



## **SIMPLE MODELS OF ADSORBED POLYMERS: VIBRATIONAL PROPERTIES**

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### **Abstract**

The vibrational properties of polymers adsorbed on surfaces are investigated within the frame of two simple models. First the surface is modelled as a one-dimensional infinite harmonic chain. Polymeric " molecules " are represented as harmonic chains of finite length. The coupling between the polymers and the surface is treated within the frame of the Interface Response Theory. Upon adsorption of polymers, resonant vibrational modes appear as well defined peaks in the variation of the density of states of the system. The effect of the interaction between adsorbed polymers via phonons is investigated and shown to lead to antiresonances in the spectral density of states and the formation of gaps in the density of states as the surface coverage is increased. A second more realistic model is introduced where the same finite harmonic chains (polymers) are grafted on a two dimensional [001] surface cut through a cubic harmonic crystal. Again the variation in density of states exhibits resonant modes between the polymers and the substrate. However, in this case, the interaction between polymers is short range. Adsorption of a film of polymers produces resonant modes which remain well-defined features within the substrate bulk band.

### **1. Introduction**

Monolayer films of macromolecules adsorbed on a surface have received in recent years a great deal of attention. As an example, Langmuir-Blodgett films show potential in a wide range of scientific and technological area from electronics to optics to biological science [1]. The properties of an adsorbed molecular film are closely related to its physical and microscopic features including the characteristics of the adsorbate/substrate interactions. In the present paper, we focus our attention on the vibrational properties of monolayer molecular films adsorbed on solid substrates and in particular on resonant phonons. Resonant phonons in adsorbed molecules or molecular films appear when the molecular vibrational modes fall within the vibrational band of the substrate. These resonant phonons

are characterized by a peak in the phonon density of states which is amenable to experimental detection. In this paper, we address the cases of resonant phonons with a finite number of adsorbed polymeric molecules as well as with an infinite monolayer polymer film adsorbed on a surface. We find in all cases that resonant phonons may exist in the polymer or polymer film at frequencies falling within the substrate bulk vibrational band.

## 2. Models of Polymers Adsorbed on a Surface

Polymeric molecules are represented by simple harmonic chains of  $L$  atoms. A chain is composed of atoms of mass,  $m_1$ , bonded through first nearest neighbor harmonic springs of force constant,  $\beta_1$ . In the most primitive model, the substrate is composed of a one-dimensional infinite harmonic chain with atomic masses,  $m_2$ , and force constant,  $\beta_2$ . A second more realistic model is also considered where the polymers are grafted at one end on a two dimensional [001] surface cut through a cubic harmonic crystal with the same physical parameters as the infinite chain substrate. For the sake of simplicity, we limit our study to the case of transverse phonons. The Green's function of a system composed of polymer chains adsorbed on a substrate can be constructed with the help of the Interface Response Theory [2]. We call,  $\vec{G}$ , the Green's function of a reference system. This reference system is constituted of the uncoupled chains and substrate and is defined in the discrete space  $D$  of the atomic sites of the finite chains and substrate. We constructed the adsorbed system by linking the chains and the substrate of the reference system with the help of a coupling operator  $\vec{V}$ . For a single finite chain linked to one atomic site on the substrate, the coupling operator is the 2x2 matrix:

$$\vec{V} = \beta_1 \begin{pmatrix} -\frac{1}{m_2} & \frac{1}{m_2} \\ \frac{1}{m_1} & -\frac{1}{m_1} \end{pmatrix} \quad (2.1)$$

where  $\beta_1$  is the force constant of the bond between polymer and substrate. This coupling operator is defined in the subspace of  $D$ ,  $M$ , of the atomic sites to be bonded. The Green's function of the adsorbed system,  $\vec{g}$ , is given by:

$$\vec{g} \cdot \vec{\Delta} = \vec{G} \quad (2.2)$$

where

$$\vec{\Delta} = \vec{I} + \vec{V} \cdot \vec{G} \quad (2.3)$$

and  $\vec{I}$  is the unit matrix. For  $N$  polymer chains grafted on a substrate  $\vec{\Delta}$  is a  $2N \times 2N$  matrix defined in  $M$ . One can finally determine the variation of the phonon density of states between the adsorbed system and the reference system from:

$$\Delta n(\omega) = -\frac{1}{\pi} \frac{d}{d\omega} \left[ \text{Im} \left( \log(\det \vec{\Delta}) \right) \right] \quad (2.4)$$

### A. One-dimensional substrate

In Fig.1 we report the variation in density of state of a single polymer attached on a one-dimensional infinite substrate.

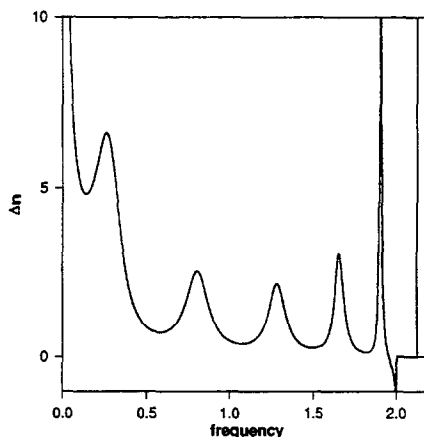


Fig. 1. Variation in density of states, one polymer adsorbed on a 1-D substrate.

To calculate  $\Delta n(\omega)$ , we have used expressions for the Green's functions of the finite and infinite harmonic chains reported by Akjouj et al. [3]. The polymer chain is composed of  $L=5$  atoms. The masses of the finite and infinite chains are taken to be identical. The harmonic force constants,  $\beta_1$ ,  $\beta_2$ , and  $\beta_I$  are also assumed to be the same. The frequencies are expressed in units of  $\sqrt{\beta/m}$  and the bulk vibrational band of the substrate extends over the interval of frequencies 0 to 2. Since the five normal modes of an unadsorbed polymer molecule fall within the entire band of the substrate, the variation of density of states exhibits five resonances in the form of five well defined peaks. A localized vibrational mode exists above the substrate bulk band. Decreasing the mass  $m_1$  and/or increasing the force constant  $\beta_1$  results in fewer normal modes of the polymer lying within the band of the substrate and therefore fewer resonant peaks in the variation of density of states. We now consider the case of two polymeric chains adsorbed on the substrate. Here, interaction between the adsorbed chains mediated by phonons via the substrate leads to a splitting of the resonant peaks.

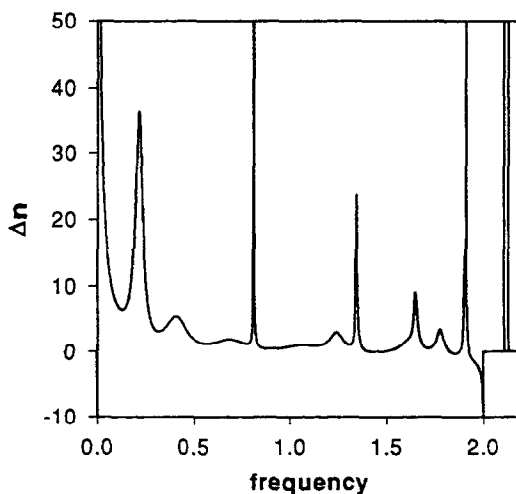


Fig. 2. Variation in density of states, two polymers on a 1-D substrate.

Fig. 2 illustrates this splitting for two adsorbed polymers separated by four atomic sites of the substrate. In addition to resonant peaks, there exist two localized vibrational modes identifiable by the two delta peaks above the substrate band.

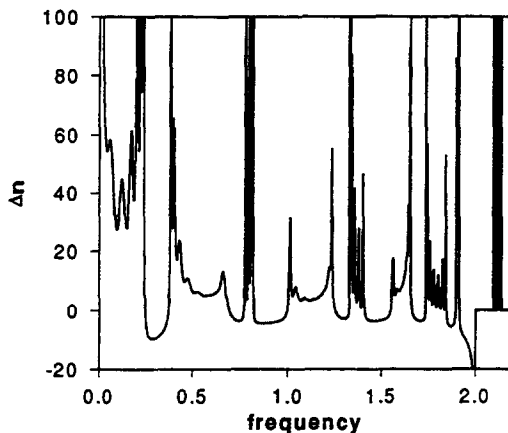


Fig. 3. Variation in density of states, 8 chains adsorbed on a 1-D substrate.

As one increases the substrate coverage further the resonant peaks split in multiple narrower peaks. Fig. 3 shows the variation of density of state in the case of 8 adsorbed chains separated by four substrate sites. Antiresonant phonons appear as depressions in the density of states forming between resonant peaks. These antiresonances are characterized by negative variations of the density of states. Again, eight delta peaks above the top of the substrate band identify localized vibrational modes.

In the limit of a complete coverage of the substrate by polymer chains, the antiresonances may form gaps in the density of states of the substrate. Fig. 4 illustrates the band structure of a polymer film constituted of finite chains of five atoms adsorbed on the one-dimensional substrate and separated by four substrate sites. The polymer chains are arranged periodically on the substrate with a period equal to four substrate atomic sites. The bands are calculated as the zeros of  $\det \bar{\Delta}_k$  where the subscript  $k$  indicates the one-dimensional  $k$ -Fourier transform of  $\bar{\Delta}$ . The wave vectors are expressed in units of  $1/a$  where  $a$  is the interatomic distance.

Eight absolute gaps are identifiable in the band structure. These correspond to the eight antiresonances observed in the variation of density of states of Fig. 3, and resulting from interactions between polymers. Some of these gaps possess the particularity of being indirect band gaps. The band structure is composed of nine bands, five of which are associated with dispersed resonant phonons in the chains. The folding of the substrate band due to the  $4a$  period of the adsorbed system produces the remaining four bands. These bands can be for instance associated with the peaks in the variation in density of state calculated for a finite polymer coverage of figure 3. The uppermost band results from the dispersion of the vibrational modes which were localized in the case of a finite coverage of the substrate.

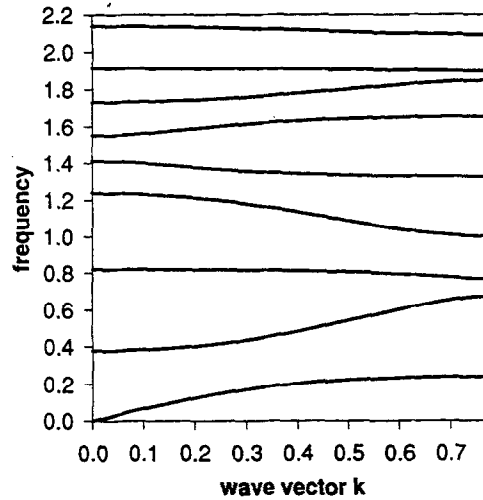


Fig. 4. Band structure of polymer film adsorbed on a 1-D substrate

### B. Three-dimensional substrate

In this section, we investigate the more realistic case of polymer molecules adsorbed on a [001] two-dimensional surface cut through a three-dimensional simple cubic crystal. One-dimensional finite chain of length  $L=5$  are again used to represent the polymer molecules. As in the previous model, for the sake of simplicity, all masses and force constants are taken to be identical. The substrate possesses translational periodicity parallel to the surface. Let the vector  $\mathbf{x}/=(x_1, x_2)$  refer to coordinates on the surface. From the expression of the Green's function of the substrate in the two-dimensional,  $k//$ -Fourier space given in Ref. [3], we calculate numerically the Green's function in real space at any site on the surface. The variation in density of states of a single polymer chain adsorbed at site,  $\mathbf{x}/=(0,0)$ , on the two-dimensional surface is readily computed using expression (2.4).

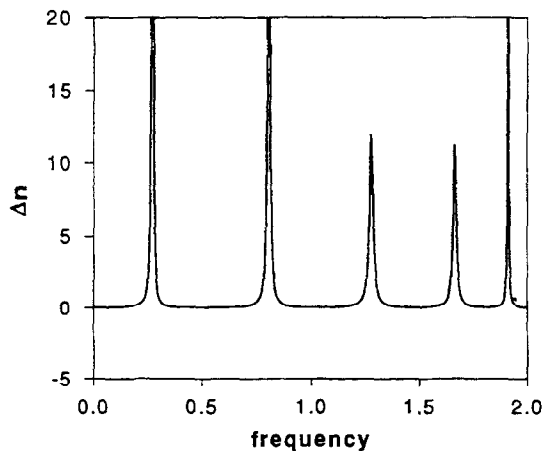


Fig. 5. Variation in density of states, one polymer adsorbed on a 3D substrate.

Similarly to the case of a single chain adsorbed on a one-dimensional substrate, the variation in density of state of Fig. 5 shows five well defined peaks corresponding to resonant phonons in the adsorbed chain. The width of these peaks has however decreased.

The adsorption of additional polymer molecules at some neighboring site is expected to produce multiple resonant modes resulting from the polymer/polymer interaction. The introduction of a second chain adsorbed at site,  $\mathbf{x}/a=(0,a)$ , leads to a splitting of the resonant peaks (see Fig. 6). The interaction between adsorbed polymers is short range as the splitting of the resonant peaks becomes barely perceptible for distances exceeding two atomic spacings of the substrate.

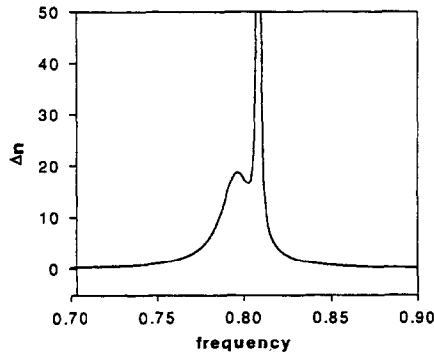


Fig. 6. Second resonant peak for two chains adsorbed on a 3-D substrate.

The adsorption of an additional polymer at  $(0,2a)$  has for effect to deepen the depression between the two peaks. A third peak is not observed as the interaction between chains separated by a distance of  $2a$  is too weak.

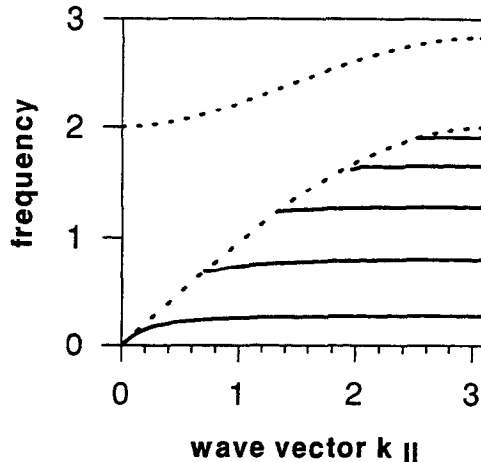
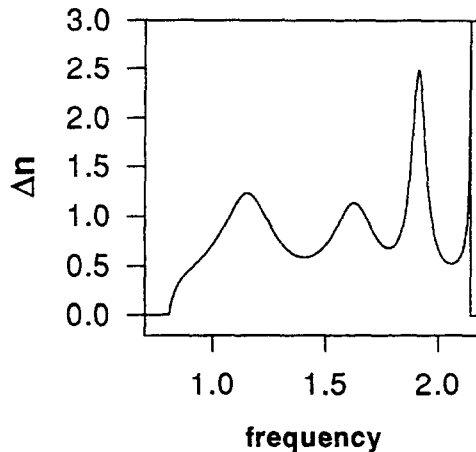


Fig. 7. Band structure of a polymer film adsorbed on a 3D substrate.

Using the  $k_{//}$ -Fourier transformed of the substrate Green's function we calculate the band structure of a monomolecular thick film of polymers adsorbed at every site of the two-dimensional surface. In Fig. 7, we report the band structure of the adsorbed system in the region of the Brillouin

zone corresponding to  $k_{//}=(k_1,0)$ . The wave vectors are in units of  $1/a$  where  $a$  is the nearest neighbor distance in the substrate.

The bulk phonon band of the substrate lies within the dotted lines. Below it there are five branches of phonons associated with the polymers. These branches correspond to localized modes. At the upper edge of the Brillouin zone where interaction with the bulk band is minimum, the frequencies of the localized modes approach the frequencies of the resonant phonons of a single adsorbed polymer molecule.



**Fig. 8.** Resonant phonons in a polymer film adsorbed on a 3-D substrate at  $k_{//}=(\pi/4a,0)$ .

The branches become resonant modes when they penetrate within the substrate bulk band. In order to study if these resonances remain well-defined features and could be detected experimentally, we calculate the corresponding variation of the density of states at the wave vector  $k_{//}=(\pi/4a,0)$ . At this value, only three polymer branches intercept the bulk band. Fig. 8 indicates that resonances are well defined features. This behavior is reminiscent of resonant phonons associated with the adsorption of slabs on a substrate [4].

We observe that the amplitude of the resonant peaks increases with the frequency. Calculations of the variation in density of states for other values of the wave vector show that the resonant peaks broaden and become ill defined as their position is further away from the bottom of the bulk band. Far away from this limit the resonant modes have completely vanished within the bulk band and have lost all specific identity.

### 3. Conclusions

We have studied with the help of a simple model resonant phonons in adsorbed polymer molecules and adsorbed polymer film. Resonances between the adsorbate and the substrate appear as well defined peaks in the variation in density of state of the adsorbed system. The detailed features of the resonant peaks are related to the physical characteristic of the adsorbate. This study therefore

suggests the possibility of structural characterization of adsorbed polymer films via experimental observation of these resonances.

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