) the fact that bubbles partly relieve the stress and may thus hinder further bubble nucleation.

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Defects.—We do not consider the nucleation process itself. We simply assume that each point in the adhesive material can sustain a certain maximum tensile hydrostatic stress before it gives birth to a bubble (such a threshold stress is predicted, for instance, by Gent and Tompkins [7] for the growth of a single spherical cavity within an infinite, perfectly elastic medium). We introduce a distribution $n(\sigma)$, defined as the number of defects per unit volume whose threshold stress is σ. The exact form of the distribution should depend on how the material has been prepared. If it is very homogeneous, $n(\sigma)$ is likely to be zero at small σ and to increase very sharply above some value σ_0 of the stress. If a very polydisperse population of defects is present in the material, $n(\sigma)$ will increase slowly, until it eventually diverges at the stress that characterizes the matrix of the material. In the present model, for simplicity, we choose a linear expression for the distribution:

$$n(\sigma) = B(\sigma - \sigma_0) \qquad (\sigma \geq \sigma_0), \tag{1}$$

where σ_0 is the threshold stress of the weakest defects. A large value constant B reflects a large number of defects, which is equivalent to a homogeneous material: the number of defects is too large to determine the number of bubbles by itself, and other mechanisms come into play, essentially stress relief from existing bubbles, as we shall see later. Conversely, a small value of B corresponds to a material with very few defects: they are likely to control the number of bubbles that appear.

If the film is stretched up to a thickness $h + \delta$, where h is its original thickness, then the stress can be expressed as

$$\sigma = \Lambda\delta/h, \tag{2}$$

where Λ is a combination of Lamé's moduli ($\Lambda = \lambda/2 + \mu$) and is on the order of the compression modulus for almost incompressible materials such as those usually used for making adhesives. By omitting numerical coefficients, $\Lambda \approx \lambda \gg \mu$. In the *defect-controlled* regime, the number of bubbles per unit surface area is then given by the number of defects that have nucleated over the entire film thickness:

$$1/d^2 = h \int n(\sigma)\, d\sigma = hB(\sigma - \sigma_0)^2/2, \tag{3}$$

where d is the typical distance between neighboring bubbles and where σ is given by Eq. (2). The number of bubbles is then zero up to the displacement δ_0 for which the stress reaches σ_0. It increases continuously thereafter, and at large displacements it is essentially proportional to δ^2, unless some other mechanism stops it at some point. Note that it is also possible to consider surface defects, e.g., interfacial air bubbles trapped during formation of contact with a rough surface [6]: we would then rather use a number $n_s(\sigma)$ of defects per unit surface.

Stress relief.—The number of defects given by the above equation increases during traction. At some point, bubbles start to interact, since each bubble partly relieves the stress in its neighborhood. In order to estimate the size ξ of the region influenced by one bubble, one has to visualize the deformation modes in the adhesive film, assumed to be horizontal. Far away from the bubble, the film is stretched vertically and does not deform horizontally. The deformation therefore contains both an elongational and a dilatational component with the same order of magnitude. Because of the small compressibility of the material, however ($\Lambda \gg \mu$), the deformation energy comes essentially from the dilatation mode: $\Lambda(\delta/h)^2$ per unit volume. Conversely, not far from the bubble, the dilatation mode is relieved by the additional volume brought by the bubble, and the material is sheared in a Poiseuille-like deformation, in order to distribute the bubble volume over the influence region of size ξ. The horizontal displacement of the material at midheight is of order $\delta\xi/h$ not far from the bubble, then decreases as the inverse distance from the bubble. The elastic energy in the whole region of size ξ can be shown to be $\mu\delta^2\xi^4/h^3$, where a logarithmic factor is omitted. If the region of size ξ were expanded instead, its energy would be $h\xi^2\Lambda(\delta/h)^2$. Minimizing the difference between both expressions, we find the dimension of the region whose stress is relieved by the presence of the bubble,

$$\xi_{\mathrm{el}} \simeq h\sqrt{\Lambda/\mu} \simeq h/\sqrt{1 - 2\nu}, \tag{4}$$

where ν is Poisson's ratio. Of course, the dimension ξ of the influence zone will have a different expression after some time when the material flows [see Eq. (9) below]. Once a bubble has developed, other bubbles are not likely to appear within a distance ξ_{el} since the stress is partly relieved there. Hence, as more and more bubbles appear, they remain at a distance greater than ξ_{el} from one another, and, in a first approach, we can postulate that the final number of bubbles is given by

$$1/d^2 \simeq 1/\xi_{\mathrm{el}}^2 \simeq (1 - 2\nu)/h^2. \tag{5}$$

Continuous nucleation.—Even when the entire film is covered by the regions influenced by the bubbles, the stress can in fact still increase when separation proceeds further. More precisely, when the distance d between neighboring bubbles is smaller than ξ_{el}, the main contribution to the deformation energy in the film comes now from shear modes, and it can be shown that the tensile hydrostatic stress halfway between bubbles is on the order of

$$\sigma \simeq \mu d^2\delta/h^3. \tag{6}$$

From the distribution of available defects [Eq. (1)], we can determine whether this stress induces the nucleation of a new bubble halfway between existing bubbles. For instance, if there is a very large number of defects (infinite B), the stress always remains equal to σ_0 since bubbles nucleate as soon as it increases further. Thus, new bubbles appear as the separation proceeds: this regime is some kind of *continuous nucleation*. By using the above equation for the stress, we find that the number of bubbles then increases linearly with the displacement:

$$1/d^2 \simeq \mu\delta/\sigma_0 h^3. \quad (7)$$

A similar expression is obtained if the number of defects is also a limiting factor (*mixed regime*). In the limit of large displacements $\delta \gg \delta_0$, combining expressions (1) and (6),

$$1/d^2 \simeq \delta^{2/3} B^{1/3} \mu^{2/3}/h^{5/3}. \quad (8)$$

Viscoelasticity.—When a bubble is nucleated, it deforms the film within a distance ξ, essentially in shear modes. After a time τ has elapsed, the material flows: the shear deformation near the bubble is no longer a steady one, and the elastic stress is replaced by a viscous stress. One can show that the size of the influence region now increases with time:

$$\xi_{\text{visc}}(t) \simeq \xi_{\text{el}}\sqrt{t/\tau} \simeq h\sqrt{\Lambda t/\eta}\,. \quad (9)$$

In both situations where the number of defects is large or when it is small, eventually two conditions are fulfilled: (a) the influence regions use up all available space, i.e., $d \leq \xi$, and (b) the time elapsed since the last bubbles were nucleated is of order τ. Indeed, if the number of bubbles is small, after time τ [condition (b)], their influence regions will grow and eventually they will cover up the entire film [$\xi(t) \simeq d$, condition (a)]. This occurs at small velocities if there are few defects. Conversely, if the material is homogeneous or if the traction velocity V is high, condition (a) is fulfilled when the bubbles appear (at time t_0), and later continuous nucleation even lowers the distance d between bubbles. Condition (b) is fulfilled at time $t_0 + \tau$.

Conditions (a) and (b) in fact determine the point when bubble nucleation stops. Indeed, it can be shown that the maximum tensile stress in the film is then similar to Eq. (6), where the modulus and the displacement are replaced by the viscosity and the velocity:

$$\sigma \simeq \eta d^2 V/h^3. \quad (10)$$

Since the velocity V is a constant, combining this equation with the number of defects [Eq. (3)] shows that the number $1/d^2$ of bubbles remains constant. (Correspondingly, the volume of the bubbles increases linearly with displacement).

Final number of bubbles.—By using the above ingredients, we can picture how the number of bubbles evolves during the entire displacement until the system reaches the constant regime, whatever the velocity or the number of defects.

For instance, if few defects are present (small B), the first bubbles appear at time t_0 when the stress reaches σ_0 (see Fig. 1). Progressively, the tensile stress increases and new bubbles are nucleated [see Eq. (3)]. Meanwhile, each bubble relieves the stress in a region (size ξ) which starts broadening at a time τ after the bubble has appeared [Eq. (9)]. Eventually, the stress is relieved by bubbles in the entire film ($d \simeq \xi$) and increases no more [viscous flow, Eq. (10)]. The number of bubbles then remains constant. One can deduce the final number of bubbles in the film. It depends both on the separation velocity and on the number of defects:

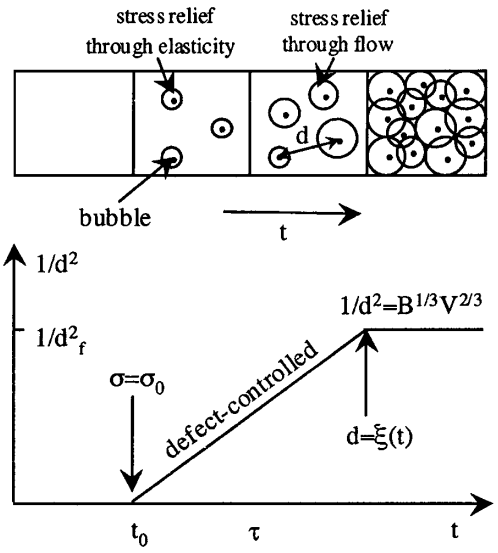

FIG. 1. Evolution of the number $1/d^2$ of bubbles per unit surface area during traction (time t), when few defects are present. At time t_0, the first bubbles appear. Each bubble relieves the stress in a region which starts broadening at a time τ after the bubble has appeared. Progressively, the tensile stress increases in regions yet unaffected by bubbles, and new bubbles are nucleated [see Eq. (3)]. Eventually, the stress is relieved by bubbles in the entire film ($d \simeq \xi$) and no longer increases (viscous flow). The number of bubbles then remains constant.

$$\frac{1}{d_f^2} \simeq \frac{1}{\xi_{\text{el}}^2}\left[\frac{V\tau}{\delta_0}\right]^{2/3}\left[\frac{B\Lambda h^3\sigma_0^2}{\mu}\right]^{1/3} \simeq \frac{V^{2/3}\eta^{2/3}B^{1/3}}{h^{5/3}} \left(B \leq \frac{\mu}{\Lambda h^3\sigma_0^2}\frac{V\tau}{\delta_0} \quad \text{or} \quad B \leq \frac{\mu}{\Lambda h^3\sigma_0^2}\frac{\delta_0^2}{V^2\tau^2}\right). \quad (11)$$

Other situations are summarized in Fig. 2. If there are a few more defects in the material, the mixed regime [Eq. (8)] is observed between the defect-limited regime [Eq. (3)] and the constant regime. If the number of defects is slightly higher, continuous nucleation occurs [Eq. (7)] instead of the defect-limited regime. It turns out that, in both cases, the final number of bubbles is still given by Eq. (11) derived for very few defects.

Let us now suppose that the velocity is high ($V \geq \delta_0/\tau$) and that there are many defects (large B). The first bubbles also appear when $\delta = \delta_0$ and there is at once a finite number of them [Eq. (5)]. From that point, continuous nucleation occurs and the number of bubbles follows Eq. (7). The constant regime is reached when $t \simeq \tau$. The final number of bubbles is therefore given by

$$\frac{1}{d_f^2} \simeq \frac{1}{\xi_{\text{el}}^2}\frac{V\tau}{\delta_0} \qquad \left(1 \leq \frac{V\tau}{\delta_0} \leq \frac{B\Lambda h^3\sigma_0^2}{\mu}\right). \quad (12)$$

If the velocity is low ($V \leq \delta_0/\tau$) and if the material still has a large number of defects, the initial number of bubbles

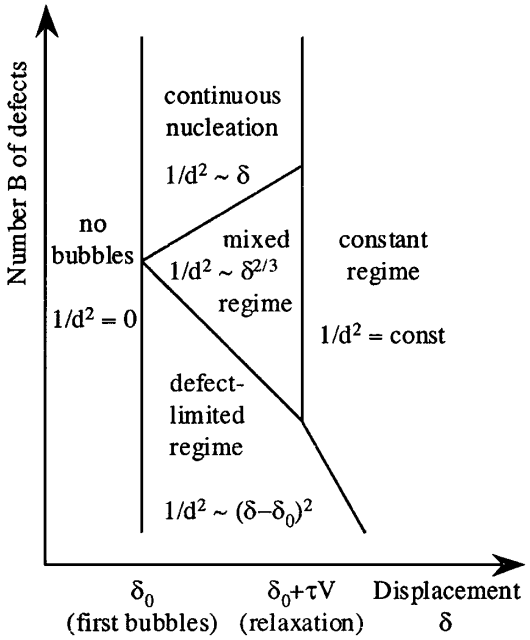

FIG. 2. Evolution of the number $1/d^2$ of bubbles per unit surface area during traction (displacement $\delta = Vt$), depending on the number B of defects [see Eq. (1)]. At small displacements, no bubbles have appeared. The evolution then depends on the number of defects. If there are few defects, they determine the number of bubbles (see Fig. 1). If there are many defects, they do not play any role and there is a continuous nucleation of new bubbles [see Eq. (7)]. For intermediate numbers of defects, the number of bubbles is determined from both effects [mixed regime, see Eq. (8)]. In all cases, at large displacements, the material flows and the number of bubbles remains constant, which defines the final number of bubbles, summarized in Fig. 3.

[Eq. (5)] has not yet increased when $t \simeq t_0 + \tau$ (constant regime):

$$\frac{1}{d_f^2} \simeq \frac{1}{\xi_{\mathrm{el}}^2} \qquad \left(\frac{\mu}{B\Lambda h^3 \sigma_0^2} \leq \frac{V^2\tau^2}{\delta_0^2} \leq 1\right). \tag{13}$$

Our model thus provides the final number of bubbles in the film, depending on the number of defects in the material and on the traction velocity (see Fig. 3). If there are few defects, they influence the final number of bubbles [Eq. (11)]. If, on the opposite, the material is almost homogeneous, the number of bubbles depends only on the traction velocity [Eqs. (12) and (13)].

By observing an adhesive film, even only *after* the separation is complete, one can estimate the number of bubbles that have appeared. The fact that it should increase with velocity [Eqs. (11) and (12)] is clearly confirmed by experiments [8,9], as well as the fact that it should be greater for thinner films and the fact that there exists an influence region (two bubble centers are never very close to each other [9]).

Our model is thus consistent with the general trends observed in an adhesive film during traction, concerning the

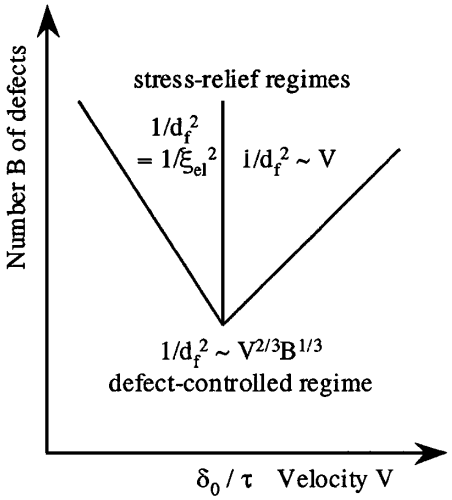

FIG. 3. Final number of bubbles per unit surface area, depending on the number B of defects and on the traction velocity V. If there are many defects, they do not play any role and the final number of new bubbles depends only on velocity [see Eqs. (13) and (12)]. If there are few defects, they too affect the number of bubbles [see Eq. (11)].

number of bubbles that appear, and could be tested in more detail through *in situ* observations [4,9]. It is therefore a first step towards determining the dissipation occurring in the polymeric material when it is strongly deformed around the bubbles. Meanwhile, it provides guides for obtaining the desired number of bubbles by adjusting the separation velocity or the number of defects in the adhesive material.

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