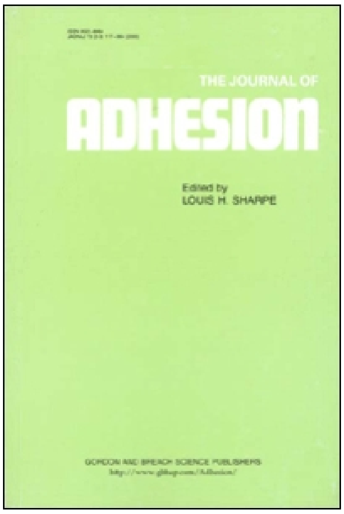

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M. E. R. Shanahan[a]
[a] Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux P. M. Fourt, EVRY Cédex, France

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A Novel Test for the Appraisal of Solid/Solid Interfacial Interactions*

M. E. R. SHANAHAN

Centre National de la Recherche Scientifique, Ecole Nationale
Supérieure des Mines de Paris, Centre des Matériaux P. M. Fourt,
B. P. 87, 91003 EVRY Cédex, France

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The Johnson, Kendall and Roberts (JKR) technique has been used with considerable success for assessing solid/solid interfacial interactions over the past 25 years or so. Nevertheless, the contact zone between the two spherical solids is often small and the energy of adhesion scales with the cube of the contact radius (at low load), thus potentially magnifying errors in adhesion assessment. The theoretical aspects of a novel technique are presented here, in which a hollow, slightly inflated, spherical membrane replaces a full sphere, and is placed in contact with a flat rigid solid. A judicious choice of experimental conditions should lead to increased contact radius and the energy of adhesion scales with its square (at low load), thus reducing possible errors. An added advantage is that the effective elasticity of the sphere depends on internal gas pressure. Thus surface and bulk effects are decoupled.

Keywords: Adhesion hysteresis; "balloon" test; contact mechanics; elastomer; JKR test; membrane; spherical surface; van der Waals adhesion

INTRODUCTION

Adhesion and wetting are two closely related subjects in that the physical contact between the two phases, respectively solid/solid and solid/liquid, is largely governed by intermolecular forces of a physical nature. Although strong solid/solid adhesion may, in some cases, result from chemical, or covalent, bonds across the interface, the initial contact, as with wetting, depends essentially on longer range, essen-

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tially physical attractions. The potential surface activity of a liquid may be readily assessed by direct measurement of its surface tension, equivalent for a pure liquid to its surface free energy, using tensiometric methods. However, in the case of a solid, the situation is far more complicated due to its lack of molecular mobility. For this reason, it has been common practice now for many years to estimate the surface free energy of a solid using the indirect method of wetting in which, for example, a sessile drop is placed onto the solid surface and its contact angle, θ, measured and used in Young's equation:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \tag{1}$$

where γ_S and γ_L are the surface free energies (tensions) of solid and liquid and γ_{SL} is their common interfacial free energy (tension). (Equation (1) is, of course, a slight simplification neglecting complications due to surrounding vapour and adsorption phenomena.) The terms γ_L and θ are readily available but, in order to ascertain γ_S, a functional form for γ_{SL} must be assumed. This has constituted a major problem over the years and although no definitive, general solution has yet been established, one of the major contributors to the advancement of knowledgde in this field has been Robert J. Good, along with his various coworkers. In the 1950s, with Girifalco, Good proposed a relation for γ_{SL} involving the geometric mean of γ_S and γ_L and a function of molar volume [1, 2], later extended by Fowkes [3], which had considerable success. Later, Good, together with Chaudhury and van Oss, were amongst the first to consider the importance of acid/base interactions at an interface [4].

Surface free energies are fundamental to adhesion as well as wetting and, in certain cases, van der Waals forces alone may lead to significant interfacial strength. However, the adhesion of a polymer, in particular an elastomer, to a second solid, rigid or not, represents a complex phenomenon involving not only the surface properties of the substrates in contact but also certain aspects of their bulk mechanical behaviour. During separation of an interface, viscoelastic dissipation in the vicinity of the failure front effectively "amplifies" the intrinsic Dupré energy of adhesion and the increase may be considerable, a factor of several thousand being possible [5–8]. Since the extra energy dissipated obeys time-temperature superposition principles [9], it is to be expected that quasi-static tests will lead to values of adhesion close to those predicted by the Dupré relation:

$$W_0 = \gamma_1 + \gamma_2 - \gamma_{12} \tag{2}$$

where γ represents the surface (interfacial) free energies of the solids 1 and 2. Thus, in principle, one may approach the surface free energies of solids *via* adhesion directly. However, this is not always the case and it would seem that the effective energy of adhesion decreases with increasing degree of crosslinking [10] when measuring separation, rather than formation, of an interface. A common test of separation is that of peel, but when quasi-static data are required, a more suitable set-up, as used in Ref. 10, is that depending on the Johnson, Kendall and Roberts (JKR) principle [11]. When two spherical, elastic surfaces are pushed into contact, the overall free energy pertaining to elastic stored energy, mechanical potential energy and adhesion energy, is minimised at equilibrium. In the case of an elastomeric sphere of radius, R, and Young's modulus, E, in contact with a flat, rigid solid, the energy of adhesion, W_0, is given by:

$$W_0 = \frac{3}{32\pi E a^3}\left(\frac{16Ea^3}{9R} - F\right)^2 \tag{3}$$

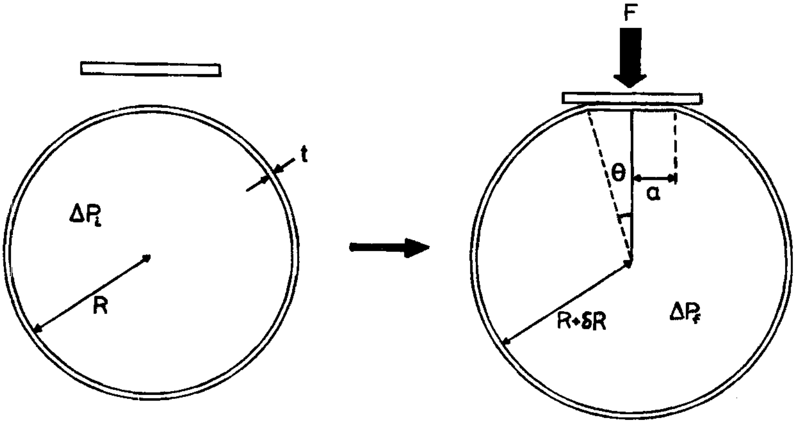
where a is contact radius and F is applied force. One significant advantage of this method is that viscoelastic "amplification" of the fundamental energy of adhesion is largely avoided. However as $F \rightarrow 0$, W scales with a^3, thus potentially introducing significant errors when a is small (when a is too large, the theory is no longer applicable, anyway). Although the now classical JKR theory is indubitably of great value and has been often successfully used [10–15], the $W \sim a^3$ law is a drawback. The purpose of this article is to propose a modification, or variant, on the JKR test in which an elastomeric, full sphere is replaced by a spherical membrane under slight internal pressure. Despite certain potential practical difficulties, the simple analysis presented demonstrates the advantage of a scaling law of the type $W \sim a^2$. In addition, the effective elasticity of the system and the adhesion properties are decoupled, leading to a potentially more versatile test.

BASIC EQUATIONS OF THE SPHERICAL MEMBRANE OF "BALLOON"

The JKR theory amounts to a modification of the Hertz theory [16] of contact mechanics in which the adhesion term, neglected by Hertz, has been incorporated. At high applied loads, the Hertz relation is essentially correct. It is only at low loads that the deviations due to surface terms appear.

Assuming the specific geometry of a deformable, elastomeric, spherical surface in contact with a flat, rigid solid (radius of curvature of the latter $\rightarrow \infty$), it is intuitively obvious that when pressing a hollow sphere against the flat, a larger contact area will result than when pushing a full sphere of the same material and radius and with the same force. This is the basis of of the following theory.

Consider Figure 1, which shows schematically a spherical, elastomeric membrane (i) before and (ii) after contact with a flat, rigid solid. Despite certain experimental difficulties manifestly related both to the production and the set-up of this system, we shall postulate that the initial hollow, spherical membrane has an intrinsic radius of ρ (internal for definiteness, but the thickness is considered much less than ρ), but



(i) (ii)

FIGURE 1 Schematic diagram of spherical membrane and flat, rigid solid, (i) before contact and (ii) at equilibrium.

that the membrane is partially inflated and a slight overpressure of gas is contained leading to a radius of R and membrane thickness t. We thus effectively have a spherical "balloon". Taking the overpressure within the balloon to be $\Delta P_i = P_i - P_0$ where P_i is the internal pressure and P_0 the external (atmospheric) pressure, and the (biaxial) tension within the membrane as T_i, from simple equilibrium considerations we have:

$$T_i = \frac{R.\Delta P_i}{2} \tag{4}$$

The quantity of gas contained is fixed and, assuming the ideal gas law to apply in the following, we have:

$$P_i V_i = \frac{4}{3}\pi R^3 P_i = n\tilde{R}\tilde{T} = K(\text{constant}) \tag{5}$$

where V_i is the initial, or spherical, internal volume, n is the number of moles of gas contained and $\tilde{R}$ and $\tilde{T}$ are, respectively, the ideal gas constant and absolute temperature.

In Figure 1(ii) we consider that a flat, rigid solid has been pushed against the balloon with small force, F, leading to a circular contact area of radius a, subtending an angle θ at the centre of the sphere ($a \ll R$ and $\theta \ll 1$).

Due to the compression of the internal gas and the elasticity of the membrane, the balloon will adopt the form of a sphere, now of radius $R + \delta R$, with a small flattened area. We must determine δR. Strains in the membrane are considered small and, thus, treated using linear elasticity theory.

The initial strain of the membrane before contact, ε_i, is given by:

$$\varepsilon_i = \frac{R-\rho}{\rho} = \frac{T_i(1-v)}{Et} = \frac{R(1-v).\Delta P_i}{2Et} \tag{6}$$

where v is Poisson's ratio, leading to:

$$\rho = \frac{2EtR}{2Et + R(1-v)\Delta P_i} \tag{7}$$

Similarly, the strain after contact, ε_f, will be given by:

$$\varepsilon_f = \frac{R+\delta R-\rho}{\rho} = \frac{T_f(1-\nu)}{Et} = \frac{(R+\delta R)(1-\nu)\,\Delta P_f}{2Et} \tag{8}$$

where T_f refers to membrane tension after contact and $\Delta P_f = P_f - P_0$, P_f represents the final internal pressure. Elimination of ρ from Equation (8) using Equation (7) leads to:

$$\delta R = \frac{R^2(1-\nu)\,(P_f - P_i)}{2Et - R\,(1-\nu)\,(P_f - P_i)} \tag{9}$$

The final internal volume after contact, V_f, is given by:

$$V_f \approx \frac{4}{3}\pi(R+\delta R)^3\left(1-\frac{3\theta^4}{16}\right) \approx \frac{4}{3}\pi R^3\left(1+\frac{3\delta R}{R}\right)\left(1-\frac{3\theta^4}{16}\right) \tag{10}$$

Since, by analogy with Equation (5), we have $P_f V_f = K$, we may write:

$$P_f \approx P_i\left(1-\frac{3\delta R}{R}\right)\left(1+\frac{3\theta^4}{16}\right) \tag{11}$$

Substitution of Equation (11) into Equation (9) leads, to order δR and θ^4, to:

$$\delta R \approx \frac{3R^2 P_i(1-\nu)\theta^4}{16[2Et + 3RP_i(1-\nu)]} \equiv \lambda R\theta^4 \tag{12}$$

where λ is a constant for a given balloon (at given temperature and pressure).

EQUILIBRIUM OF THE BALLOON/FLAT SOLID

We shall consider the free energy of the system, G, pertaining to four sources: (a) the elastic, stored energy of the membrane, G_E; (b) the energy of adhesion, G_S; (c) the mechanical, potential energy associated with F, the force of contact of the flat solid, G_M; and (d) the energy corresponding to the gas compressed within the membrane, G_P.

(a) The elastic stored energy is $T_f^2\ (1-\nu)/(Et)$ per unit area of surface, where ν is Poisson's ratio ($\approx 1/2$ for an elastomer) and E is Young's modulus. Since the volume of the membrane itself $(4\pi R^2 t)$ remains essentially constant, we have:

$$G_E \approx \frac{T_f^2(1-\nu).4\pi R^2}{Et} \approx \frac{\pi(1-\nu)(\Delta P_f)^2 R^3(R+2\delta R)}{Et} \tag{13}$$

where ΔP_f and δR may be given explicitly using Equations (11) and (12) above. The second equality of expression (13) follows by analogy with equation (4) for the case of T_f. It should be noted here that an underlying assumption is made in that the state of tension in the membrane is supposed to be the same in the contact zone as in the free zone. In practice, this may depend on the manner in which contact has been effected.

(b) The free energy of the interfacial zone is γ_{12} during contact, compared with $\gamma_1+\gamma_2$ before contact. Using Equation (2), we see that:

$$G_S = -\pi a^2 W_0 \tag{14}$$

where a is contact radius.

(c) The mechanical energy corresponding to movement of the force of application, F, is given by:

$$G_M \approx -F[R-(R+\delta R)\cos\theta] \tag{15}$$

(d) The volume of the interior of the balloon in its final configuration is given by Equation (10). Since the gas inside is assumed to be ideal, the increase in free energy due to compression, G_P, is related to the internal pressure and the volume by:

$$G_P = -\int \Delta P\, dV = -\int_{V_i}^{V_f}\left(\frac{K}{V}-P_0\right)dV \approx 3\Delta P_i V_i\left(\frac{\theta^4}{16}-\frac{\delta R}{R}\right) \tag{16}$$

In order to determine equilibrium, we must minimise the sum:

$$G = G_E + G_S + G_M + G_P$$

$$\approx \frac{\pi(1-\nu)R^4.\Delta P_i}{Et}\left\{\Delta P_i + \theta^4\left[3P_i\left(\frac{1}{8}-2\lambda\right)+2\lambda.\Delta P_i\right]\right\} - \pi R^2 W_0\left(\theta^2 - \frac{\theta^4}{3}\right)$$

$$- FR\left(\frac{\theta^2}{2} - \frac{\theta^4}{24} - \lambda\theta^4\right) + 3V_i.\Delta P_i\left(\frac{\theta^4}{16} - \lambda\theta^4\right) \qquad (17)$$

where G corresponds to the overall free energy of the system (to within an additive constant).

At equilibrium, $dG/d\theta = 0$, and after some algebra and using the simplification $a \approx R\theta$, we obtain:

$$W_0 \approx \frac{a^2}{2\pi R^4}\left\{3V_i\Delta P_i\left[\frac{R(1-\nu)}{Et}\left(\frac{3}{8}P_i(1-16\lambda) + 2\lambda\Delta P_i\right) + \frac{(1-16\lambda)}{4}\right]\right.$$

$$\left. - FR\left(\frac{1}{2} - 4\lambda\right)\right\} - \frac{F}{2\pi R} \qquad (18)$$

As will be seen in the following, the balloon test should be of most use when ΔP_i is small. Thus, on neglecting terms of order $(\Delta P_i)^2$, we have:

$$W_0 \approx \frac{a^2}{2\pi R^4}\left\{\frac{3V_i\Delta P_i}{8}(1-16\lambda)\left[2 + \frac{3RP_i(1-\nu)}{Et}\right]\right.$$

$$\left. - FR\left(\frac{1}{2} - 4\lambda\right)\right\} - \frac{F}{2\pi R} \qquad (19)$$

Clearly Equation (19) (or (18)) will only be valid when ΔP_i is positive and when F is sufficiently small (this latter condition applies equally to (Equation (13)) but an advantage is that as $F \to 0$, we obtain:

$$W_0 \sim a^2 \qquad (20)$$

This dependence on a^2 rather than a^3 should be of use in reducing potential errors. The difference in scaling law can perhaps be appreciated conceptually by considering that, in the JKR system, adhesion is "battling" against a volume of solid ($\sim a^3$) whereas, with the balloon, the resistance trying to separate membrane and rigid solid is essentially a surface phenomenon.

APPLICATION TO A MODEL CASE: COMPARISON WITH JKR

The equilibrium corresponding to Equations (19) (or (18)) depends on the minimisation of the free energy function, G, of Equation (17). It is instructive to consider the various components of G as a function of the angle θ or, alternatively, the contact radius, a. We shall consider this for a model case using plausible values for the various parameters of the system balloon/rigid solid. Typically we may take W_0 to be of the order of 50 mJ.m^{-2} and Young's modulus for a soft rubber, E, to be about 10^6 Pa with $\nu \approx 1/2$. Let us consider a membrane radius, R, of 2×10^{-2} m and thickness, t, of 10^{-4} m. We shall assume that the system is at atmospheric pressure ($P_0 = 10^5$ Pa) and that $\Delta P_i = 10^2$ Pa-a slight overpressure. This leads to a value of $\lambda = 0.059$. We shall assume an applied load, F, of 10^{-2} N. The various contributions to G may be calculated from Equations (11) to (16). These are given in Figure 2, together with G itself, as a function of contact radius, a. It can be seen that a minimum in G is obtained at $a \approx 7$ mm. Using the same data (where applicable) in Equation (3), we find an equivalent JKR contact radius of $a \approx 0.7$ mm. It can, thus, be seen how the balloon presents a distinct advantage with its greater contact zone. (Although an order of magnitude difference is manifest in this case, in practice it may be better to choose parametric values so that a/R is somewhat smaller).

Nevertheless, it should be noted that for the balloon test to prove advantageous, the overpressure ΔP_i must be relatively small. If we adopt a figure of $\Delta P_i = 10^4$ Pa, a value of a of 0.6 mm results, which is slightly smaller than that found with the JKR system!

With the JKR system it is possible to make F negative and still have adhesion, *i.e.* the applied force tends to separate sphere and

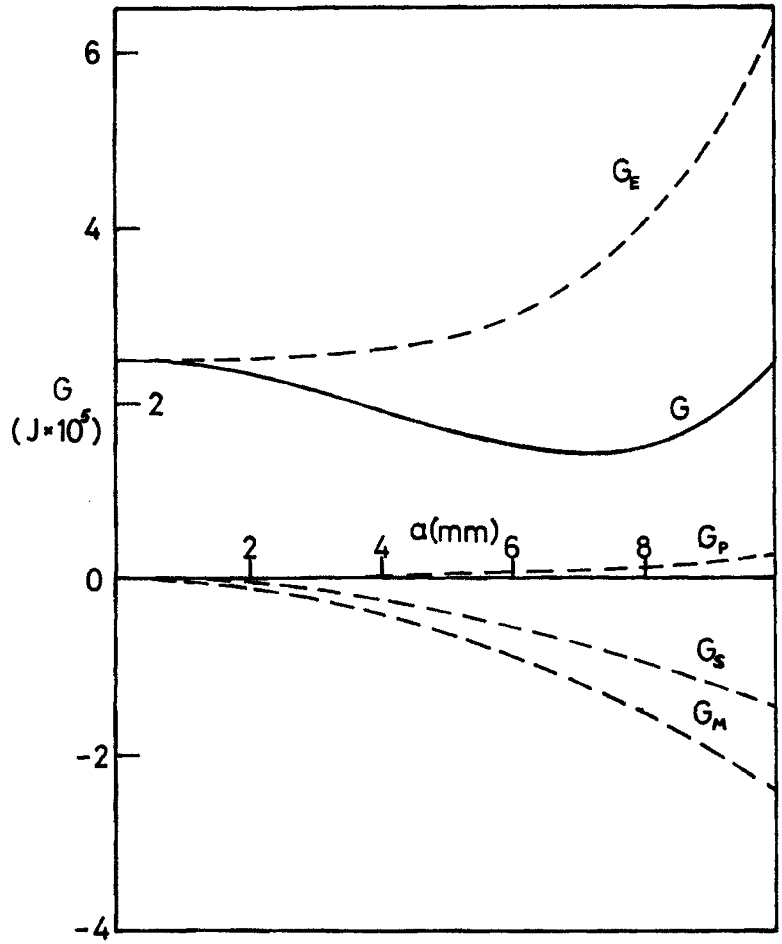


FIGURE 2 Curves of, G, the overall free energy (to within an additive constant) and its various components: G_E, G_P, G_S and G_M, as a function of contact radius, a. Equilibrium corresponds to $a \approx 7$ mm (see text for values of parameters used).

rigid solid, yet, provided F in tension is not too great, contact is maintained. The limiting value of negative F (pull-off force) is well established and given by [11]:

$$F = -\frac{3}{2}\pi R W_0 \tag{21}$$

An equivalent limiting negative force at separation occurs for the balloon/rigid solid and is given by:

$$F = -2\pi R\, W_0 \tag{22}$$

In both cases, the (negative) force at separation is independent of the elastic characteristics of the sphere and, in the case of the balloon, also of the overpressure of gas. [In effect, ΔP_i may be considered to represent "part" of the elastic modulus of the balloon]. Comparison of Equation (21) and (22) shows that the separation force is 33% greater in the case of the balloon test.

It is of interest to consider the equilibrium contact radius, *a*, as a function of force, *F*, for the JKR and balloon/rigid solid systems. This is done in Figure 3, where *a* is on a logarithmic scale. With the exception of (variable) *F*, the same values of the parameters have been used as for Figure 2. It can be seen that, typically, the balloon/rigid solid test gives contact radii *ca.* 10 times larger than for the JKR system, although values of *a* corresponding to *F* greater than *ca.*

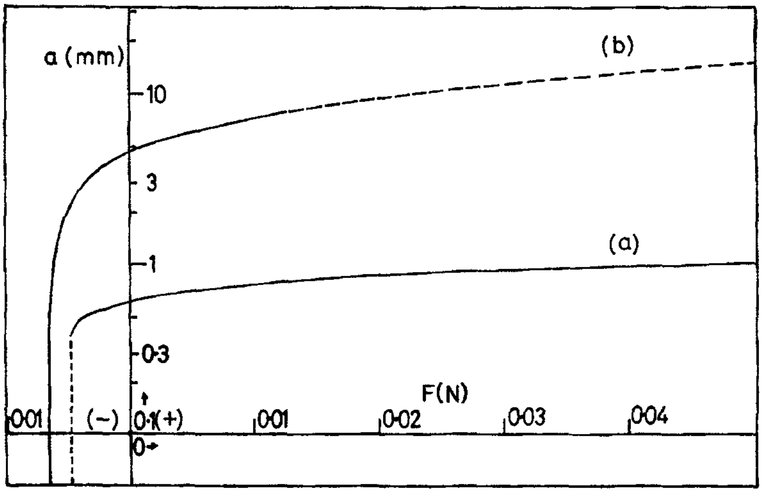


FIGURE 3 Curves of contact radius, *a*, as a function of applied force, *F*, for both (a) the JKR and (b) the balloon/rigid solid systems. The dotted line above $F = ca.$ 0.01 N for (b) indicates that limitations of the theory are being approached, and that for (a) is the (negative) pull-off force.

1.5×10^{-2} N are represented by a dotted line since the hypothesis of $a \ll R$ starts to become doubtful. The pull-off force for JKR is *ca.* -4.7×10^{-3} N and that of the balloon/rigid solid system, *ca.* -6.3×10^{-3} N.

DISCUSSION

The above theory suggests that the use of a hollow, slightly inflated sphere, instead of a full sphere, may be advantageous for contact experiments in the investigation of the (feeble) adhesion between a relatively soft solid, such as an elastomer, and a more rigid material. Although the above theory was aimed specifically at this case, in principle, polymer/polymer adhesion may possibly be evaluated using two inflated spheres in contact with each other. The proposed test has something in common with the well-known blister test [17, 18], commonly used for assessing the adhesion of coatings, in that a fluid under pressure is resisting adhesion. An important difference, however, is that the method presented here considers adhesion on the curved surface of the spherical membrane, whereas the blister test involves separation at the rim of an essentially spherical protrusion of membrane from an otherwise flat coating.

The potential advantages of the proposed method are manifest. A larger contact zone may be expected when a judicious choice of parametric values (dimensions, elastic characteristics and gas overpressure) has been made. This will both render measurement easier and reduce potential errors, the second advantage also being aided by the energy of adhesion scaling essentially with the square, rather than the cube, of the contact radius. In the JKR test, a given elastic sphere has intrinsic surface and bulk properties. With the balloon test, these two are effectively decoupled. Although the surface properties will be intrinsic for a given membrane material, by changing the initial internal overpressure of gas, effectively the elastic, or mechanical, properties of the sphere may be modified. This may be effected by manufacturing a series of spheres of the same material with various initial, internal pressures. Alternatively, by conducting experiments at different temperatures, the same sphere may be used and the product $P_i V_i$ simply changed *via* Charles' law. Such cycles of temperature could perhaps be exploited in order to gain a better understanding of adhesion hysteresis [10, 13, 14].

Nevertheless, the method envisaged could present certain delicate experimental problems. It may not be easy to manufacture the requisite spheres and their clamping during measurements could prove difficult. One possible technique for at least reducing the experimental difficulties of clamping could be to use two identical flat rigid solids parallel to each other and apply these to the spherical membrane, as shown schematically in Figure 4 (as suggested personally to the author by C. Creton). The above theory would have to be slightly modified but this is a trivial affair.

As far as the theory is concerned, we have remained with the same basic school of thought as Johnson, Kendall and Roberts, *i.e.* adhesion forces outside the area of contact are neglected and, thus, stress singularities may exist at the contact edge. Another type of analysis exists, known

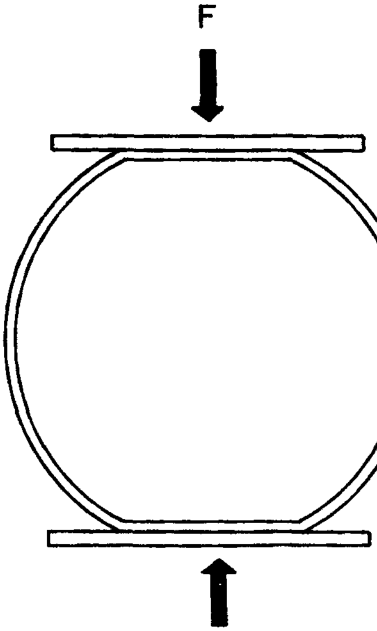


FIGURE 4 Schematic diagram of a possible variant on the simple balloon test, in which two identical flat, rigid solids are applied to "sandwich" the sphere.

as the DMT theory [19], which makes rather different assumptions. Adhesion (long-range forces) outside of the zone of contact are taken into consideration. For a full description of the JKR and DMT models and a theory for the transition between them, the reader is referred to Maugis [20]. In the present context, since we are principally dealing with soft solids, it is believed that the JKR approach is more suitable.

An implicit assumption has been made in the development. It has been taken the state of tension in the membrane will be the same in the contact area as elsewhere on the free membrane. This point is delicate and may well depend on the method of contact. The adhesion itself may impede any modification of the position of the membrane with respect to the flat solid in shear, and this may modify the tension locally. This could potentially have some impact on the fracture mode. The separation front is assumed to behave in mode 1 but the last point, together with the fact that the membrane tension is biaxial, may lead to a contribution in mode 2. (This latter point is also true for the JKR test, especially when $\nu \neq 0.5$.) These problems are not trivial and, for the moment at least, no answers are forthcoming. Nevertheless, use of two identical elastomeric spheres, as suggested above, could alleviate this problem at least to some extent.

Finally, despite the potential drawbacks discussed above, it is believed that the balloon test may well be of use in investigations of fundamental adhesion problems. Clearly, variants on the test are also possible. Apart from the possibility of using two, symmetically disposed, rigid flats, or identical elastomeric spheres, as mentioned above, it may be possible to fill the balloon with an incompressible fluid, *i.e.* a liquid, instead of a gas. Equivalently, a variant of the blister test may be used where interest is concentrated on the apex of the separated blister adhering to an imposed flat solid.

CONCLUSION

The classical theory of Johnson, Kendall and Roberts (JKR) [11] has proved enormously useful over the past decades for the investigation of adhesion, particularly feeble adhesion due to van der Waals forces. Nevertheless, it has drawbacks, notably the dependence of the deduced energy of adhesion on the cube of the contact area between the two adhering spherical surfaces. In this article, a variant of the JKR is suggested in which a hollow, spherical membrane, slightly inflated, is placed in contact with a flat, rigid solid. It is shown that the energy of adhesion scales with the square of contact radius, *a* (at low applied load), and, with a suitable choice of parameters, the contact zone can be relatively large (compared with the equivalent JKR value), thus potentially reducing experimental errors. In addition, by changing the overpressure of the gas within the spherical membrane, or balloon, the effective elastic modulus is varied. The technique, thus, should permit decoupling of surface and bulk effects.

References

[1] Girifalco, L. A. and Good, R. J., *J. Phys. Chem.* **61**, 904 (1957).
[2] Good, R. J. and Girifalco, L. A., *J. Phys. Chem.* **64**, 561 (1960).
[3] Fowkes, F. M., *J. Phys. Chem.* **66**, 382 (1962).
[4] van Oss, C. J., Chaudhury, M. K. and Good, R. J., *Chem. Rev.* **88**, 927 (1988).
[5] Gent, A. N. and Petrich, R. P., *Proc. Roy. Soc. London* **A310**, 433 (1969).
[6] Gent, A. N. and Schultz, J., *J. Adhesion* **3**, 281 (1972).
[7] Andrews, E. H. and Kinloch, A. J., *Proc. Roy. Soc. London* **A332**, 385 (1973).
[8] Maugis, D. and Barquins, M., *J. Phys. D: Appl. Phys.* **11**, 1989 (1978).
[9] Ferry, J. D., *Viscoelastic Properties of Polymers*, 2nd edition (Wiley, New York, 1970), p. 314.
[10] Shanahan, M. E. R. and Michel, F., *Internat. J. Adhesion Adhesives* **11**, 170 (1991).
[11] Johnson, K. L., Kendall, K. and Roberts, A. D., *Proc. Roy. Soc. London* **A324**, 301 (1971).
[12] Carré, A. and Roberts, A. D., *J. Nat. Rubber Res.* **2**, 152 (1987).
[13] Chaudhury, M. K. and Whitesides, G. M., *Langmuir* **7**, 1013 (1991).
[14] Israelachvili, J. N., Chen, Y. L. and Yoshizawa, H., *J. Adhesion Sci. Tech.* **8**, 1231 (1994).
[15] Creton, C., Brown, H. R. and Shull, K. R., *Macromolecules* **27**, 3174 (1994).
[16] Hertz, H., *J. Rein. Angew. Math.* **92**, 156 (1881).
[17] Danneberg, H., *J. Appl. Polymer Sci.* **5**, 125 (1961).
[18] Williams, M. L., *J. Adhesion* **5**, 81 (1973).
[19] Derjaguin, B. V., Muller, V. M. and Toporov, Yu. P., *J. Coll. Interface Sci.* **53**, 314 (1975).
[20] Maugis, D., *J. Coll. Interface Sci.* **150**, 243 (1992).