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Friction between two misoriented crystalline monolayers

Pierre-Gilles de Gennes

Institut Curie recherche, 26, rue d'Ulm, 75231 Paris cedex 05, France

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Abstract

Friction between two ideal single crystals is expected to be very small if there is an incommensurate orientational mis-setting θ between the crystals (provided that the interlayer couplings are small). We consider here a different case: two identical *monolayers* (of materials such as MoS_2 or graphite) in ideal conditions (high purity; high vacuum; no dislocations in both layers).

Two dimensional crystals have anomalous fluctuations, analyzed long ago by B. Jancovici. The Bragg reflections are not sharp, but diffuse. The X-ray (or neutron) scattering near the nominal Bragg peaks is singular, and dominated by multiphonon processes. Incorporating this form of dynamics, we construct a scaling prediction for the viscous friction stress expected at slow relative velocities V. It is predicted to be *very large*! This conclusion would also hold for *one* monolayer facing a bulk crystal. Our discussion is qualitative (ignoring all numerical coefficients) but relatively simple. ***To cite this article: P.-G. de Gennes, C. R. Physique 7 (2006).***

Résumé

Friction entre deux monocouches cristallines d'orientations différentes. La friction entre deux cristaux de graphite (quand l'un des cristaux a tourné par rapport à l'autre d'un angle θ) est connue pour être faible. Nous discutons ici un cas différent : celui de deux *monocouches* graphitiques, dans des conditions idéales (pureté, ultravide, pas de dislocations préexistantes dans une couche).

Un cristal à deux dimensions a des fluctuations géantes, analysées jadis par B. Jancovici. La diffusion X n'a plus de pics de Bragg, mais des réflexions diffuses, dominées par des processus multiphonons. Or, un système désordonné a souvent un coefficient de frottement élevé. Nous construisons des lois d'échelle pour la friction visqueuse (à basse vitesse V) dans la situation décrite par Jancovici ; la friction s'avère effectivement forte. Il en serait de même pour un cristal opposé à une seule monocouche. ***Pour citer cet article : P.-G. de Gennes, C. R. Physique 7 (2006).***

Keywords: Misoriented crystalline monolayers; Viscous friction stress

Mots-clés : Monocouches cristallines d'orientations différentes ; Friction visqueuse

E-mail address: pgg@curie.fr (P.-G. de Gennes).

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Deux cristaux de graphite (tournés l'un par rapport à l'autre d'un angle θ) engendrent, au plan graphitique de contact, une structure incommensurable. Si les interactions interplans sont au-dessous d'un certain seuil, les deux cristaux sont « découplés » et on attend seulement une faible friction visqueuse.

Nous discutons ici un cas différent (et plutôt académique) : celui de deux monocouches graphitiques. La couche du haut glisse à une vitesse $\vec{V}$ sur celle du bas. Elle crée un potentiel sinusoïdal de vecteur d'onde $\vec{\tau}_+$ (où $\vec{\tau}_+$ est un vecteur du réseau réciproque de la couche supérieure). Ceci engendre une perturbation mécanique sur la couche du bas, modulée à la fréquence $\Omega = \vec{V}.\vec{\tau}_+$. Il en résulte des émissions (ou absorptions) de phonons dans la couche du bas. Avec des cristaux *massifs*, ces processus seraient sévèrement limités par les règles de conservation (sur le vecteur d'onde et la fréquence). Mais avec des *monocouches* bidimensionnelles, on a affaire à des fluctuations *géantes* (analysées jadis par B. Jancovici) et à des procesus multiphonons importants. En construisant les fonctions de réponse dynamiques associées à ces fluctuations géantes, on arrive à une estimation de la friction (omettant tous les coefficients numériques) : la friction prédite est *forte*.

1. Superlubrication

Certain crystals (graphite, MoS_2, ...) have strong compact layers, but weak interlayer interactions. We put two such crystals into contact, through their compact layers, after having rotated one of them by a certain angle θ ('mis-setting').

The measured friction between 'up' and 'down' crystals has been found to be weak [1–6] if the situation is truly ideal (no impurities on the contact planes, imposing high vacuum; no dislocations in the bulk crystals). This low friction is often described by the (slightly misleading) word 'superlubrication'.

On the theoretical side, there is a wide spectrum of possibilities:

(a) For some (very rare) choices of θ the compact planes 'up' and 'down' may be commensurate with some large common unit cell: then we expect solid friction, with a threshold stress inversely proportional to the area of the common cell.
(b) Usually, the two faces are incommensurate. They tend to build up two orthogonal sets of screw dislocations (in the contact plane), first discussed by F.C. Frank [7]. The resulting behaviour depends on the mis-setting θ and on the strength of the interlayer interactions. The two limiting cases are:
   (i) *decoupling*, when $\theta \lesssim U_1/U_L$, where U_1 (U_L) are interlayer (intralayer) interactions. Here, the dislocations are spread out ('infinitesimal'). The 'up' and 'down' crystals are essentially unperturbed.
   (ii) *strong coupling* ($\theta > U_1/U_L$): here the infinitesimal dislocations cluster into quantized dislocations of finite Burgers vector. Strong coupling leads to solid friction even if the dislocation pattern is incommensurate with the crystal lattices.

A recent review on these general features is in press (J. Friedel, P.-G. de Gennes, Phil. Mag.). In the present text we focus on the decoupled regime, which is probably realised with strong layers like graphite or MoS_2.

In the decoupled regime we expect to observe mainly a viscous friction: the 'up' crystal creates a perturbing potential $U_1 \exp(i\vec{\tau}_+\vec{r})$ on the lower surface, where $\vec{\tau}_+$ is a (short) reciprocal lattice vector of 'up'. Sliding at slow velocity $\vec{V}$ induces a time modulation of the perturbation at the (low) frequency $\Omega = \vec{\tau}_+ \cdot \vec{V}$. This leads to the emission of phonons in the region 'down', and was analysed long ago [8,9].

(i) One phonon processes are severely limited by the conservation of energy and momentum. There are at most 3 phonon modes which can resonate: they do not form a continuous spectrum and can lead to no dissipation.
(ii) Two phonon processes (Raman) allow for more flexibility, and lead to some damping.

In the present Note, instead of two crystals we consider two *monoatomic sheets* (e.g.: two graphitic planes) with no solid support in the region of contact. It is difficult to realize this, but one possible set up is shown on Fig. 1. The sheet-sheet friction should be anomalous, because two dimensional crystals have giant fluctuations, analysed long

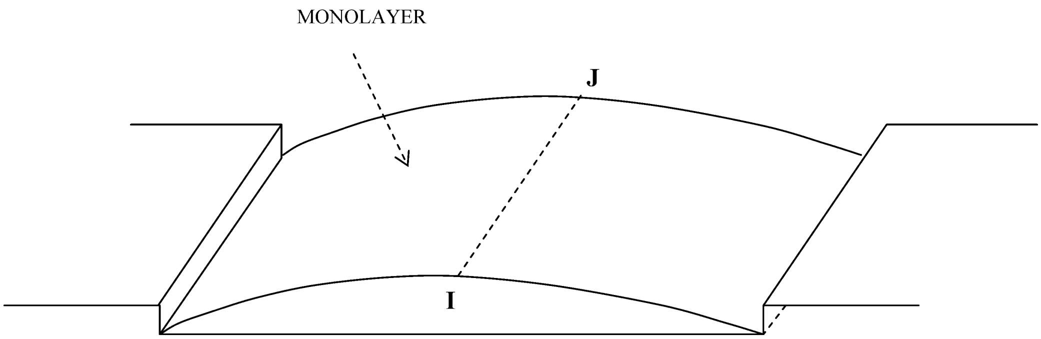

Fig. 1. A tentative set up for the study of friction between two graphite monolayers. One layer (shown on the figure) is slightly bent. The other layer (not shown) is horizontal and is brought into contact with the first along the line IJ. A similar (and possibly simpler) set up would be based on two layers bent into cylinders (the macroscopic analog of a nanotube).

Fig. 1. Un montage (de principe) permettant de mesurer la friction entre monocouches de graphite. Chaque couche est courbée par un système compressif comme le montre la figure (qui n'exhibe qu'une des deux couches). La deuxième couche serait déformée vers le bas, tournée par rapport à la première, et appliquée au-dessus d'elle. Un autre montage consisterait à enrouler chaque monocouche en forme de cylindre (l'analogue macroscopique d'un nanotube).

ago by B. Jancovici [10]. There are no sharp Bragg peaks: they are replaced by a diffuse peak. The static correlation function $S(\vec{k})$ for a wave vector $\vec{\tau}+\vec{k}$ ($\vec{\tau}=$ reciprocal lattice vector, k small) has the form

$$S(\vec{k}) = const \frac{1}{(ka)^{2-m}} \tag{1}$$

$$m = \frac{k_B T}{2\pi M c^2}(\tau a)^2 \tag{2}$$

where a is a unit cell size, M is the mass of the unit cell, c is a sound velocity, and $k_B T$ is the thermal energy.

We know that disordered surfaces lead to strong frictions [11]: thus we may expect that the large fluctuations described by Eq. (1) will increase the friction. This is confirmed in the next section: with free monolayers, we do not expect superlubricity.

2. Scaling estimates of the layer-layer friction

We consider the dissipation $T\mathring{S}$ in the bottom sheet due to a sliding potential of the top sheet $U_1 \exp(\mathrm{i}\vec{\tau}_+.\vec{r} + \vec{\tau}_+ \cdot \vec{V}t)$. Following the arguments of Sacco, Sokoloff and Widom [8], we find (per unit contact area):

$$T\mathring{S} \cong \frac{(U_1)^2}{a^2}\frac{\Omega^2}{k_B T} S(\vec{k}, \Omega) \tag{3}$$

where $S(\vec{k}, \Omega)$ is the dynamic structure factor of the bottom layer, with a vector $\vec{k} = \vec{\tau}_+ - \vec{\tau}_-$ ($k \cong \tau\theta$) and a frequency $\Omega = \vec{\tau}_+ \cdot \vec{V}$. We are interested in low velocities V and low frequencies Ω. Ideally $S(\vec{k}, \Omega)$ could be measured by neutron inelastic experiments. Eq. (3) ignores all numerical coefficients. The calculation of $S(\vec{k}, \Omega)$ is an extension of the Jancovici argument. The time Fourier transform of $S(\vec{k}, \Omega)$ is

$$S(\vec{k}, t) = \frac{1}{N}\sum_{i\ j} \mathrm{e}^{\mathrm{i}\vec{\tau}_-.\vec{R}_j} \langle \mathrm{e}^{\mathrm{i}\vec{k}[\vec{u}_i(t)-\vec{u}_j(0)]} \rangle \tag{4}$$

where $\vec{u}_i$ is the displacement of unit (i) and N is the overall number of units. Since the variables are (coupled) Gaussian variables, we have $\langle \mathrm{e}^{\mathrm{i}\vec{k}[\vec{u}_i(t)-\vec{u}_j(0)]} \rangle = \exp -\frac{1}{2}k^2 \langle \vec{u}_i(t) - \vec{u}_j(0)^2 \rangle$. Performing the integral over phonon modes as in Ref. [10], we arrive at an approximate interpolation formula

$$S(k, t) \cong \int \frac{R\,\mathrm{d}R}{a^2} \exp(\mathrm{i}\vec{k}.\vec{R}) \left(\frac{a}{ct+R}\right)^m \tag{5}$$

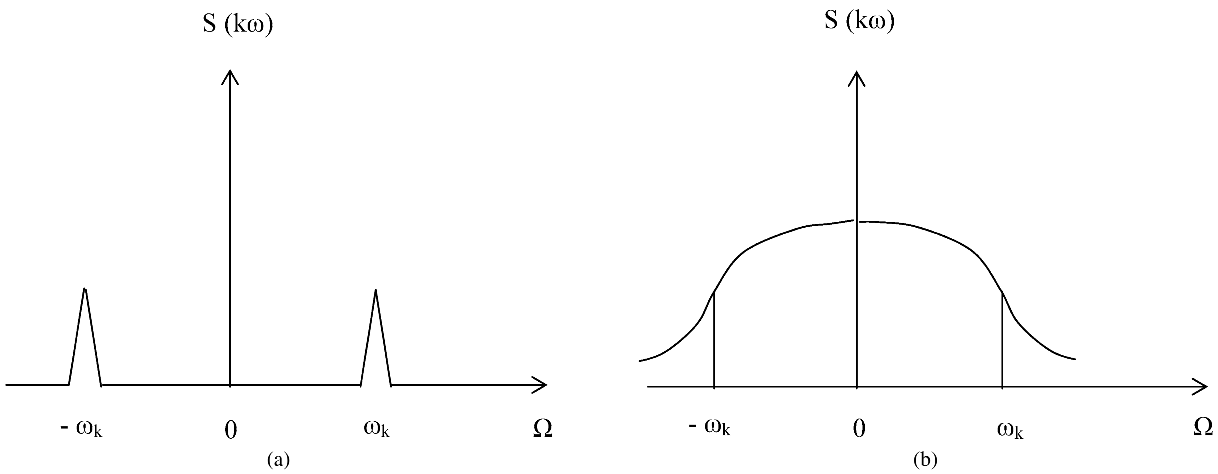

Fig. 2. Frequency spectrum of the density fluctuations at a fixed wave vector (k): (a) For a 3-dimensional solid the dominant feature is a one phonon peak at a frequency ω_k. (There is also a small 2 phonon contribution for a 2-dimensional monolayer distributed over all frequencies—not shown here.) (b) For a 2-dimensional monolayer we expect a broad central peak, of width $\sim\omega_k$.

Fig. 2. Spectre de fréquence des fluctuations de densité à un vecteur d'onde k fixé. (i) À 3 dimensions, on a un pic à $\pm\omega_k$ (1 phonon), plus un faible fond continu. (ii) À 2 dimensions, on attend un pic central large (d'une largeur $\sim\omega_k$).

We constructed Eq. (5) by looking at the two extreme cases: (i) static $(ct = 0)$; (ii) long times $(ct \gg R)$

$$S(kt) = \begin{cases} S(k), & (\omega_k t) < 1 \\ S(k)/(\omega_k t)^m, & (\omega_k t) > 1 \end{cases} \tag{6}$$

where $\omega_k = ck$ is the phonon frequency associated with wave vector k.

The Fourier transform $S(k, \Omega)$ plotted at fixed k versus Ω is a broad line of width $\sim \omega_k$, very different from what we have classically in a 3d crystal, within the one phonon approximation (Fig. 2). This is clearly a multiphonon effect.

Thus, for $\Omega < \omega_k$

$$S(k\Omega) \cong \frac{1}{\omega_k} S(k) \tag{7}$$

We can then write the dissipation $T\mathring{S} = \sigma V$ (where σ is the friction stress) in the form

$$T\mathring{S} \cong a^{-2}|U_1|^2\left(\vec{\tau}_+.\vec{V}\right)^2 \frac{2}{k_B T} S\left(\vec{k}\right)\frac{1}{\omega_k} \quad (\Omega < \omega_k) \tag{8}$$

giving a friction stress

$$\sigma = \sigma_1 \frac{cV}{v_{\text{th}}^2} \theta^{-3+m} \tag{9}$$

where

$$\sigma_1 = U_1^2/Mc^2 a^{-3} \tag{10}$$

$$M v_{\text{th}}^2 = k_B T \tag{11}$$

3. Discussion

For a general presentation of the orders of magnitude in friction, our reader may be referred to Refs. [13,14].

(1) Let us estimate the order of magnitude of the viscous friction stress σ at a velocity $V = 100$ microm./s for a pair of *hard* layers.
We choose:
- $U_1/Mc^2 \equiv$ (interlayer/intralayer interactions) $= 0.1$;

- $Mc^2 = 5$ eV;
- $m \cong 10^{-3} \cong 0$;
- $\theta = 0.1$ radians;
- $v_{th} = 300$ m/s.

This would correspond to $\sigma_1 \sim 10^4$ atm, and $\sigma = 10^2$ atm. Thus the predicted friction is high!

(2) Can we extend the argument to systems thicker than a monolayer? Here are a few remarks:
  (a) A monolayer in good contact with a solid support will be stiffened by the support, and the Jancovici fluctuations will be suppressed. Thus, the adsorbed layers discussed by M. Robbins and coworkers [15] do not belong to our discussion.
  (b) A nanotube lying on a solid surface will also be stiffened. Also the phonon modes running around a circular section are quantized, and this tends to reduce the friction.
  (c) In a free n layer system the Jancovici exponent m of Eq. (2) is divided by n.

(3) An analogy may be mentioned at this point. Experiments on the inelastic scattering of neutrons in a *liquid* (measuring $S(Q, \Omega)$ as a function of ω for a fixed wave vector Q) show that the frequency distribution is *narrow* near the static scattering peak ($Q = \tau_-$). This was predicted nearly 50 years ago by the present author [12]. In the two-dimensional crystals, a form of narrowing is also present (the width $\omega_k \to 0$ when $k \to 0$). However, the Lorentzian form of $S(q\omega)$ used in [12] is not correct for the present purposes: as shown by Eq. (6) there are singular power laws in $S(qt)$.

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References

[1] C. Mate, G. McClelland, R. Erlandsson, S. Chiang, Phys. Rev. Lett. 59 (1987) 1942.
[2] J. Ruan, B. Bhushan, J. Mat. Res. 8 (1993) 3019.
[3] U. Schwarz, O. Zworner, P. Koster, E. Wiesendanger, Phys. Rev. B 56 (1997) 6987.
[4] M. Dienwiebel, G. Verhoeven, N. Pradeep, J. Frenken, J. Heimberg, H. Zandbergen, Phys. Rev. Lett. 92 (2004) 126101.
[5] A. Socoliuc, R. Bennewitz, E. Gnecco, E. Meyer, Phys. Rev. Lett. 92 (2004) 134301.
[6] Consult the sessions on superlubrication in "Proceedings of World Tribology Congress III" (Washington, September 13–16, 2005). CD ROM available from ASME, ISBN 0-7918-3767-X, Order no I734CD (2005).
[7] F.C. Frank, in: Proc. Pittsburgh Conf. ONR, Office of Naval Research 2 (1949) 542.
[8] J. Sacco, J. Sokoloff, A. Widom, Phys. Rev. B 20 (1979) 5071.
[9] J. Sokoloff, Phys. Rev. B 42 (1990) 760;
See also: J. Sokoloff, Phys. Rev. B 42 (1990) 6745.
[10] B. Jancovici, Phys. Rev. Lett. 19 (1967) 20.
[11] B. Persson, Sliding Friction, second ed., Springer-Verlag, Berlin, 2000.
[12] P.-G. de Gennes, Physica 25 (1959) 825.
[13] J. Krim, Comments Cond. Matt. Phys. 17 (1995) 263.
[14] J. Krim, Science 500 (2002) 741.
[15] M. Muser, L. Wenning, M. Robbins, Phys. Rev. Lett. 86 (2001) 1295.