Molecular-Dynamics Calculations for Ethylene Adsorbed on Graphite

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The structural and dynamical behavior of overlayers of ethylene physisorbed on the graphite basal plane, has been investigated via computer simulation. The dynamics of various surface phases has been revealed by examination of the power spectra appropriate to molecular translational and rotational motion. Our results are discussed in the light of recent experimental work on the ethylene-graphite system.

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There is intense interest in the behavior of simple molecules physisorbed on the graphite basal plane.[1–7] Such systems not only exhibit structural transitions involving changes in the orientational order of the ad-molecules[1–3] but also provide a means of studying different crystal growth mechanisms.[4–7] Despite a wealth of experimental data on the ethylene-graphite system,[8–11] only rudimentary information is presently available concerning molecular arrangement and comportment in the various adsorbed phases.[5] This is in part due to the apparent absence of any superlattice lines in the diffraction experiments.[6] Nevertheless, a detailed phase diagram has been established, particularly for the monolayer region.[5,6]

The present paper describes the results of computer-simulation calculations which were carried out in order to cast some light on the structural and dynamical behavior of physisorbed ethylene molecules. Anticipating our results we shall see that a relatively simple potential model not only is able to embrace much of the rich variety of phase behavior already revealed in diffraction experiments[5,6] but it also predicts dynamical behavior that has been detected in inelastic-scattering experiments.[10]

Before describing our calculations we digress to remind the reader of the salient features of the ethylene-graphite phase diagram which is shown in Fig. 1. (We define coverage $n = 1$ to be a triangular net of physisorbed molecules, with lattice constant $a = 4.26$ Å.) At low T and for $n < 0.8$, ethylene adopts a low-density (LD) incommensurate structure with $a \sim 4.65$ Å, while for $n > 1.05$ it exists as a high-density (HD) phase with $a \sim 4.22$ Å. The HD phase coexists with bulk crystallites. For $0.82 < f < 1.05$ two-phase (HD + LD) coexistence is observed.[5,6]

On the basis of static calculations employing empirical atom-atom potentials[12] and in analogy with the behavior of O_2 on graphite[3] it was concluded that in the HD (LD) phase the molecular C=C axis is perpendicular (parallel) to the graphite basal plane.[6]

In our calculations the ethylene molecules interact with the same atom-atom (exp-6) potentials.[12] Using the new constant-pressure molecular dynamics (NMD) technique[13] we tested the intermolecular potential by studying the structure of *bulk* (monoclinic) ethylene. In particular, at $p = 0.23$ (0.19) GPa and $T = 107$ (99) K we find $a = 4.71$ (4.51) Å, $b = 6.46$ (6.56) Å, $c = 4.12$ (3.98) Å, and $\beta = 94.8°$ (95.2°), where the experimental values are given in parentheses.[14] The adsorbed ethylene molecules were assumed to interact with a planar, energetically homogeneous surface via atom (H or C) -surface potentials. The latter were constructed by integrating the exp-6 potentials of Ref. 12 over the basal plane only. The calculated gain of potential energy upon adsorption of one molecule on the basal plane is about 4.8 kcal mol^{-1}

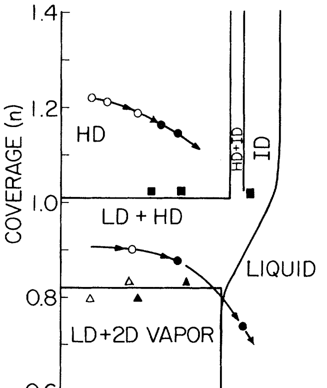

FIG. 1. Phase diagram for ethylene on grafoil taken from Ref. 6. HD (LD) denote phases where C=C is perpendicular (parallel) to the surface. The circles denote simulations carried out by the NMD method (Ref. 13); the triangles and squares refer to conventional calculations. Solid symbols denote the presence of rotation about at least one axis.

compared with the experimental value of 4.6 kcal mol^{-1} derived from isosteric heat data.[15]

Two types of MD calculation were carried out, each with 96 molecules: conventional constant-n investigations and NMD runs at constant spreading pressure, ϕ, using a two-dimensional version of the NMD technique.[13] All calculations started from ordered triangular (herringbone) lattices with the ethylene $C=C$ axes either parallel (LD phase) or perpendicular (HD phase) to the surface. The equations of motion were followed with use of a predictor-corrector algorithm, periodic boundaries being assumed parallel to the surface (X, Y), with a perfectly reflecting wall at $Z = 20$ Å. Typically, phase-space trajectories were followed for 5 ps using a time step of 2.5 fs, about 1 ps being used for equilibration. The nature of each simulated state point (see Fig. 1) was established by examining the CC, CH, and HH radial-distribution functions parallel to the surface, the distribution of C and H atoms normal to the surface, and certain orientational order parameters referring to vectors drawn along $C=C$ and $H-H$ in individual molecules. The distinction between fully ordered, orientationally disordered, and rotator phases was aided by examination of the autocorrelation functions (acf) of the linear and angular velocities. The significance of these acf's is that their integrals yield the diffusion constants associated with molecular translation and rotation while their Fourier transforms yield the translational (phonon) and rotational (libration) spectra.

We now describe our results. At constant spreading pressure $\phi = 0$ an initial $(n = 0.8)$ LD-phase triangular lattice (which can be regarded equivalently as a centered $1\times\sqrt{3}$ rectangular lattice) evolved spontaneously to a denser $(n = 0.9)$ orientationally ordered solid (centered $1\times\sqrt{2}$ lattice), in which the molecules are canted with respect to the surface [Fig. 2(a)]. Heating to ~50 K (at $\phi = 0$) restored

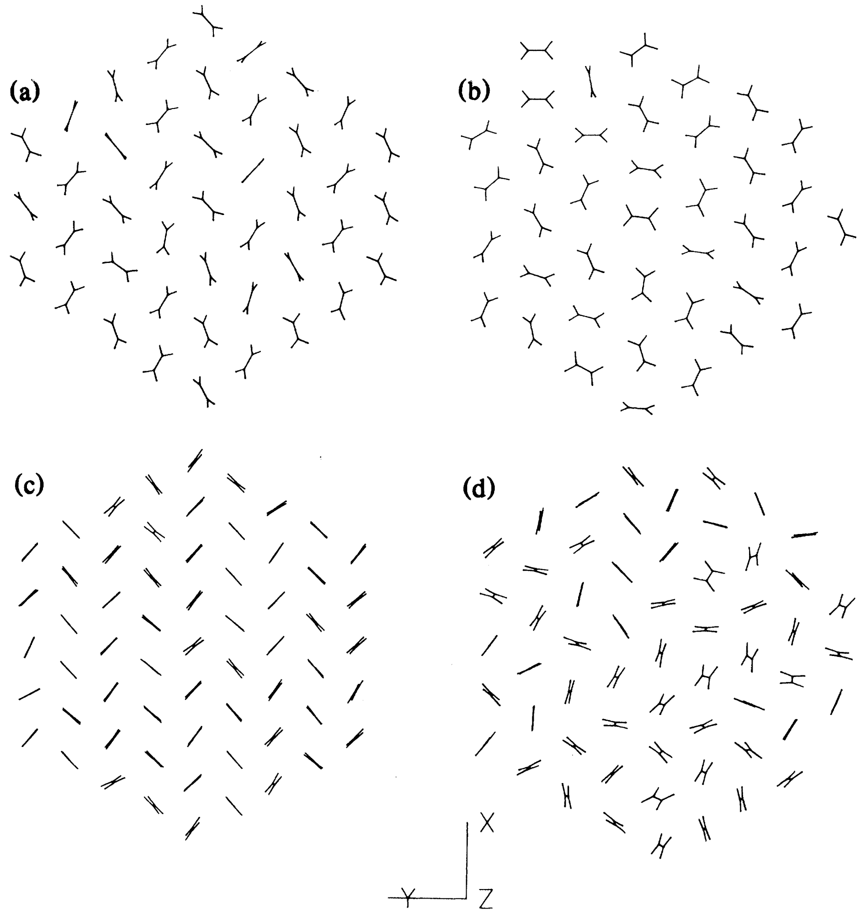

FIG. 2. Instantaneous configurations for ethylene on graphite. (a) The $\phi = 0$, LD $(1\times\sqrt{2})$ ordered phase $(n = 0.9)$ at $T = 30$ K, (b) the LD $(1\times\sqrt{3})$ orientational disordered phase $(n = 0.8)$ at $T = 12$ K, (c) the $\phi = 0$ HD ordered phase $(n = 1.22)$ at $T = 12$ K, (d) the $\phi = 0$ HD rotator phase $(n = 1.15)$ at $T = 48$ K.

the triangular $(1\times\sqrt{3})$ lattice with $n\sim0.85$ and in so doing produced a rotator-phase solid. Further heating to 75 K (with $\phi=0$) eventually generated a liquid phase ($n\sim0.75$) with a translational self-diffusion coefficient 2.8×10^{-5} cm^2/s and rotational diffusion coefficients $D_X=12.5$, $D_Y=2.0$, and $D_Z=1.3$ in units of 10^{11} s^{-1}, typical errors being 25%.

Different behavior was observed in constant-n calculations carried out using the experimental value $n\simeq0.8$ (triangles in Fig. 1). At all temperatures the simulations yield orientationally disordered structures with a broad distribution of center-of-mass separations [Fig. 2(b)]. At low temperatures reorientation is slow but by 50 K a predominantly two-axis rotator phase is formed with $D_X=3.1\times10^{11}$, $D_Y=1.0\times10^{11}$, and $D_Z=0.3\times10^{11}$ s^{-1}, the latter being barely statistically significant.

In calculations carried out at 12 K by the NMD method[13] with $\phi=0$, the HD phase retained an ordered herringbone structure with $n=1.22$ [Fig. 2(c)], but by 48 K a uniaxial rotator phase with $n=1.15$ ($D_X=3.3\times10^{11}$ s^{-1}) was formed [Fig. 2(b)].

Finally, in conventional MD calculations carried out at intermediate coverage ($n=1.03$) the system evolved from an initial HD structure to a phase-separated mixture of molecules either standing on end or lying down (squares in Fig. 1).

We now turn to a brief discussion of the dynamics of the various surface phases. Typical power spectra of the translational and rotational excitations, obtained from the Fourier transform of appropriate acf's, are shown in Fig. 3. The significance of these spectra is that those features which involve large-amplitude motion of the H atoms should be detected in incoherent inelastic neutron-scattering experiments.[10] In the LD phases, although translation modes (T_X, T_Y, T_Z) are much lower in frequency than the rotational modes (R_X, R_Y, R_Z), there is clear evidence for translation-rotation (TR) coupling. Essentially, a rigid-body translation of any C_2H_4 molecule inevitably results in atom-atom "collisions" which in turn lead to molecular rotation. Thus for example, the low-frequency structure in the R_X spectrum is also present in the T_X spectrum. In the HD phase the translational modes are shifted to higher frequencies. Here there is also evidence for TR coupling, the low-frequency peaks in the R_X spectrum being nothing more than the T_Y response. Because of the presence of TR coupling incoherent inelastic neutron scattering from C_2H_4[10] should contain contributions from these coupled modes.

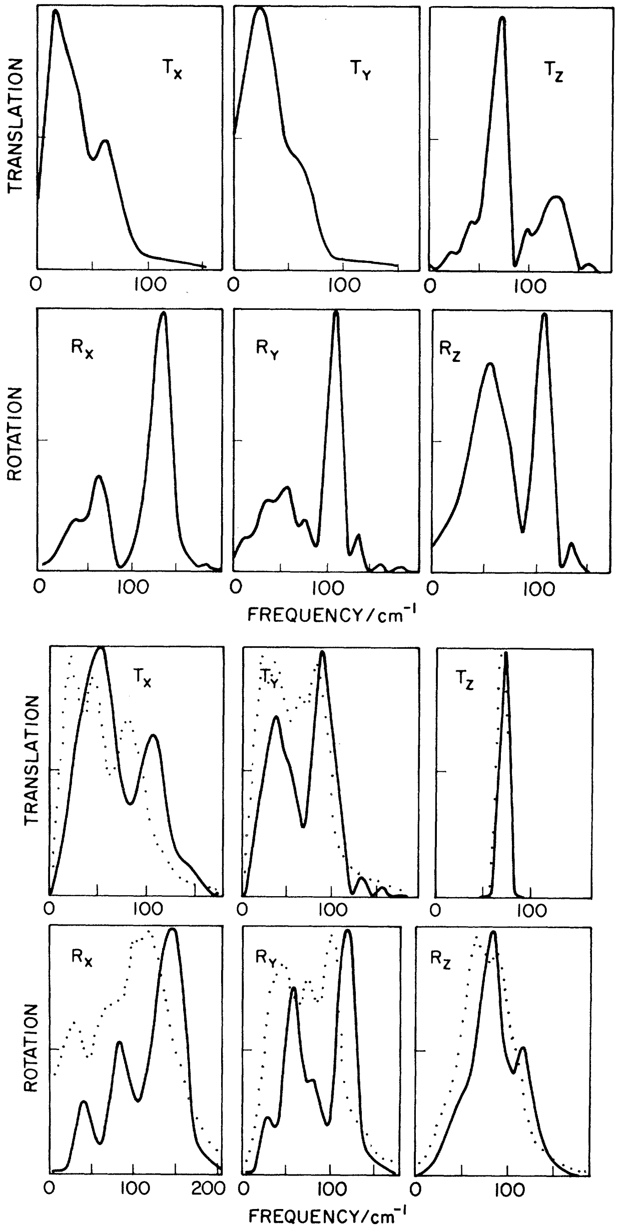

FIG. 3. Power spectra for translational phonons parallel (T_X,T_Y) and perpendicular (T_Z) to the basal plane. The librational motion is characterized by rotation about the C=C (R_X) and two orthogonal axes in (R_Y) and perpendicular to (R_Z) the molecular plane. The upper curves correspond to the LD phase at $T=12$ K and the lower curves and dots to the HD ordered ($T=12$ K) and rotator ($T=48$ K) phases, respectively.

In summary, we have presented the results of molecular dynamics calculations on the structure and dynamics of ethylene molecules on a graphite surface. While the simulations yield two-phase coexistence at intermediate coverage and confirm the presence of high temperature LD and HD rotator phases,[6,10] as yet there is no experimental evidence for either a LD or HD ordered low-temperature structure. In addition, our simulated structures are all too dense. Several possible reasons for this immediately come to mind. For example, in order to apply the NMD method[13] we have neglected the surface corrugation. Moreover, our classical simulations omit the dilation due to the large librational zero point energy. There are clearly also residual errors in the intermolecular potential which lacks the quadrupole-quadrupole interaction.[16] Future work will be directed not only towards resolving these questions but also to a more detailed investigation of the collective modes. Predictions based upon the results of the present model are compared with experiments in the accompanying article.[10]

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