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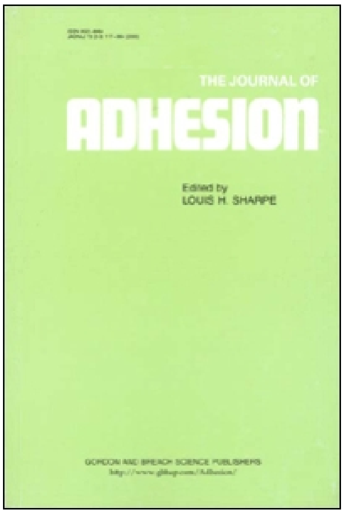

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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Online publication date: 08 September 2010

To cite this Article Shanahan, Martin E. R.(2003) 'Adhesion of a liquid-filled spherical membrane', The Journal of Adhesion, 79: 10, 881 — 891

To link to this Article: DOI: 10.1080/714906141

URL: http://dx.doi.org/10.1080/714906141

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The Journal of Adhesion, 79: 881–891, 2003
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ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460390247699

ADHESION OF A LIQUID-FILLED SPHERICAL MEMBRANE

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Solid/solid interfacial interactions have been successfully characterised using the Johnson, Kendall, and Roberts (JKR) analysis for many years now. Following a suggestion and accompanying analysis by the present author to replace a solid sphere by a gas-filled, hollow, spherical membrane in contact experiments, we now propose a liquid-filled "balloon." Free energy changes due to stretching, bending, the mechanical contact force and adhesion are assessed and minimised to obtain an exploitable equation permitting estimation of the energy of adhesion of the system as a function of various, in principle more easily measured, parameters.

Keywords: Adhesion; "Balloon" test; Capsule; Cell; Contact mechanics; Elastomer; Spherical membrane

INTRODUCTION

Although adhesion, or adherence, has been recognised as a physical phenomenon since time immemorial, successful attempts to understand the underlying principles are relatively recent, probably having commenced some 80 years ago with McBain and Hopkins' "mechanical theory of adhesion" [1]. Amongst several complicating factors rendering adhesion delicate to assess is the fact that the "value" obtained depends to a large extent on the way it is measured [2]. The reason that the removal of a sticking-plaster from the skin at low peel rates is less painful than at high rates does not mean that the intrinsic

Received 26 March 2003; in final form 9 June 2003.

One of a Collection of papers honoring Jacob Israelachvili, the recipient in February 2003 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

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adhesion is greater in the latter case, but that energy-dissipating mechanisms are more significant, as shown in early pioneering work by Gent and Petrich [3]. Overall resistance to separation reflects both surface and bulk properties. Although bulk energy dissipation phenomena, usually of a viscoelastic or of a plastic nature, contribute enormously to macroscopic, pragmatic adhesion effects, they can tend to cloud the issue as far as the understanding of fundamental interfacial bonding is concerned. Early attempts to understand bonding mechanisms with mica date back to 1930 [4], but later significant developments were made in Cambridge (GB) with the work of Tabor and Winterton [5] and later Israelachvili and Tabor [6, 7], culminating in the "surface force apparatus" (see also Kendall [2]). In both Australia and in the United States, Israelachvili and colleagues have over the last 30 years continued research in this fundamental domain of surface forces, leading to considerable advances in understanding [8].

As hinted at above, dynamic adhesion can be largely dominated by dissipative mechanisms, and thus static adhesion measurements would, in general, seem better suited for fundamental investigation of surface forces. An important step was made with the introduction of the Johnson, Kendall, and Roberts (JKR) [9] theory explaining the contact of two spheres and allowing for adhesion between the contiguous materials (neglected in the original Hertz theory [10]). Since the theory is applicable to (quasi-) static conditions, values of the energy of adhesion close to that of Dupré, or fundamental, thermodynamic adhesion, W_o, should be accessible:

$$W_o = \gamma_1 + \gamma_2 - \gamma_{12}, \tag{1}$$

where γ represents the surface (interfacial) free energies of the solids 1 and 2, related directly to surface forces.

The JKR theory has been much exploited over recent years and has been of immense use in data interpretation for the contact of soft solids (for two hard solids the Derjaguin, Muller, and Toporov (DMT) theory [11] is probably better suited). However, a possible disadvantage is that contact areas between the spheres are usually rather small and, as contact force tends towards zero, the calculated energy of adhesion scales with the cube of the contact radius, a. In a fairly recent article, Shanahan suggested a modification of the JKR test in which a hollow sphere, rather than a solid sphere, is put into contact with a rigid flat [12], representing a second sphere of infinite radius. With a slight gas overpressure within the "balloon," the radius of the contact area may not only be greater than for the equivalent JKR test, reducing potential relative errors in measurement, but also it should be possible to decouple surface and volume effects, by changing internal gas pressure. However, it may be a delicate procedure to make the "balloons" in question! This contribution is a sequel to the earlier article in which, instead of considering the "balloon" to be gas filled, we assume it to be liquid filled. Such "balloons" may possibly be easier to manufacture. In addition, there is some resemblance to cellular adhesion [13]* and that of microcapsules [16].

ELASTIC DEFORMATION OF A LIQUID-FILLED 'BALLOON'

Stretching

We commence by considering a spherical membrane of thickness, t, and radius, R, enclosing a volume V ($= 4\pi R^3/3$) of a liquid (Figure 1(a)). No distinction is made between outer and inner radius since we assume $t \ll R$. The spherical membrane, or "balloon," is then brought to bear on a flat, rigid solid (Figure 1(b)). We shall assume that the

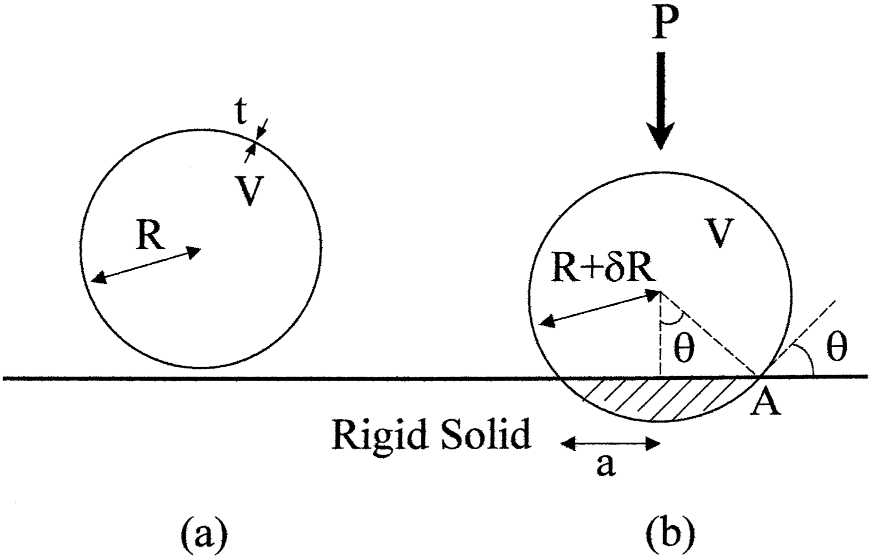

FIGURE 1 Schematic representation of "balloon" containing volume, V, of liquid (a) before and (b) after contact with flat, rigid solid.

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[*] Although our development here is basically from an engineering, or macroscopic, standpoint, it has since come to the author's attention that somewhat similar approaches to the present have been suggested in a specifically biological, microscopic context, *e.g.* Dietrich *et al.* [14] and Tordeux *et al.* [15].

balloon retains a spherical form, except in the flattened zone in direct contact with the solid, which subtends an angle of 2θ. Such a simplification implies sharp bending at the triple line (A) separating balloon, solid, and exterior. Although compatible with the assumptions of membrane theory [17], in which stretching is deemed to dominate over bending, this discontinuity in membrane orientation is physically unreal and will therefore be addressed below.

To a very good approximation, we may consider the liquid to be incompressible and, thus, the volume of the flattened balloon remains as V. As a consequence, the radius of the truncated sphere becomes $\mathrm{R}' = \mathrm{R} + \delta\mathrm{R}$, and the shaded zone of Figure 1(b) ("within" the rigid solid, and corresponding to the continuation of the slightly expanded sphere) is of volume $\delta\mathrm{V}$:

$$\delta V = \frac{\pi \mathrm{R}'^3}{3}(1-\cos\theta)^2(2+\cos\theta) \approx \frac{\pi \mathrm{R}'^3 \theta^4}{4}, \tag{2}$$

where the approximation is valid for θ sufficiently small. Thus, for assumed constant volume V we have:

$$\frac{4\pi \mathrm{R}^3}{3} \approx \frac{4\pi(\mathrm{R}+\delta\mathrm{R})^3}{3} - \frac{\pi(\mathrm{R}+\delta\mathrm{R})^3\theta^4}{4}, \tag{3}$$

leading to

$$\frac{\delta\mathrm{R}}{\mathrm{R}} \approx \left(\frac{\theta}{2}\right)^4, \tag{4}$$

where terms of order $(\delta\mathrm{R})^2$, or alternatively or order θ^8, have been neglected.

The spherical balloon has an initial surface area, S, of $4\pi\mathrm{R}^2$, and in its slightly flattened state after contact its total surface area becomes $\mathrm{S} + \delta\mathrm{S}$:

$$\mathrm{S} + \delta\mathrm{S} = \pi\mathrm{R}'^2\left[4 - 2(1-\cos\theta) + \sin^2\theta\right] \approx 4\pi\mathrm{R}'^2\left(1 - \frac{\theta^4}{16}\right). \tag{5}$$

After substituting from Equation (4) and simplifying, neglecting terms of order $(\delta\mathrm{R})^2$, we obtain

$$\mathrm{S} + \delta\mathrm{S} \approx 4\pi\mathrm{R}^2\left(1 + \frac{\delta\mathrm{R}}{\mathrm{R}}\right) \approx 4\pi\mathrm{R}^2\left[1 + \left(\frac{\theta}{2}\right)^4\right]. \tag{6}$$

We could consider that the initial, undeformed spherical membrane is just filled with volume V of liquid, without stretching. However, this would only be useful under special conditions. If there is no initial tension in the membrane, then even under its own weight alone it will deform, somewhat in the style of sessile drop (except, of course, that a liquid drop has a constant "membrane tension," or more precisely, surface tension, whereas an elastic membrane under no intrinsic tension will initially manifest a linearly increasing tension with strain). Thus, only if there are negligible body forces will the assumption of retained sphericity be applicable. (This approach could, however, be useful if the balloon models a cell and is immersed in another liquid of the same density, where buoyancy alleviates the problem.)

We shall therefore assume an intrinsic, isotropic tension, T, in the spherical membrane, due to slight overfilling. This tension will be related to the slight overpressure of the liquid, Δp, by the expression $T = R, \Delta p/2$. Provided $\delta R/R \ll 1$, the increase in free energy of the membrane due to stretching is proportional to the increase in surface area [18], and thus the supplementary energy, U_E, is given by

$$U_E \approx T.\delta S \approx 4\pi TR.\delta R \approx 4\pi R^2 T \left(\frac{\theta}{2}\right)^4. \tag{7}$$

We shall assume as a first approximation that the flattening after contact leads to a homogeneous stretching of the membrane, although in practice this will not be quite correct, as discussed elsewhere [19], due in part to the method of establishing contact. (The gradual stretching of the membrane during the establishment of contact will lead to a (slight) tension gradient, the tension increasing with radial distance in the contact circle.)

Bending

The above, approximate expression for elastic energy, Equation (7), neglects any bending effects. This will be reasonable, for a very thin membrane, everywhere except near the triple line denoted by A in Figure 1(b). An exact appraisal of bending effects in the vicinity of the triple line would be complex, so we shall make some simplifying assumptions. (There will be some interplay in reality: the bending moment will slightly perturb the sphericity of the free membrane which will, in turn, diminish bending to some extent.) The "instantaneous" change from the flattened membrane in contact with the rigid solid to the free membrane, at an angle θ with respect to the solid, will occur over a length comparable with the membrane thickness, t (Figure 2). Thus, the local radius of curvature, ρ, is of order t/θ. We may treat the membrane locally using beam theory. Then the elastic energy, per unit length perpendicular to the figure, u_B, is given by

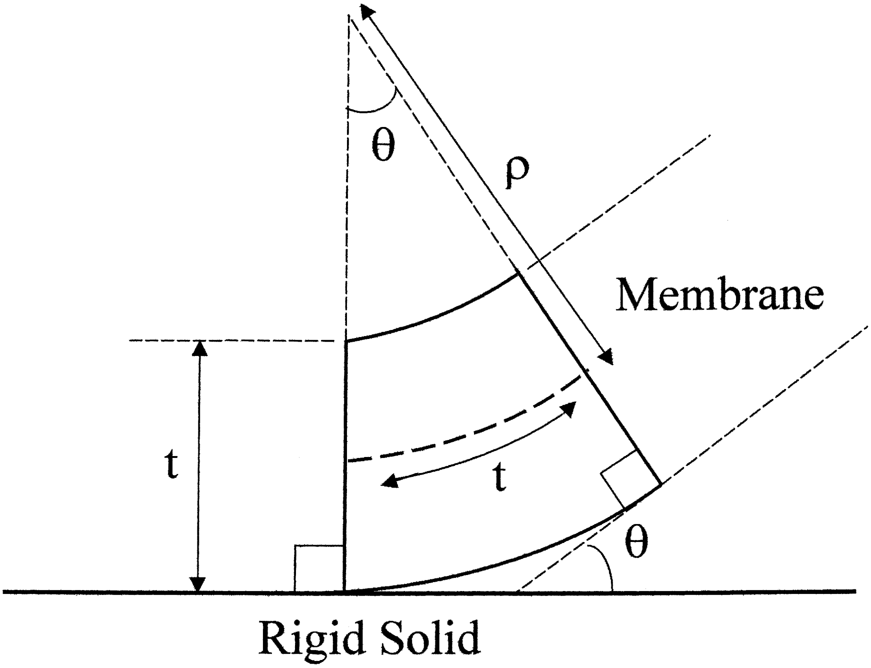

FIGURE 2 Bending of membrane near triple line A in Figure 1(b).

$$u_B \approx \frac{EI}{2} \cdot \frac{1}{\rho^2} \cdot t, \tag{8}$$

where $I = t^3/12$ is the second moment of area of the 'beam' cross section (per unit width, perpendicular to the figure) and E is Young's modulus. Since the total length of triple line involved is given by $2\pi R \sin\theta$ (neglecting the increment from R to $R + \delta R$), we obtain the total energy due to bending, around the triple line, U_B, as

$$U_B \approx \frac{EI}{2} \cdot \frac{1}{\rho^2} . t . 2\pi R \sin\theta \approx \frac{\pi t^2 E R \theta^3}{12}, \tag{9}$$

for θ sufficiently small (say, < *ca.* 1 radian).

We can thus see that

$$\frac{U_B}{U_E} \approx \frac{Et^2}{3TR\theta}. \tag{10}$$

We may conclude that as θ decreases, bending effects become more important. Also, a very thin membrane reduces the relative importance of U_B.

ENERGY BALANCE FOR EQUILIBRIUM

The basics of determining equilibrium have been considered in an earlier article [12]. We consider the various sources of free energy change attributable to contact between the liquid-filled membrane and a flat, rigid solid, *i.e.*, the transition from Figure 1(a) to Figure 1(b). Defining U as the total free energy, to within an additive constant, we have

$$\mathrm{U} = \mathrm{U_E} + \mathrm{U_B} + \mathrm{U_M} + \mathrm{U_S}, \tag{11}$$

where $\mathrm{U_E}$ and $\mathrm{U_B}$ are the elastic strain energies dealt with above, $\mathrm{U_M}$ is the mechanical energy corresponding to movement of the force of application, P, in Figure 1(b) (which may simply be the weight of the membrane plus contained liquid, in the geometry shown), and $\mathrm{U_S}$ is the energy of adhesion:

$$\mathrm{U_M} \approx -\mathrm{P}[\mathrm{R} - (\mathrm{R} + \delta\mathrm{R})\cos\theta], \tag{12}$$

$$\mathrm{U_S} = -\pi \mathrm{a}^2 \mathrm{W_o} \approx -\pi \mathrm{W_o}(\mathrm{R} + \delta\mathrm{R})^2 \sin^2\theta, \tag{13}$$

where a is contact radius, and $\mathrm{W_o}$ is defined by Equation (1), 1 and 2 representing membrane and rigid solid.

Using Equations (7), (9), and (11)–(13), and truncating at the leading term in θ for each contribution in order to simplify, we find

$$\mathrm{U} \approx \frac{\pi \mathrm{R}^2 \mathrm{T}\theta^4}{4} + \frac{\pi \mathrm{t}^2 \mathrm{ER}\theta^3}{12} - \frac{\mathrm{PR}\theta^2}{2} - \pi \mathrm{W_o R}^2\theta^2. \tag{14}$$

At equilibrium, $\mathrm{dU/d}\theta$, and thus

$$\mathrm{W_o} \approx \frac{\mathrm{T}\theta^2}{2} + \frac{\mathrm{t}^2\mathrm{E}\theta}{8\mathrm{R}} - \frac{\mathrm{P}}{2\pi\mathrm{R}}. \tag{15}$$

Clearly, Equation (15) will only be valid for evaluating adhesion energy, $\mathrm{W_o}$, for reasonably small values of θ, since higher powers have been neglected, but the principle is clearly shown. Anyway, if θ is too large, the hypotheses adopted at the outset will become invalid. This would occur, for example, if P were too large.

DISCUSSION

Equation (15) is the main result of this article, and it is instructive to inject a few reasonable values into it to see what behaviour may be expected. Let us take $\mathrm{R} = 10^{-2}\,\mathrm{m}$, $\mathrm{t} = 10^{-4}\,\mathrm{m}$, and $\mathrm{E} = 1\,\mathrm{MPa}$. We must assume a suitable value for intrinsic tension, T. By analogy with the treatment of sessile, or pendant, liquid drops, we may define a "balloon number," B, equivalent to a capillary number [20]:

$$B = \frac{\tilde{\rho} g R^2}{T}, \tag{16}$$

where $\tilde{\rho}$ is effective (average) density of the balloon (with $t \ll R$, essentially the density of the liquid contained, reduced by the density of the exterior medium, to allow for buoyancy) and g is gravitational acceleration. For sphericity to be well approximated, B should be less than *ca.* 1 (membrane tension then dominating over gravity). Taking the balloon to be water-filled, this condition leads to a value of $T \geq 1\,\mathrm{Nm}^{-1}$. How do we obtain this tension in practice? One method may be to prepare the balloon above the temperature at which it is to be used and then, on cooling, with a coefficient of thermal expansion greater than that of the contained liquid, shrinking will lead to a tension. (Or conversely, if the thermal expansion coefficient of the liquid is greater than that of the membrane, prepare the balloon at reduced temperature.) A tension of, say, $3\,\mathrm{Nm}^{-1}$ in a rubber membrane of thickness $10^{-4}\,\mathrm{m}$, means a stress of $T/t \approx 3 \times 10^4\,\mathrm{Pa}$, or 3% of the (assumed) Young's modulus, which is quite reasonable.

Let us assume that the balloon remains in contact with the rigid solid under its own weight alone; $P = 4\pi R^3 \tilde{\rho} g/3$. Neglecting air buoyancy, the weight and thickness of the membrane, and assuming the balloon to be water filled, we find $P \approx 4.1 \times 10^{-2}$ N.

Equation (15) can now be rearranged to give a quadratic in θ to establish this value for a given set of parameters:

$$\theta^2 + \frac{t^2 E \theta}{4TR} - \frac{P}{\pi TR} - \frac{2W_o}{T} = 0, \tag{17}$$

or

$$\theta = \frac{t^2 E}{8TR}\left\{\left[1 + \frac{64TR^2}{t^4 E^2}\left(\frac{P}{\pi R} + 2W_o\right)\right]^{1/2} - 1\right\}, \tag{18}$$

where the positive root has been taken for physical reasons. With the above values, and treating W_o, the intrinsic energy of adhesion, as a variable, we may compare values of θ (and equivalently, contact radius, a) for differing degrees of adhesion. Values are presented in Table 1. In addition, values are given of the ratio U_B/U_E, obtained from Equation (10). It can be seen that even at (assumed) zero adhesion, there is some flattening of the spherical membrane in contact with the flat, rigid surface. This is, of course, simply due to the force

P (weight). If adhesion is zero and total buoyancy prevails ($P = 0$), Equation (18) shows indeed that θ becomes zero, as expected. Comparing values of W_o, θ, and a in Table 1, it can be seen that the sensitivity of subtended semiangle, θ, or contact radius, a, to variations in energy of adhesion, W_o, is perhaps not as great as may be hoped for from an experimental standpoint. Nevertheless, θ and a clearly do rise with W_o. It is clear from Table 1 that the bending energy, U_B, is quite comparable with the stretching energy, U_E, in order of magnitude, if tending to be somewhat smaller in the given examples. Thus, bending effects near the contact triple line must be taken into account.

Towards higher values of θ, the validity of values of W_o clearly decreases due to the approximations made in the foregoing analysis. If the analysis presented here is exploited experimentally, it is suggested that the available parameters be adjusted (within the realms of possibility!) such that angle θ is not too large, in order to minimise truncation errors in the development. The membrane thickness, pretension, and radius may possibly be chosen as a function of the range W_o expected.

Finally, note from Equation (18) that if the applied force, P, becomes negative (inversion of system discussed above), then θ becomes zero for

$$P = -2\pi R W_o. \qquad (19)$$

Thus, the pull-off force is given by Equation (19), which is the same expression as previously found in the DMT theory [11] and with a gas-filled balloon [12]. This is different from the JKR theory [9], where the pull-off force is 25% smaller.

TABLE 1 Calculated Values of Angle, θ, Corresponding to Half of Flattened Contact Zone of "Balloon" (from Equation (18)), Equivalent Contact Radius, a, and Ratio, U_B/U_E, of Bending to Stretching Elastic Energies (from Equation (10))

W_o (mJm^{-2})	θ (rad.)	a($m \times 10^2$)	U_B/U_E
0	0.620	0.58	0.18
20	0.630	0.59	0.18
50	0.645	0.60	0.17
100	0.670	0.62	0.17
200	0.715	0.65	0.16
500	0.835	0.74	0.13
1000	1.010	0.85	0.11

$E = 1$ MPa; $t = 10^{-4}$m; $t = 3\,Nm^{-1}$; $R = 10^{-2}$m; $P \approx 4.1 \times 10^{-2}$ N.

CONCLUSION

Following the analysis of a gas-filled balloon in contact with a flat, rigid solid, which may possibly supplement the JKR analysis of solid sphere contact in surface force research, we suggest here an analysis of a contacting liquid-filled balloon. Free energy (to within an additive constant) is attributed both to stretching and to bending of the initially spherical liquid-filled membrane, as contact is made with a flat, rigid solid. The remaining free energy changes are related to mechanical force causing contact and to adhesion. Minimisation of overall free energy leads to an expression relating the angle subtended by the flattened, contacting zone of the membrane, to the energy of adhesion membrane/solid. Putting typically expected values of the various parameters into the final equations shows the test to be quite plausible and possibly useful in various areas of research into surface forces, including cell adhesion and the contact of liquid-filled capsules. As in the earlier analysis of a gas-filled balloon, the present system possesses the advantage of having potentially decoupled surface and volume effects.

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