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PHONON GAP ENERGY AS A FUNCTION OF TEMPERATURE FOR COMMENSURATE MONOLAYERS ON GRAPHITE

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Gases physisorbed on adequate substrates present a large variety of phases and phase transitions. Graphite has been one of the most frequently studied substrates, since well characterized samples with a large surface to mass ratio can easily be produced. The observed phase transitions are the result of a delicate balance between the interaction of the adsorbed gas and the substrate, and between the adsorbed molecules themselves. Unfortunately, the knowledge of the details of these interaction potentials is sparse since not many experimental techniques are available. The adsorption potential itself has been determined mainly with molecular beam scattering, but the magnitude of the in-plane corrugation of the adsorption potential is very difficult to obtain in this way. It is this corrugation that forces some physisorbed substances into a commensurate phase and produces, due to the lost translational invariance, an energy gap at the zone centre in the acoustic branches of the phonon spectrum. Thus, the determination of this gap is a direct measure of the adsorption potential corrugation. The temperature renormalization of the phonon spectrum gives insight into the anharmonic terms of the adsorption and intermolecular potentials. Recently, several measurements of the gap became available and allowed a quantitative comparison with theoretical models of the adsorption potentials[1].

We present here the results of inelastic neutron scattering experiments that determined the phonon gap (Δ), and its dependence on temperature, for various substances, together with a model that reproduces the observed features. The studied adsorbates present all a registered $\sqrt{3}\cdot\sqrt{3}$ R30 phase (a_{nn} = 4.26Å) and can be grouped mainly into two classes according to their quantum character. The hydrogen isotopes (H_2, HD, D_2) and ^3He are typical quantum gases: their interaction potential is weak, they exhibit a large zero point motion and a very large compressibility. Nitrogen (N_2) and deuterated-methane (CD_4), on the other hand, are much heavier molecules, with consequently a smaller zero point motion forming less compressible monolayers. These differences are evidenced in the 2-dimensional phonon spectra as shown in Table I. The quantum gases present very little dispersion and resemble, to a first approximation, Einstein oscillators. The reason for this behaviour is the large zero point motion which

	H_2	HD	D_2	^3He	N_2	CD_4
Phonon Gap	47.3	43.2	40.0	13.5	19.3	15.9
DOS width	27.5	14.7	9.5	-	64.2	76.7
DOS centre	61.0	50.6	44.2	-	51.4	55.3
W/C ratio	0.45	0.29	0.21	-	1.25	1.39
T_m	20.5	19.4	18.5	3.05	~50*	~55*

Table I: Some characteristic values of the 2-dimensional phonon density of states (DOS) and melting temperature (T_m) of the commensurate phase. (Values are given in Kelvin. Row 4 gives the ratio of the values in rows 2 and 3).

*The phase diagrams for N_2 and CD_4 present a commensurate region that extends to higher temperatures when the coverage is slightly higher than the commensurate one. Details of the respective phase diagram can be found in ref. [2] and [3].

favours the commensurate phase, even if the nearest neighbour distance is ~20% larger than that of the 3D solid. Due to the strong interaction between the adsorbed molecules, the dispersion curves of N_2 and CD_4 cover a wider energy range. In this case the 3D lattice parameter matches within some percent the one of the 2D commensurate phase.

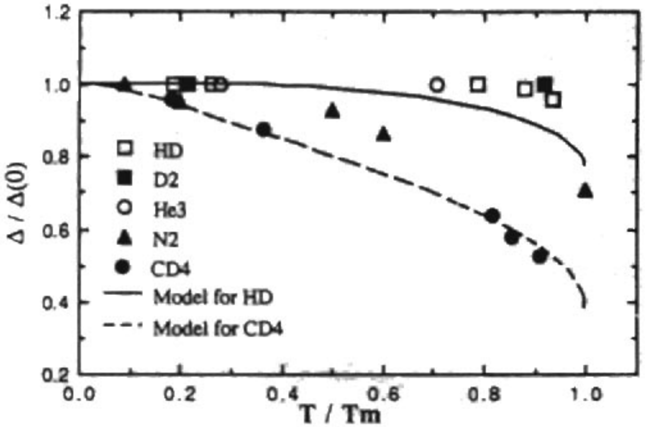

Figure 1: Normalized zone centre phonon gap vs. reduced temperature for several gases. The lines are the result of the model calculation. (Δ stands for the zone center phonon gap)

Figure 1 shows the temperature renormalization of the phonon gap due to the strong anharmonicity of the adsorbate potential. The q=0 mode depends only on the curvature of the adsorption potential and not on the intermolecular forces. The effective curvature is a weighted average over the root mean square amplitude of vibration, which is in turn determined by the effective curvature of the potential. This quasi-harmonic approximation must thus be solved in a self-consistent way. On the other hand, the intermolecular potential is also anharmonic and can be expanded in terms of the two-particle correlation function. This additional anharmonicity renormalizes the whole frequency spectrum of the phonons.

More insight into the problem can be gained using the following model hamiltonian to obtain the corresponding dispersion curves [4,5]:

$$H = \frac{1}{2}\sum_{l\alpha} m\,\dot{u}^2_{l\alpha} + \frac{1}{2}\sum_{\substack{l\alpha\\ l'\beta}} \phi_{ll'\alpha\beta}\, u_{l\alpha} u_{l'\beta} + \frac{1}{2}\sum_{\substack{l\alpha\\ \beta}} \theta_{l\alpha\beta}\, u_{l\alpha} u_{l\beta}$$

where α, β = 1,2 are the coordinate components, and l, l´ designate the molecular sites,

$$\phi_{ll'\alpha\beta} = \frac{\partial^2 U}{\partial u_{l\alpha}\partial u_{l'\beta}} + \frac{1}{2}\frac{\partial^4 U}{\partial^2 u_{l\alpha}\partial^2 u_{l'\beta}}\left\langle \left|\bar{u}_l - \bar{u}_{l'}\right|^2 \right\rangle , \quad \theta_{l\alpha\beta} = \frac{\partial^2 V}{\partial u_{l\alpha}\partial u_{l\beta}} + \frac{1}{2}\frac{\partial^4 V}{\partial^2 u_{l\alpha}\partial^2 u_{l\beta}}\left\langle \left|\bar{u}_l\right|^2 \right\rangle$$

with $U(r_l - r_{l'})$ the inter-molecular potential and $V(r_l)$ the substrate-adsorbate interaction. The anharmonic part of the potential is partially taken into account by the bi-quadratic term. All the derivatives are evaluated at the equilibrium position. A similar treatment for several gases can be found in ref. [4] The two thermal averages are expressed as:

$$\left\langle \left| \bar{u}_l - \bar{u}_{l'} \right|^2 \right\rangle = \frac{\hbar}{Nm} \sum_j \sum_{BZ} \coth\left(\frac{\beta \hbar \omega_j(\bar{q})}{2} \right) \frac{1}{\omega_j(\bar{q})} \left\{ 1 - \cos\left(\bar{q} \cdot (\bar{R}_l - \bar{R}_{l'}) \right) \right\}$$

$$\left\langle \left| \bar{u}_l \right|^2 \right\rangle = \frac{\hbar}{2Nm} \sum_j \sum_{BZ} \coth\left(\frac{\beta \hbar \omega_j(\bar{q})}{2} \right) \frac{1}{\omega_j(\bar{q})}$$

where $\beta = 1/k_B T$.

The dynamical matrix was evaluated using this ansatz for the potentials and the structure of the $\sqrt{3} \cdot \sqrt{3}$ R30 hexagonal lattice. The corresponding expressions were iterated until convergence was obtained for each temperature. The resulting temperature renormalization of the phonon gap obtained with this model for HD and CD_4 are also indicated in fig.1. The melting of this structure was defined as the temperature at which $<u^2>$ diverged. For HD we used the Silvera-Goldman[6] intermolecular potential and for the CD_4 molecule a 6-12 Lennard-Jones potential (ε=137K, σ=3.68Å). The adsorbate-substrate potential was modeled after Steele[7]. A calculation done for D_2 using the same microscopic model as in ref. 8 indicates that the gap is less affected by temperature[9], more in agreement with the experimental data.

The agreement between the data and the model is reasonable taking into account the incomplete knowledge of the potential parameters involved. In this treatment a mean field approach has been used which should break down near the melting transition. Nevertheless the qualitative features of the temperature dependence of the phonon gap are reproduced: for the quantum gases, the rms vibrational amplitude is determined by their zero point motion and is little affected by thermal population of phonons resulting in a very weak variation of the gap with temperature. For the heavier gases, on the other hand, $k_B T_m$ at the melting temperature lies well above the cutoff energy of the phonon DOS and the melting transition is driven by thermally excited phonons.

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