Influence of frozen capillary waves on contact mechanics

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Free surfaces of liquids exhibit thermally excited (capillary) surface waves. We show that the
surface roughness which results from capillary waves when a glassy material is cooled below the
glass transition temperature can have a large influence on the contact mechanics between the solids.
The theory suggest a new explanation for puzzling experimental results [L. Bureau, T. Baumberger
and C. Caroli, arXiv:cond-mat/0510232] about the dependence of the frictional shear stress on the
load for contact between a glassy polymer lens and flat substrates. It also lends support for a recently
developed contact mechanics theory.

Many technological applications require surfaces of solids to be extremely smooth. For example, window
glass has to be so smooth that no (or negligible) diffusive scattering of the light occur (a glass surface with
strong roughness on the length scale of the light wavelength will appear white and non-transparent because of
diffusive light scattering). For glassy materials, e.g., silicate glasses, or glassy polymers, e.g., Plexiglas, extremely
flat surfaces can be prepared by cooling the liquid from well above the glass transition temperature \( T_g \), since in
the liquid state the surface tension tends to eliminate (or reduce) short-wavelength roughness. Thus, float glass
(e.g., window glass) is produced by letting melted glass flow into a bath of molten tin in a continuous ribbon.
The glass and the tin do not mix and the contact surface between these two materials is (nearly) perfectly flat. 
Cooling of the melt below the glass transition temperature produces a solid glass with extremely flat surfaces.
Similarly, spherical particles with very smooth surfaces can be prepared by cooling liquid drops of glassy materi-
als below the glass transition temperature. Sometimes glassy objects are “fire polished” by exposing them to a
flame or an intense laser beam[1] which melt a thin surface layer of the material, which will flow and form a very
smooth surface in order to minimize the surface free energy. In this way, small-wavelength roughness is reduced
while the overall (macroscopic) shape of the solid object is unchanged.

However, surfaces of glassy materials prepared by cooling the liquid from a temperature above \( T_g \) cannot be
perfectly (molecularly) smooth, but exhibit a fundamental minimum surface roughness, with a maximum height
fluctuation amplitude of typically 10 nm, which cannot be eliminated by any changes in the cooling procedure.
The reason is that at the surface of a liquid, fluctuations of vertical displacement are caused by thermally
excited capillary waves (riplons)\[2, 3\]. At the surface of very viscous supercooled liquids near the glass transition
temperature these fluctuations become very slow and are finally frozen in at the glass transition\[2\].

The roughness derived from the frozen capillary waves is unimportant in many practical applications, e.g., in
most optical applications as is vividly evident for glass windows. However, in other applications they may be of
profound importance. In this letter I show that they are of crucial importance in contact mechanics. For elastic
hard solids such as silica glass, already a roughness of order 1 nm is enough to eliminate the adhesion, and re-
duce the contact area between two such surfaces to just a small fraction of the nominal contact area even for high
squeezing pressures\[4\]. In this letter I will show that this is the case even for elastically much more compliant solids
such as Plexiglas (PMMA). The results presented below suggest a new explanation for the puzzling experimen-
tal result of Bureau et al\[5\] for PMMA, and in addition lends support for a recently developed contact mechanics
theory\[6\]. Bureau et al observed that the nominal shear stress \( \sigma \) when a PMMA lens was slid on a flat substrate,
depends strongly on the nominal pressure (or perpendicular stress) \( p_{nom} \). They assumed that perfect (molecular)
contact occurred in the nominal contact area \( A_0 \), and interpreted the experimental results as a strong depen-
dence of the frictional shear stress on the local pressure. However, the analysis below shows that the experimen-
tal results can be understood assuming that the area of real contact \( A \) is smaller than the nominal contact area \( A_0 \),
and assuming a constant (pressure independent) shear stress \( \sigma_i \) in the area of real contact in such away that
the friction force \( F_i = \sigma_i A = \sigma A_0 \) and the normal load \( F_N = pA = p_{nom} A_0 \), where \( p \) is the (average) pressure in
the area of real contact.

The most important property of a rough surface is the surface roughness power spectrum which is the Fourier
transform of the height-height correlation function\[7\]:

\[
C(q) = \frac{1}{(2\pi)^2} \int d^2x \langle h(x)h(0) \rangle e^{-iq \cdot x}
\]

Here \( z = h(x) \) is the height of the surface at the point \( x = (x, y) \) above a flat reference plane chosen so that
\( \langle h(x) \rangle = 0 \). The angular bracket \( \langle \cdot \rangle \) stands for ensemble averaging. The surface roughness power spectra due to
capillary waves is of the form\[8, 9\] (1):

\[
C(q) = \frac{1}{(2\pi)^2} \frac{k_B T}{\rho g + \gamma q^2 + \kappa q^4}
\]
where $\gamma$ is the surface tension, $\kappa$ the bending stiffness, and $\rho$ the mass density of the glassy melt. The smallest relevant wavevector $q = q_0 \approx 2\pi/L$, where $L$ is the diameter of the nominal contact area $A_0$. In the applications below $L \approx 0.1$ mm and (for PMMA) $\gamma \approx 0.04$ J/m², giving $\gamma q^2 > 10^6$ J/m² $\gg \rho g$. Thus, the gravity term in (1) can be neglected. The mean of the square of the surface height fluctuation is given by

$$\langle h^2 \rangle = \int d^2 q \, C(q) = 2\pi \int_{q_0}^{q_1} dq \, qC(q)$$

$$= \frac{k_B T}{\pi^2}\ln \left[ \frac{q_1}{q_0} \left( \frac{q_0^2 + q_c^2}{q_1^2 + q_c^2} \right)^{1/2} \right]$$

(2)

where $q_c = (\gamma/\kappa)^{1/2}$ is a cross-over wavevector. For the polymer surface which interests us below (PMMA), Eq. (2) gives the rms roughness $\approx 0.5$ nm which correspond to a maximum roughness amplitude of about 3 nm. I will now show that even this small roughness has a large influence on the contact mechanics.

![FIG. 1: An elastic (e.g., rubber) block (dotted area) in adhesive contact with a hard rough substrate (dashed area). The substrate has roughness on many different length scales and the rubber makes partial contact with the substrate on all length scales. When a contact area is studied at low magnification ($\zeta = 1$) it appears as if complete contact occurs in the macro asperity contact regions, but when the magnification is increased it is observed that in reality only partial contact occurs.](image)

Recently, a contact mechanics theory has been developed which is valid not only when the area of real contact is small compared to the nominal contact area, but which is particularly accurate when the squeezing force is so high that nearly complete contact occurs within the nominal contact area. All other contact mechanics theories were developed for the case where the area of real contact is much smaller than the nominal contact area. The theory developed in Ref. 6, 10 can also be applied when the adhesional interaction is included.

Fig. II shows the contact between two solids at increasing magnification $\zeta$. At low magnification ($\zeta = 1$) it looks as if complete contact occurs between the solids at many macro asperity contact regions, but when the magnification is increased smaller length scale roughness is detected, and it is observed that only partial contact occurs at the asperities. In fact, if there would be no short distance cut-off, the true contact area would vanish. In reality, however, a short distance cut-off will always exist since the shortest possible length is an atomic distance. In many cases the local pressure at asperity contact regions at high magnification will become so high that the material yields plastically before reaching the atomic dimension. In these cases the size of the real contact area will be determined mainly by the yield stress of the solid.

The stress distribution $P(\sigma, \zeta)$ at the interface when the interface is studied at the magnification $\zeta = L/\lambda$, where $L$ is the diameter of the nominal contact area between the solids and $\lambda$ the shortest surface roughness wavelength which can be detected at the resolution $\zeta$, satisfies the diffusion-like equation

$$\frac{\partial P}{\partial \zeta} = D(\zeta) \frac{\partial^2 P}{\partial \sigma^2}$$

(4)

where

$$D(\zeta) = \frac{\pi}{4} \left( \frac{E}{1 - \nu^2} \right)^2 q_0 q^3 C(q)$$

(5)

where $E$ is Young modulus and $\nu$ the Poisson ratio, and where $q_0 = 2\pi/L$ and $q = \zeta q_0$. The stress distribution function $P(\sigma, \zeta)$ must vanish for $\sigma < -\sigma_a$, where $\sigma_a(\zeta)$ is the highest tensile stress possible at the interface when the system is studied at the magnification $\zeta$. Substituting (1) in (4) gives

$$D(\zeta) = \frac{k_B T}{16\pi\gamma} \left( \frac{E q_0}{1 - \nu^2} \right)^2 \frac{\zeta}{1 + \zeta^2 (q_0/q_c)^2}$$

(6)

If one assume, as is expected from the theory of cracks, that the (tensile) stress diverge as $r^{-1/2}$ with the distance $r$ from the boundary line between a contact island and the surrounding non-contact region, then one can easily prove the boundary condition $P(-\sigma_a(\zeta), \zeta) = 0$. When the adhesion is neglected $\sigma_a = 0$ and $P(0, \zeta) = 0$. The (normalized) area of (apparent) contact when the system is studied at the resolution $\zeta$ is given by

$$\frac{A(\zeta)}{A_0} = \int_{-\sigma_a(\zeta)}^{\infty} d\sigma \, P(\sigma, \zeta)$$

(7)

where $A_0$ is the nominal contact area. The area of real contact is obtained from (7) at the highest (atomic) resolution, corresponding to the magnification $\zeta_1 = L/a$, where $a$ is an atomic distance.
The detachment stress $\sigma_a$ can be determined using the theory of cracks which gives

$$\sigma_a(\zeta) \approx \left( \frac{\gamma_{\text{eff}}(\zeta) E q}{2(1-\nu^2)} \right)^{1/2}$$  \hspace{1cm} (8)

Here $\gamma_{\text{eff}}(\zeta)$ is the (effective) interfacial binding energy when the system is studied at the magnification $\zeta$. At the highest magnification (corresponding to atomic resolution) $\gamma_{\text{eff}} = \Delta \gamma$, where $\Delta \gamma = \gamma_1 + \gamma_2 - \gamma_{12}$ is the change in the energy (per unit area) when two flat surfaces of the solids are brought into adhesive contact. An explicit expression for $\gamma_{\text{eff}}$ is given in Ref. [10].

In the experiment by Bureau et al. [2], the PMMA lens was prepared by cooling a liquid drop of PMMA from 250 $^\circ$C to room temperature. In the liquid state the surface fluctuations of vertical displacement are caused by thermally excited capillary waves (ripplons). When the face fluctuations of vertical displacement are caused by solids into adhesive contact. An explicit expression for $\gamma_{\text{eff}}$ is given in Ref. [10].

The (upper) solid line in Fig. 2 shows the calculated relative contact area as a function of the (nominal) pressure $p_{\text{nom}} = F_S / A_0$ (where $F_S$ is the squeezing force). In the calculation we have used the equations above with the measured elastic (Young) modulus $E = 2.9$ GPa and surface tension $\gamma = 0.04$ J/m$^2$. We have also used the glass transition temperature $T_g \approx 370$ K, the short-distance cut-off wavevector $q_1 = 7 \times 10^9$ m$^{-1}$ and $q_c = 1.7 \times 10^9$ m$^{-1}$. The cross-over wavevector $q_c$ (or the bending stiffness $\kappa$) has not been measured for PMMA, but has been measured for other systems. Thus, for alkanes at $T \approx 100$ $^\circ$C for C20 and C36, $q_c \approx 4.4 \times 10^9$ and $\approx 2.7 \times 10^9$ m$^{-1}$, respectively [12]. There are also some studies of polymers [16, 17] (using the atomic force microscope) giving $q_c \approx 1 \times 10^8$ m$^{-1}$. The interfacial binding energy $\Delta \gamma$ can be estimated using [18] $\Delta \gamma \approx 2(\gamma_1 \gamma_2)^{1/2} \approx 0.07$ J/m$^2$, where $\gamma_1 = \gamma \approx 0.04$ J/m$^2$ is the surface energy of PMMA and $\gamma_2 \approx 0.02$ J/m$^2$ the surface energy of the (passivated) substrate. In the calculations we used $\Delta \gamma = 0.06$ J/m$^2$.

If one assumes that, in the relevant pressure range (see below), the frictional shear stress $\sigma_f$ between PMMA and the substrate is essentially independent of the normal stress $p$ in the asperity contact regions, then the calculated curve in Fig. 2 is also the ratio between the nominal (or apparent) shear stress $\sigma$ and the true stress $\sigma_t$; $A/A_0 = \sigma / \sigma_t$ (note: the friction force $F_1 = \sigma_t A = \sigma A_0$).

The circles and squares in Fig. 2 show the measured data of Bureau et al. [2] for $\sigma/\sigma_t$. They performed experiments where a PMMA lens, prepared by cooling a liquid drop of PMMA, was slid on silicon wafers (which are nearly atomically smooth) covered by a grafted silane layer. Two different types of alkylysilanes were employed for surface modification, namely a trimethylsilane (TMS) and octadecyltrichlorosilane (OTS). The circles in Fig. 2 are the shear stress, divided by $\sigma_t = 50$ MPa, for PMMA sliding on TMS as a function of the (nominal) pressure $p_{\text{nom}}$. The shear stress $\sigma_t = 50$ MPa was deduced from multi-contact experiments [10] (where the local pressure in the asperity regions is so high as to give rise to local plastic deformation) using $\sigma_t \approx \sigma H / p_{\text{nom}}$, where $H \approx 300$ MPa is the hardness (yield stress) of PMMA as determined from indentation experiments. This equation follows from $\sigma A_0 = \sigma_t A$ and $AH = A_0 p_{\text{nom}}$. The squares in Fig. 2 show $\sigma/\sigma_t$ for PMMA sliding on OTS as a function of the (nominal) pressure $p_{\text{nom}}$. For this system no multic和平ctact experiments were performed, and we have divided the apparent shear stress by $\sigma_t = 5$ MPa, chosen so as to obtain the best agreement between the theory and experiment. Hence, in this case $\sigma_t$ represent a theoretically predicted shear stress for the multic和平ctact case; we suggest that multic和平ctact experiments for the system PMMA/OTS are performed in order to test this predic-
tion.

The calculation presented above shows that the local pressure in the asperity contact regions is of order $\sim 2$ GPa, which is much higher than the macroscopic yield stress (about 300 MPa) of PMMA. However, nanoscale indentation experiments[21] have shown that on the length scale ($\sim 10$ nm) and indentation depth scale ($\sim 1$ nm) which interest us here, the indentation hardness of PMMA is of order $\sim 10$ GPa, and no plastic yielding is expected to occur in our application.

The study above has assumed that the frictional shear stress at the PMMA-substrate interface is independent of the local pressure $p$, which varies in the range $p \approx 50 - 100$ MPa. This result is expected because the shear stress will in general exhibit a negligible pressure dependence as long as $p$ is much smaller than the adhesional pressure $p_{ad}$. The adhesional pressure is defined as follows: In order for local slip to occur at the interface, the interfacial molecules must pass over an energetic barrier of magnitude $\delta \epsilon$. At the same time the spacing between the surfaces must locally increase with a small amount (some fraction of an atomic distance) $\delta h$. This correspond to a pressure work $pa^2\delta h$, where $a^2$ is the contact area between the molecule, or molecular segment, and the substrate. Thus the total barrier is of order $\delta \epsilon + pa^2\delta h = a^2\delta h(p_{ad} + p)$ where $p_{ad} = \delta \epsilon / (a^2\delta h)$. For weakly interacting systems one typically have[21] $\delta \epsilon / a^2 \approx 1$ meV$/$Å$^2$ and $\delta h \approx 0.01$ Å giving $p_{ad} \approx 10$ GPa, which is at least one order of magnitude larger than the pressures in the present experiment. We note that the pressure $p_{ad}$ is similar to the pressure $p$ which must be applied before the viscosity of liquid hydrocarbon oils start to depend on the applied pressure. The reason for the pressure dependence of the viscosity of bulk liquids is similar to the problem above, involving the formation of some local “free volume” (and the associated work against the applied pressure) in order for the molecules to be able to rearrange during shear.

To summarize, I have shown that the surface roughness which result from capillary waves when a glassy material is cooled below the glass transition temperature can have a large influence on the contact mechanics between the solids, even for relatively (elastically) soft solids such as PMMA. This fact suggest a new explanation for puzzling experimental results about the dependence of the frictional shear stress on the load for contact between a PMMA lens and flat passivated silica substrates. It also lend support for a recently developed contact mechanics theory.

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$\delta \varepsilon / a^2$ and the adhesion pressure would be about 1 order of magnitude smaller than for TMS. This analysis does not take into account that the (measured) shear stress $\sigma_i$ involves \textit{thermally-assisted} stress-induced dissipative events (i.e., $\sigma_i$ would be larger at lower temperatures), so the estimation of $\delta \varepsilon / a^2$ is a lower bound.