tion energy should be smaller than $\Delta E_f$ as the kinetic energy is expected to increase below the superconducting state. Taking this into account, we see that the spectral weight of the $\pi$ resonance peak can quantitatively account for the condensation energy measured from $H_c$ and specific-heat experiments, in reasonable agreement with the prediction based on our mechanism.

We now compare our mechanism for HTSC with the spin fluctuation pairing mechanism$^{23-25}$. All these mechanisms are based on the antiferromagnetic exchange interaction $E_I$. Our analysis of the neutron data confirms that a large part of the condensation energy indeed arises from such an exchange interaction$^6$. However, our mechanism differs from the spin fluctuation pairing mechanism, both conceptually and quantitatively. The idea of spin fluctuation pairing is directly borrowed from the phonon-mediated pairing in the traditional BCS superconductors. It requires sizeable antiferromagnetic spin fluctuations in the normal state, in order to pair the Fermi liquid like quasiparticles. In contrast, in our mechanism, the antiferromagnetic spin fluctuations in the normal state do not play an important role in driving superconductivity. In the superconducting state, the $\pi$ resonance can be viewed as a kind of spin fluctuation in a particular frequency and momentum range. From the point of view of the SO(5) theory$^7$, the superconducting state is obtained from the antiferromagnetic state by a rotation, so it is natural to expect it to have more antiferromagnetic correlation than the normal state. The crucial conceptual difference between these two mechanisms therefore lies in the fact that normal state antiferromagnetic spin fluctuations are not required in our mechanism. This conceptual difference has a direct quantitative consequence. From equation (4), we see that the presence of spin fluctuation spectral weight in the normal state contributes negatively to the condensation energy. It is not clear why the spin fluctuation model would predict a change in the frequency-integrated weight of $S(q,\omega)$ near $q = Q$. In fact, most theories of the neutron resonance peak based on the spin fluctuation models$^{26,27}$ assume a pre-existing overdamped spin fluctuation mode in the normal state and only predict a reduction of damping below $T_c$ with essentially conserved weight.

Our mechanism provides a natural explanation for the doping dependence of the condensation energy. We attribute the condensation energy to the difference in exchange energies in superconducting and normal states. More-underdoped materials have considerably more antiferromagnetic correlations in the normal state, as known from neutron scattering$^{28}$. Although in the superconducting state the weight of the resonance is enhanced$^2$, the difference between the normal and the superconducting exchange energies becomes smaller.

This is consistent with the results of Loram et al.$^{30}$ who find a decrease in the condensation energy with decreased doping in $Y_{1-x}Ca_xBa_2Cu_3O_{7+\delta}$. Until this point we have been discussing the relation between the condensation energy and the resonant peaks in neutron scattering at zero temperature. It would be interesting to see whether this idea also works at finite temperature. Without going into details, we would like to point out a striking similarity between the temperature dependence of $H_c$ (ref. 2) and that of the resonance intensity$^{29,31}$ for the underdoped copper oxides: both quantities scale similarly below $T_c$ and both have ‘tails’ extending above $T_c$, presumably arising from significant pairing fluctuations in the pseudogap regime. These phenomena await future investigations.

Received 4 June; accepted 16 September 1998.


In 1773 Coulomb$^*$ recognized that the static properties of granular systems can be discussed in terms of the frictional properties between different layers, leading to his relationship between the angle of repose of a granular pile ($\theta_0$) and the coefficient of static friction $\mu_s$ : $\tan \theta_0 = \mu_s$. Two centuries later, solid friction and granular media still present many puzzles. One such is that the coefficient of static friction depends on the time during which the solids remain in contact before the measurement. Here we show that this ageing effect is manifested too in the angle of repose of granular media and originates from capillary condensation of water vapour between the packed particles, leading to the formation of water bridges. By assuming that the kinetics of this process are governed by the thermally activated nucleation of bridges, we can reproduce both the time- and humidity-dependence of the ageing behaviour. Our results also clarify the kinetics of adsorption in porous media more generally.

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Ageing is said to occur in systems for which the relaxation time becomes so long that it may not reach equilibrium on a laboratory timescale (typically hours). The measured properties of such a system therefore depend on the time at which the measurement is made. This is the case for solid friction: the friction coefficient depends on the time elapsed after the surfaces have come into contact \( t > 1 \). This dependence of \( \mu \) on waiting time is observed with almost all materials (from paper to rocks) and is found universally to be logarithmic. Although solid friction is related to the properties of granular media, as emphasized by Coulomb's analogy, ageing in granular media has previously received little attention.

We have studied the effect of waiting time on the angle of first avalanche \( \theta_w \) of a granular system of small (typically 200-\( \mu \))m spherical glass beads contained in a rotating drum (Fig. 1a). We observe logarithmic ageing of the maximum static angle \( \theta_w \) (Fig. 2a). This logarithmic behaviour spans more than three orders of magnitude in time, ranging from 5 seconds to more than 2 hours. Ageing was not observed for beads with a diameter larger than 0.5 mm, except at very large humidities. It is known that humidity can exert an important influence on granular media. Addition of small quantities of wetting liquid has been shown to change enormously the repose angle of a pile \( \theta^* \); a brief discussion of moisture effects can even be found in Coulomb's treatise. We repeated our experiments at various humidities \( P_v/P_{sat} \) (\( P_v \) and \( P_{sat} \) being respectively the vapour pressure and saturated water pressure), and found humidity to be the crucial parameter controlling the ageing of \( \theta_w \): no ageing is observed at low humidity, and the magnitude of the ageing effect increases dramatically with humidity (Fig. 2b).

This humidity dependence leads to the intuitive idea that the ageing effect originates from the condensation of small liquid bridges between the beads. Liquid bridges induce a significant cohesion between the beads, which can increase the friction between different layers of the granular system and result in a higher value of \( \theta_w \). However, the physical justification for such a dependence of ageing on humidity. a. Logarithmic ageing of the angle of first avalanche. The ageing property is analysed by plotting \( \tan(\theta_w(t)) \) as a function of \( \log(t_w) / \cos(\theta_w) \), for different values of the water vapour pressure \( P_v \) (see equation (3)). The time is in units of seconds. From bottom to top, humidity is: 15\% (triangles), 27\% (pentagons), 36.1\% (squares) and 45.6\% (circles). In these measurements, times range typically over nearly four orders of magnitude. The dotted lines are least-square fits of the experimental data, whose slope is \( \alpha \). b. Variation of the slope \( \alpha \) characterizing the ageing behaviour of the first avalanche angle (see equation (3)) with humidity \( P_v/P_{sat} \). Open symbols, the polydisperse system; filled symbols, the monodisperse system. The dashed line is the theoretical prediction \( \alpha = a_0 \ln(P_{sat}/P_v) \), where \( a_0 = 0.079 \) and \( P_{sat} = 0.68P_{wet} \). The validity of the previous theoretical prediction is best confirmed by the measured linear dependence of \( 1/\alpha \) as a function of \( \ln(P_{sat}/P_v) \) (see inset): in this plot, a linear least-squares fit thus provides unambiguously values of \( a_0 \) and \( P_{sat} \). The lowering observed in the saturating pressure \( P_{sat} \) might be an effect of the long-range attractive forces exerted by the walls, and/or of dissolved species in the condensed water.
behaviour is not so obvious. We consider first the idealized situation of two smooth beads in contact. The capillary adhesion force exerted by a small liquid bridge connecting the beads is given by the product of the liquid surface tension $\gamma$ and the radius of the beads (we note that if solid deformation occurs, the numerical prefactor changes slightly: $F_{\text{adh}} \approx 2\pi\gamma R$, regardless of the size of the (small) bridge$^9$). Therefore, the adhesion force has no humidity-dependence, and moreover would be able to stick all the beads together$^7$. This apparent difficulty disappears if one takes into account the roughness of the beads. The spatial extent of a liquid bridge is controlled by the radius of curvature $r_{\text{eq}}$ of the liquid interface, which, at liquid–vapour equilibrium, is fixed by the Kelvin relation$^{10}$

$$\frac{\gamma}{r_{\text{eq}}} = \rho_l k_B T \ln \frac{P_{\text{sat}}}{P_v} = \rho_l \Delta \mu$$

(1)

where $\rho_l$ is the density of the liquid and $\Delta \mu = k_B T \ln (P_{\text{sat}}/P_v)$ is the undersaturation of the chemical potential. Under ambient conditions, this yields a value of $r_{\text{eq}}$ of nanometre dimensions. A crucial consequence is that liquid bridges are able to form only in nanometre-scale interstices. Because the beads are not smooth at the nanometre scale, the wetted region does not spread over the whole area it would occupy if the beads were smooth, and the cohesive force is reduced in proportion. We also note the slow evolution in time of the cohesive properties, measured through the time-dependence of $\theta_w$. This indicates that the condensation of a liquid bridge occurs from a metastable state; that is, a metastable vapour phase can stay for a long time (of the order of several minutes) between the surfaces, whereas the equilibrium state is a liquid bridge$^{11,12}$.

On the basis of these considerations, we propose a model for the ageing behaviour based on the hypothesis that capillary condensation arises through an activated process. This assumption is justified by the first-order character of capillary condensation. We consider two surfaces separated by a gap, and in contact with undersaturated vapour. A thin wetting film coats both surfaces. For gaps of less than a critical distance, of the order of the Kelvin radius $r_{\text{eq}}$ this state is metastable$^{10}$; capillary condensation should occur. However, an energy barrier has to be overcome, as the coating films have to grow and coalesce in order to fill the gap between the surfaces. Along this path, the free energy of the system increases to a maximum as the films are able to merge$^{11}$. The energy barrier, $\Delta E$, is therefore the free energy cost of condensing the corresponding water volume from the undersaturated vapour phase: $\Delta E \approx \Delta \mu \gamma_0 V$, where $\gamma_0$ is the liquid volume needed to nucleate the liquid bridge. In the case of two rough beads, nucleation occurs preferentially between the asperities and the nucleation volume is $V_0 = \alpha_0 A^2$, where $\alpha_0$ is the gap between the surfaces at the nucleating site and $A^2$ is a typical nucleation area (Fig. 1b). A more sophisticated model taking the long-range forces into account confirms this estimation.

Assuming an activation process, the time $t$ needed to condense a liquid bridge in an interstitial volume is $t \approx t_0 \exp \left(\Delta E / k_B T\right)$, with $t_0$ being a microscopic time. Typically, $t_0$ is of the order of the time needed to condense one liquid layer. Because both beads are rough, many liquid bridges can form in the macroscopic contact region. One expects, moreover, that the nucleating sites will exhibit a broad distribution of gaps $\epsilon$ between solid surfaces, and that the activation times are accordingly widely distributed. After a given time $t_w$, only the bridges with an activation time $t_R$ smaller than $t_w$ have condensed. These were therefore formed at the nucleating sites with a gap $\epsilon$, verifying that $\epsilon < \epsilon_{\text{max}}(t_w) = (k_B T/\Delta \mu) (\rho_l \alpha_0^2)^{-1} \ln (t/t_0)$. Once a liquid bridge has condensed, it fills locally the volume surrounding the nucleating site, until the Kelvin equilibrium condition for the radius of curvature, equation (1), is met. Thus because of roughness, only a fraction $f(t_w)$ of the total wettable area is indeed wetted at a given time $t_w$. This fraction $f(t_w)$ is proportional to the number of activated bridges, yielding (to a first approximation) $f(t_w) \approx \epsilon_{\text{max}}(t_w) \rho_l$. Therefore, the adhesion force is proportional to the width of the distribution of distances between the surfaces. The capillary adhesion force is proportional to the wetted area and is thus reduced by the factor $f(t_w)$ from the perfectly smooth case ($F_{\text{adh}} \approx 2\pi\gamma R$), leading to

$$F_{\text{adh}}(t_w) \approx \gamma d \frac{1}{\ln (P_{\text{sat}}/P_v)} \ln \left(\frac{t_w}{t_0}\right)$$

(2)

where $d = 2\pi R (\rho_l \alpha_0)$ is a distance taking into account the geometrical characteristics of the contact. By reproducing Coulomb’s argument for the stability of the surface layer in the presence of this additional adhesive force$^1$, we obtain the following equation for $\theta_w(t_w)$:

$$\tan \theta_w(t_w) = \tan \theta_0 + \frac{\alpha(P_s)}{\cos \theta_w(t_w)} \log \left(\frac{t_w}{t_0}\right)$$

(3)

where $\alpha(P_s) = \alpha_0 / \ln (P_{\text{sat}}/P_v)$. Here $\alpha_0$ is a dimensionless parameter taking into account the relative strength of the adhesion force and the weight of the material. Thus, by plotting $\tan \theta_w(t_w)$ as a function of $\log (t_w)$, one should obtain a straight line. This expectation is indeed borne out experimentally (Fig. 2a). Moreover, the increase in the slope, $\alpha(P_s)$, of this line with humidity is in good agreement with the theoretical prediction of equation (3) (Fig. 2b).

Our model is thus able to reproduce both the waiting-time- and humidity-dependence of the measured ageing properties of a granular system.

Our results highlight the crucial role of humidity in the statics of granular systems. The similarity between ageing in granular media and ageing of the static friction coefficient in dry friction is reflected in the reported effect of humidity on the friction between rocks$^5$; in that study, the ‘standard’ ageing properties of $\mu_s$ were similarly found to disappear at zero humidity. Similar behaviour has also been observed in indentation experiments$^{13}$. The mechanism previously suggested to explain ageing behaviour in solid friction involves asperity creep$^{14}$; our work suggests that humidity-induced capillary condensation may provide an alternative explanation for this effect.

Received 26 January; accepted 2 September 1998.


Acknowledgements. We thank J.-M. Georges and M.L. Bocquet for discussions. L.B. thanks J. Duran for providing ref. 1.

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