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Simulations of the temperature dependence of static friction at the N_2/Pb interface

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Abstract

A molecular dynamics approach for studying the static friction between two bodies, an insulator and a metal, as a function of the temperature is presented. The upper block is formed by N_2 molecules and the lower block by Pb atoms. In both slabs the atoms are mobile. The interaction potential in each block describes properly the lattice dynamics of the system. We show that the lattice vibrations and the structural disorder are responsible for the behaviour of the static friction as a function of the temperature. We found that a large momentum transfer from the Pb atoms to the N_2 molecules misplaces the N_2 planes in the proximity of the interface. Around $T = 20$ K this effect produces the formation of an hcp stacking at the interface. By increasing the temperature, the hcp stacking propagates into the slab, toward the surface. Above $T = 25$ K, our analysis shows a sharp, rapid drop of more than three order of magnitude in the static friction force due to the misplacing of planes in the stacking of the fcc(111) layers, which are no longer in the minimum energy configuration. Above $T = 35$ K, we also observe a tendency for the splitting of planes and the formation of steps near the surface. By increasing the temperature we obtain the subsequent melting of the N_2 slab interface layer at $T = 50$ K. The temperature behaviour of the calculated static friction is in good agreement with recent measurements made with the quartz crystal microbalance (QCM) method on the same system.

1. Introduction

The microscopic study of friction is now becoming an important part of surface science [1] thanks to the developments in the last 20 years of many experimental techniques such as atomic force microscopy [2], friction force microscopy [3], the surface force apparatus [4] and the quartz crystal microbalance [5]. These apparatus permit us to study the friction at the microscopic level. Simultaneously, the development of fast computers allows us to study very large and realistic three-dimensional systems at the atomic scale [6–9]. The microscopic

interactions that give rise to macroscopic friction between two sliding blocks involve many physical phenomena, such as interactions due to phonons, to electrons and to the morphology of the two surfaces.

In this paper we present a three-dimensional molecular dynamics simulation of the static friction force per atom, F_s, as a function of the temperature. The system that is studied consists of two solid blocks: the top body and the bottom body. The frictional properties are investigated by considering the lattice dynamics of both the upper block and the lower block. In particular, we want to show that the release of the generally used assumption of a rigid bottom block produces a large change in the static friction, F_s. We will use two thick slabs to describe properly the lattice dynamics anharmonic effects of two semi-infinite systems.

In our model study, we will consider a thick slab of an insulator, such as N_2, on a metal substrate, such as Pb, because the interaction of the two surfaces is strong. In this way we can better evidence the role played by the phonons of the lower block on the top block's frictional behaviour. This system has been studied experimentally by Dayo *et al* [10], by Renner [11] and recently by Mistura *et al* [12].

In our molecular dynamics study we will use a model potential, so that the electronic contribution to friction is not taken into account. However, we can study in detail the phonon interaction of the two substrates and the effect of the disorder of the two surfaces.

The paper is organized as follows: in section 2 we describe the construction of the combined system formed by 24 (111) planes of Pb and 12 (111) planes of N_2. The molecular dynamics procedure for obtaining the equilibrium configuration of the two blocks at $T = 0$ K is also presented. The potentials for the Pb–Pb, N_2–N_2 and Pb–N_2 interactions are discussed. In the subsequent section 3 we present the procedure for determining the static friction force (F_s) suitable for a molecular dynamics (MD) calculation. F_s is derived for several values of the temperature. The behaviour of F_s as a function of temperature is interpreted in terms of the disorder of the upper block. The effects of the vibrations present in the lower block are also discussed. In the final section 4 we draw conclusions.

2. The model

The system is composed of a lower block formed by 24 (111) layers of Pb. The three bottom layers are held fixed to simulate a semi-infinite crystal. The interaction potential is described by the embedded atom method [13], whose parameters are fitted to *ab initio* calculations [14]. The parameters are determined to match the experimental properties of bulk Pb, such as density, cohesive energy, compressibility, elastic constants and phonon dispersions. We consider a simulation cell of 200 atoms per layer and we impose the periodic boundary conditions to the layers of the slab normal to the (111) direction. We have found that this slab of 24 layers is sufficient to describe the bulk crystal static and dynamic properties.

The N_2 slab is formed by a stacking of 12 (111) planes, with a simulation cell of 128 atoms per layer. The N_2 molecules in the present study are taken with spherical symmetry and interact via a Lennard-Jones (LJ) potential. The collision parameter σ and the well depth ϵ of the LJ potential are taken to reproduce the gas properties. Their values are $\sigma = 3.86$ Å and $\epsilon = 9.7$ meV. With this potential the melting temperature of the N_2 slab is about 65 K, which is close to the experimental value of 70 K. Periodic boundary conditions are also imposed to the N_2 slab in the planes normal to the (111) direction.

The interaction between N_2 and Pb atoms is not well known. For simplicity, we use a Lennard-Jones potential, whose parameters are chosen by taking as a guide the interaction of the N_2 molecules adsorbed on the Ag(111) surface, which is a similar system to that previously studied in [15, 16]. In this system the physisorption energy is about 110 meV and the vibration

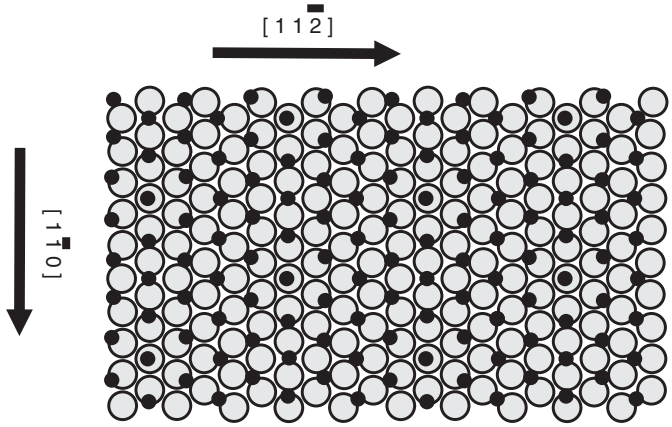

Figure 1. The top view of the interface N_2/Pb in the equilibrium configuration. Open grey circles indicate Pb atoms and black dots represent N_2 molecules. The applied forces are along the $[1\bar{1}0]$ direction.

frequency of N_2 is 8 meV. We have performed a best fit of σ and ϵ to these quantities, obtaining $\sigma = 2.23$ Å and $\epsilon = 31.90$ meV.

We then put in contact the two blocks in a global simulation cell with periodic boundary conditions in the plane normal to the (111) direction consistent with the previous ones.

We equilibrate the system by using a Parrinello–Rahman simulation of 0.4 ns with a time step of 1.47 fs. We start from a temperature of a few kelvin and, during the successive MD cycles, we perform quenching for a total simulation time of 6.0 ns, reducing the kinetic energy of the system to get as close as possible to 0 K. After this procedure, a second run of 0.3 ns is then performed without temperature control. Since in this second run the kinetic energy of the whole system remains very close to zero, we conclude that the N_2/Pb system has reached the equilibrium configuration. In this run we obtain an average N_2–N_2 distance of 5.66 Å. This distance is similar to that found by Bruch in [15]. The interplane distance at the interface between the N_2 and Pb layers is $d = 1.56$ Å. The N_2 molecules form an hexagonal structure slightly distorted in both the $[1\bar{1}0]$ and $[11\bar{2}]$ directions, as illustrated in figure 1.

The corrugation of the interface is presented in figure 2, where we have drawn the interaction N_2–Pb potential at the equilibrium distance $z(R)$ at which the normal component of the gradient of the potential vanishes. One notices that the maximum value of the corrugation is about 80 meV, so the N_2/Pb system is suitable for representing a test case to study the friction behaviour of very high corrugation systems.

3. Determination of static friction F_s and effects of the temperature

To study the static friction as a function of the temperature, we proceed as follows. We start from the system that we have built up at $T = 0$ K. Then we heat the sample at the desired temperature by rescaling the velocities of the particles at each time step ($\Delta t = 1.47$ fs) for 100 000 steps to adjust the kinetic energy to the given temperature. A second run for a total simulation time of 0.3 ns is performed without any temperature control to stabilize the system. Finally, we collect the statistics averaging over a simulation time of 500 ps. This procedure is then repeated for various temperatures in the range 0–70 K.

For a given temperature, we then apply a force in the $[1\bar{1}0]$ direction, i.e. in the direction with the highest packing of atoms in the plane (111), to the N_2 block to study the frictional behaviour of the system N_2/Pb(111).

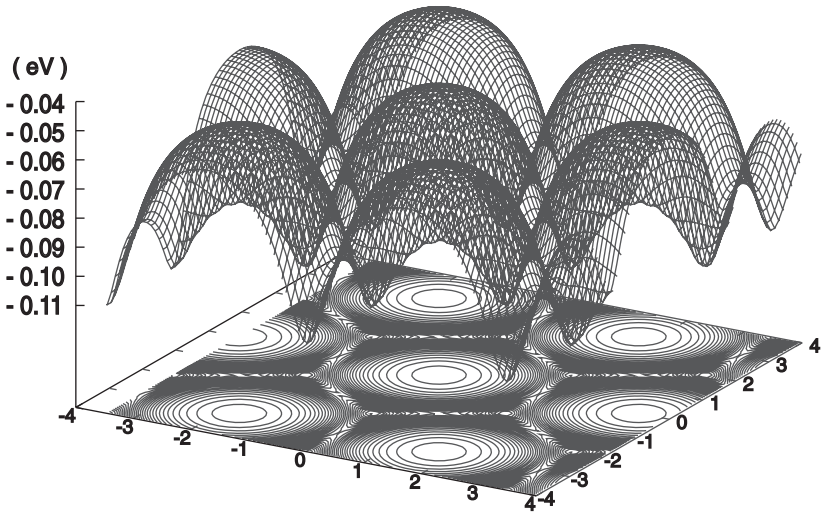

Figure 2. The interaction potential N_2/Pb evaluated at the interface for the equilibrium distance between the Pb and the N_2 layers. The vertical axis potential is in electronvolts. The in-plane axes refer to the $[1\bar{1}0]$ and the $[11\bar{2}]$ directions, respectively. The distances are in ångströms.

In the molecular dynamics calculations there are several ways [17, 18] to determine the static friction. We will use an iterative procedure similar to [17]. At first, by increasing at a constant rate the external force applied to each atom, we search for the maximum force which keeps the N_2 block stuck and the minimum force at which the sliding occurs. We then perform a run with the external force equal to the average of these values to determine whether sliding occurs. We say that the crystal does not move during the simulation time of 500 ps if the centre of mass moves by less than 2σ, while if the centre of mass of the N_2 slab moves by more than 5σ, we say that the crystal slides (see figure 3). If this trial force does not lead to sliding, it becomes the new lower bound for F_s, while if the block is sliding, it becomes the new upper bound for the friction force in our search algorithm. This procedure is repeated several times to obtain the threshold with a precision better than 2%. This force is what we call F_s.

The results of the MD simulations are presented in figure 4, where F_s is plotted as a function of the temperature.

We start by noticing that, after the thermalization, the layer of N_2 at the interface with the Pb slab is disordered even at $T = 0$ K, so we expect a smaller value of F_s with respect to the value obtained for ideal commensurate surfaces. Furthermore, the collisions between the mobile Pb atoms with the N_2 molecules at the interface produce a large momentum transfer which increases the energy of the N_2 molecules, increasing the disorder at the interface. We indeed found F_s in the range of a femtonewton, which is several orders of magnitude less than those arising in the case of a rigid substrate, as shown elsewhere [19]. We remember that in the Frenkel–Kontorova model, where the substrate is rigid with periodicity a, the transition from locked to running [20] occurs at a force F_s given by:

$$F_s = \frac{\pi \epsilon}{a}. \tag{1}$$

With the values of the parameters of our potential, this formula gives a static friction of $F_s = 0.06$ nN which, as expected, is very large compared to our simulation results.

From figure 4 we note that F_s remains practically constant in the temperature range 0–20 K. This is due to the strong corrugation of the potential (80 meV) compared with the thermal

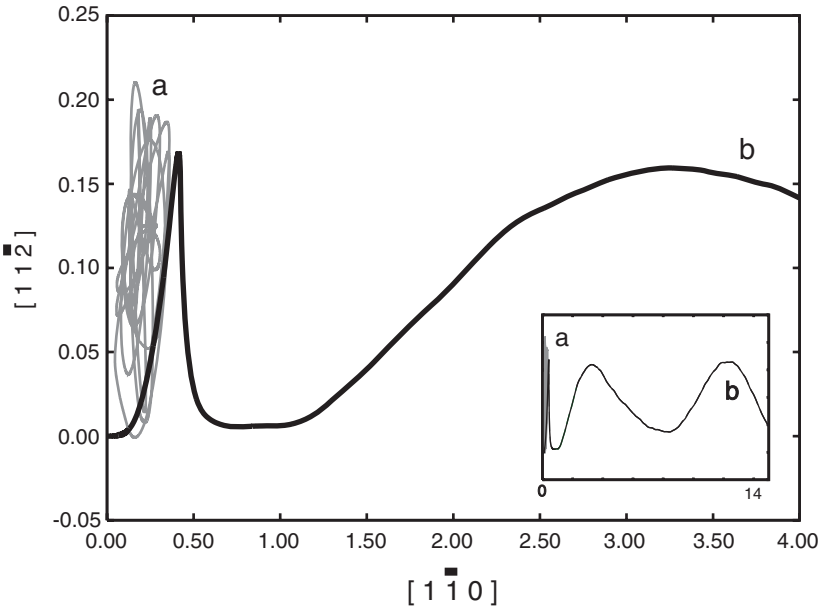

Figure 3. Motion of the centre of mass of the N_2 slab in the (111) plane for $T = 10$ K. The distances along the $[1\bar{1}0]$ and the $[11\bar{2}]$ axes are in ångströms. The trajectory corresponding to the force per atom $F_1 = 2.56$ fN, labelled by a, shows that there is no slip of the N_2 slab. For $F_2 = 2.88$ fN, corresponding to trajectory b, we have the motion of the N_2 slab, because the displacement of the centre of mass is greater than 5σ, as depicted in the insert. The static friction force F_s is in between these two forces.

energy ($k_B T \leqslant 1.7$ meV). The minimum lateral force F_s needed to move the centre of mass of the N_2 slab is not modified by the small kinetic energy acquired by the N_2 molecules. The absence of motion of the N_2 slab in this large range of temperatures is consistent with the experimental QCM analysis of Mistura *et al* [12] on the same system and with the results of Taborek *et al* for several realistic systems [21].

The disorder increases in the interval 25–35 K, producing a sharp drop of three orders of magnitude of the static friction, F_s, becoming a few thousandths of a femtonewton. This value agrees with the experimental result of 0.002 fN obtained at 19 K with the QCM measurements by Mistura *et al* [12]. To investigate the type of the disorder produced by the temperature, we have evaluated the structure factor of a given layer as

$$S_L(\vec{Q}) = \left\langle \left| \frac{1}{N} \sum_{j=1}^{N} e^{-i\vec{Q}\cdot\vec{r}_j(L)} \right|^2 \right\rangle \tag{2}$$

where N is the number of atoms in the layer and $\langle \cdots \rangle$ stands for the average over the simulation. In the calculations we have assumed $\vec{Q} = \frac{2\pi}{a}(0, \frac{4\sqrt{6}}{3}, 0)$, where a is the lattice constant of the N_2 bulk crystal.

Figure 5 plots the values of $S(Q)$ as a function of the layer index L of the N_2 slab, for different temperatures. Layer index $L = 1$ represents the N_2 plane at the interface and layer index $L = 12$ indicates the N_2 slab surface.

We first note that at $T = 0$ K the interface layer is already disordered, but the crystal is ideal in the interior, as discussed in connection with figure 1.

Notice that at $T = 20$ K the disorder for $L = 1$ is larger, then it decreases for the second layer and it oscillates in the interior toward the surface.

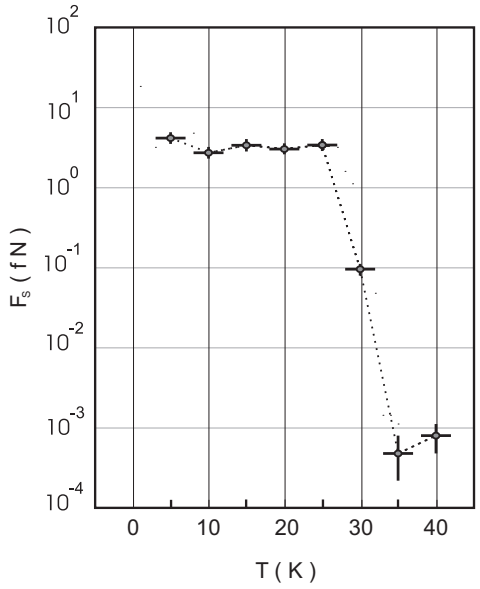

Figure 4. Static force friction per atom, as a function of the temperature. The melting of the first layer of N_2 at the interface occurs at $T = 50$ K.

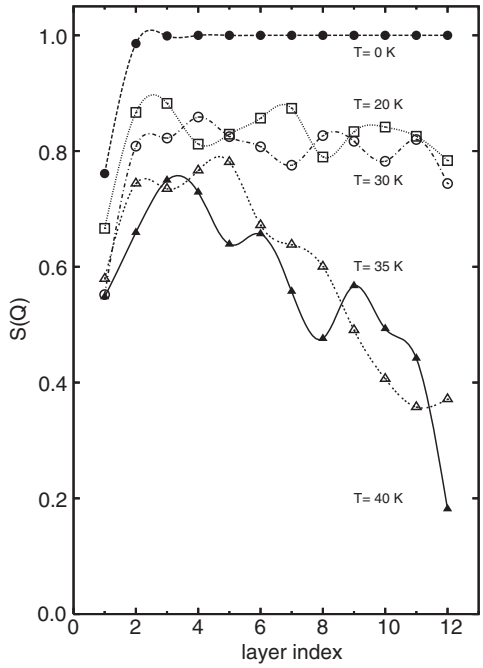

Figure 5. Structure factor $S(\vec{Q})$ as a function of the index L of the layers of the N_2 slab, evaluated for $\vec{Q} = \frac{2\pi}{a}(0, \frac{4\sqrt{6}}{3}, 0)$ for different temperatures.

At $T = 30$ K there is a strong increase in the disorder at the interface, then the disorder remains mainly constant in the rest of the crystal. At $T = 35$ K the disorder increases further

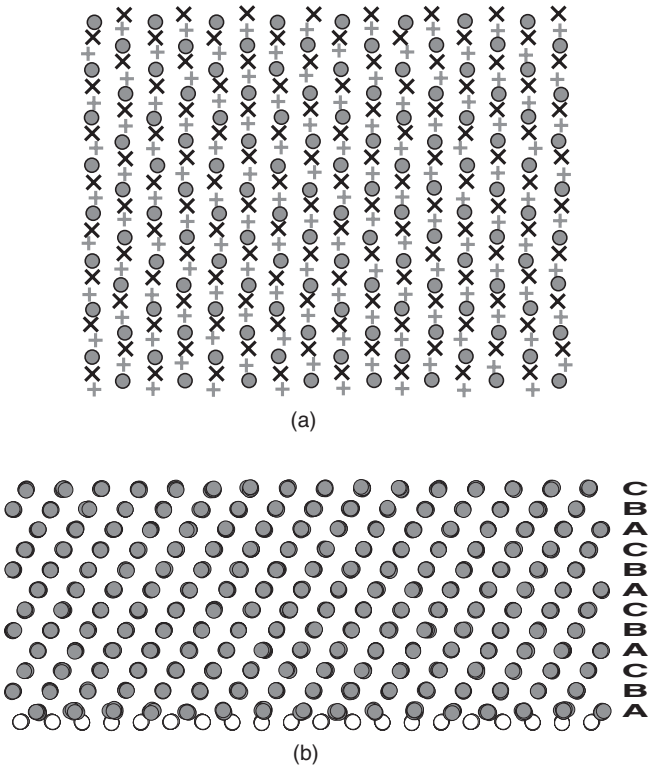

Figure 6. Panel (a): top view of the fcc(111) structure. The coordinates of the A, B, C planes are assumed as a reference to determine the stacking of the planes of the N_2 slab at different temperatures. Panel (b): side view of the N_2 slab for temperature $T = 10$ K. Notice the stacking of planes ABCABCABCABC of the fcc(111) geometry. The open circles are the Pb atoms of the underlying block.

in the first plane, decreases a little for the next four planes, and then increases rapidly toward the surface. At $T = 40$ K one notices a large drop in the structure factor $S(Q)$ at the surface, indicating that there are large changes near the surface.

To relate the disorder to the geometry of the various planes of N_2 slab, we plot snapshots taken with a simulation time of 500 ps. We show in figure 6(a) the positions of the atoms at $T = 10$ K that define the fcc structure in the (111) direction. The plane A is indicated by plus label, the plane B by the cross label, and finally the plane C by the circle label. These planes are taken as references to fix the sequence of the layers of the slab at any temperature. To obtain the label for each plane, we superimpose the layer with those drawn in figure 6(a). In this way we can see if the plane in consideration is of A or B or C type. This procedure, repeated for all planes of the slab, allows us to determine the stacking of planes at the temperature considered. Of course, this procedure fails over a certain temperature where the disorder of the planes becomes very large. The stacking of the whole slab obtained in this way at $T = 10$ K is ABCABCABCABC, which is confirmed by the side view shown in figure 6(b).

In figure 7 we present a snapshot of the side view at $T = 20$ K. The sequence that we have found is the following: BABCABCABCAB. One notes the formation of an hcp structure that produces a sequence BAB at the interface, followed by the fcc CABCABCAB structure. With this small disorder, the value of the static friction force is not yet modified.

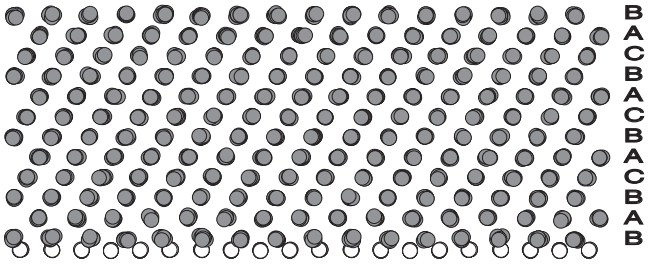

Figure 7. Side view as in figure 6(b), but for the temperature $T = 20$ K. Notice that the first three planes have an hexagonal stacking BAB, followed by a CABCABCAB sequence. The open circles are the Pb atoms of the underlying block.

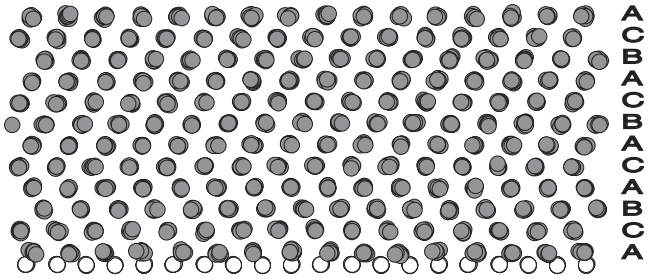

Figure 8. Side view as in figure 6(b), but for the temperature $T = 30$ K. The hexagonal stacking has moved inward into the bulk of the N_2 slab. The sequence is ACBACABCABCA. The open circles are the Pb atoms of the underlying block.

By increasing the temperature at $T = 25$ K, we found that there is an hcp stacking of the type ACA at the interface of the N_2 slab, so that we have the sequence ACABCABCABCA. The static friction does not change appreciably.

At $T = 30$ K the misplacing of planes increases, as depicted in the side view presented in figure 8, and the sequence that we obtain is ACBACABCABCA. The hcp stacking has moved to the fifth plane. The bulk planes are no longer in the configuration with minimum energy, weakening the whole crystal. Therefore a smaller static friction force F_s is obtained and the force that is needed to start to move the centre of mass of the N_2 slab drops off by more than one order of magnitude.

At $T = 35$ K the disorder increases further. By comparing the top view with the fcc reference sequence drawn in figure 6(a), we can label only the first five planes in the sequence CBACB. The next layers close to the surface start to split, with the formation of steps, regions of fcc and hcp geometry, as seen in the side view of figure 9.

Here we have the maximum drop in the static friction F_s, which becomes three order of magnitude lower than that obtained at $T = 20$ K.

By increasing the temperature, the splitting of layers near the surface is more evident and is responsible for the large decrease in the value of the structure factor $S(Q)$, but the static friction value does not change significantly.

At $T = 50$ K the layer $L = 1$ of the N_2 slab starts to melt, as proved by the evaluation of the two-body correlation function $g(r)$ plotted in figure 10. Two peaks are well resolved: one at small distances, corresponding to the Pb–N_2 first nearest neighbours (nn), and the second at the 1nn distance for N_2–N_2 molecules. At higher distances we see the structureless behaviour characteristic of the liquid phase. This melting occurs at a temperature lower than the bulk melting temperature.

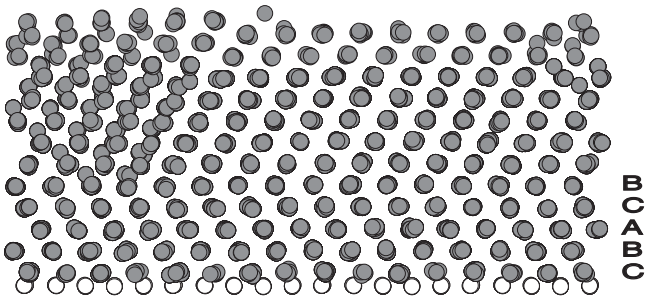

Figure 9. Side view as in figure 6(b), but for temperature the $T = 35$ K. Only the first five planes can be classified with the rule based on the geometry of figure 6(a). The sequence observed is CBACB. The open circles are the Pb atoms of the underlying block.

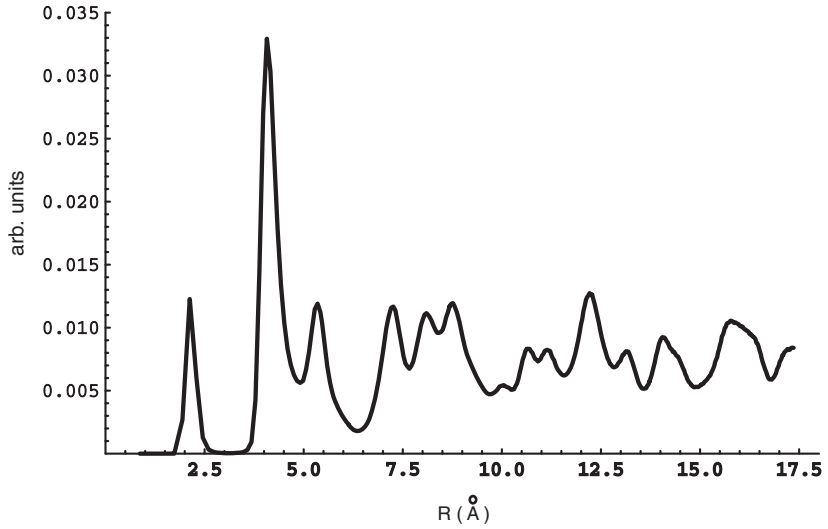

Figure 10. Two-body correlation function evaluated with a run of 500 ps for the first N_2 layer at the interface at the temperature $T = 50$ K. The structureless shape at large distances indicates that this layer is melting. The first peak, on the left, is located at the 1nn distance Pb–N_2 and the second peak gives the 1nn distance N_2–N_2.

4. Final remarks and conclusions

We have presented a theory for the static friction between two thick slabs interacting with a strong potential, which explains the main features of recent experiments. Our results hold for two blocks with a very highly corrugated interface. The interaction potentials in each block are chosen to reproduce correctly the static and dynamic bulk properties of the Pb crystal and of the N_2 crystal.

In the temperature range 0–20 K the kinetic energy of the N_2 molecules is much lower than the corrugation energy. For this reason, no temperature effects are observable and the static force friction per atom F_s remains temperature independent. A similar result has been observed by Taborek *et al* [21] for several realistic systems.

For temperatures in the range 20–25 K, aside from the thermal disorder, a misplacing of planes occurs at the interface, altering the fcc structure. Above 25 K this misplacing moves into the bulk of the slab. The misplaced planes are out of their equilibrium configuration, so

that, in order to move the centre of mass of the N_2 block, a reduced force is required and we have a sharp drop-off of F_s. This is the main result of our paper and it is in agreement with the measurements performed by Mistura *et al* [12] for a similar system composed of a few layers of N_2 on a Pb block. These authors found a sharp decrease in F_s with temperature. They found that, for temperatures less than $T = 19$ K the force applied by the microbalance is not sufficient to move the N_2 layers. Only at $T = 19$ K did they observe motion of the N_2 layers for an applied force of 0.002 fN, which has the same order of magnitude as the values of F_s after the sharp drop-off found at $T > 25$ K in our simulations.

At higher temperatures the disorder increases and we have found a region of mixed fcc and hcp structures and the splitting of planes, with the formation of steps near the surface. Finally, we have observed melting of the layer of N_2 at the interface at the temperature $T = 50$ K, which is lower than the bulk melting temperature.

Acknowledgments

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