

LATTICE DYNAMICS OF QUANTUM GASES ADSORBED ON GRAPHITE
INVESTIGATED BY INELASTIC NEUTRON SCATTERING

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INTRODUCTION

During the last decade, substantial progress in the knowledge of the properties of two-dimensional (2D) matter has been achieved thanks to studies realized on monolayers of gases adsorbed on well characterized substrates like graphite. The existence of two relevant length scales in this problem, the adsorbate-adsorbate equilibrium distance and the separation between adsorption sites, leads to a rich phase diagram, where commensurate (C) and incommensurate (IC) structures can be present^{1,2}. In a commensurate phase, the lack of translational invariance produces an energy gap (Δ) at the zone center in the acoustic branch of the phonon dispersion relation. The magnitude of this gap at low temperatures is related to the lateral variation of the adsorption potential, the so called corrugation. In an incommensurate phase, on the other hand, the translational invariance has been recovered and the phonon branches go to zero frequency at the zone center.

Changes in temperature and/or coverage induce phase transitions that are the result of a delicate balance between the interaction of the adsorbed gas and the substrate, and between the adsorbed gas molecules themselves. The interaction potential between the gas molecules is known in general in great detail. However, the knowledge of the details of the gas-adsorbate interaction potential is still sparse, since not many experimental techniques are available and it is very difficult to model it theoretically. The adsorption potential itself has been determined mainly with molecular beam scattering, but the magnitude of the in-plane corrugation is very difficult to obtain in this way. Recently, inelastic neutron scattering measurements of the corrugation have been performed for the hydrogen^{3,4} and helium⁵ isotopes, krypton⁶, methane⁷ and nitrogen⁸ adsorbed on graphite. These results have provided quantitative values against which the theoretical models of the adsorbate-substrate interaction can be compared.

The case of the quantum gases (the helium and hydrogen isotopes) is particularly interesting due to the similarity of their phase diagrams⁹⁻¹⁵. They all present a commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase at low coverages and temperatures. At higher coverages, they present an incommensurate phase which is the stable one up to monolayer completion. The C-IC transition goes through a domain wall phase (DW) at low temperatures and at higher temperatures through a domain wall liquid (DWL). The details of this C-IC transition varies slightly for the different quantum gases and the richest phase diagram is obtained for D₂. All these phases have been studied in detail by adsorption isotherms, specific heat and neutron diffraction measurements. The aim of neutron inelastic measurements is to determine the excitation spectrum of the different phases and to deduce the interaction potentials involved.

The detailed knowledge of the adsorption potential is not only relevant for adsorbed

monolayers, but is necessary to understand the gradual change of bulk properties that occur near an interface.

EXPERIMENTAL RESULTS

The measurements were performed on the three axis spectrometer IN14 and IN3 at the high flux reactor of the Institute Laue-Langevin. The spectrometer were used in the fixed final wavevector (K_F) mode with a Be filter after the sample and a horizontally curved analyzer. The sample consisted of 31.70g of Papyex¹⁶ sheets located in an aluminum container, oriented with their *c*-axis normal to the scattering plane. The total surface area was determined by adsorption isotherms and neutron diffraction.

Usually difference spectra are presented, where the scan taken with the graphite sample before adsorbing the gas is subtracted as background. For ³He, however, a corrected background must be used, since the large neutron absorption of ³He modifies drastically the signal coming from the graphite substrate. Therefore, in this case, the background scan has been multiplied by a transmission factor, *T*, to take this effect into account. This factor is a function of the sample geometry, the neutron energy-momentum transfer and the ³He coverage. The transmission per unit height has been calculated for a cylindrical sample integrating numerically the following formula:

$$T_{(R,\theta,\rho)} = \iint r \, dr \, d\phi \, \exp\left[-\left(\Sigma_{(K_I)} l_{I(r,\theta,\phi)} + \Sigma_{(K_F)} l_{F(r,\theta,\phi)}\right)\right]$$

where *R* is the radius of the sample, θ the scattering angle, ρ the ³He density, l_I and l_F the lengths of the initial and final path within the sample and Σ the corresponding inverse absorption length (coverage dependent). The transmission of the sample increases monotonically by about 30% between 0 and 1THz (1THz = 48.28K) for our experimental setup. An alternative method to determine the background is to use data obtained at the same coverage, but higher temperatures where the layer melts (above 3K for ³He). The melting, however, produces a broadening of the elastic peak due to quasielastic scattering related to the higher diffusion coefficient of the fluid. At still higher temperatures desorption occurs and again the signal from the substrate is modified. Thus, only the corrected background method can be used for this particular system. It must be pointed out that the elastic and inelastic signals are well separated, that corrections due to background subtraction are small and that the background does not show any peak in the inelastic region of interest; therefore, this procedure does not introduce significant systematic errors in the evaluation of the spectra within our present error bars.

The graphite sample, and hence the adsorbed layer, is essentially a 2D powder: the in-plane crystallographic directions are not oriented. Thus, the measured signal consists of a directional average over all phonons for which scattering is allowed (see insert in fig. 1). Scans were taken at a momentum transfer $Q = 1.70\text{\AA}^{-1}$. This corresponds to the distance between zone centers in reciprocal space for the C phase. Due to the powder average and the polarization factor, these scans focus on the phonons at the zone center (i.e., the gap region) and on the transverse phonons at the zone boundary. In scans performed at $Q = 0.85\text{\AA}^{-1}$, on the other hand, one works within the first Brillouin zone, and thus only longitudinal phonons can be excited^{3,17,18}.

The Hydrogen isotopes

In the first inelastic neutron scattering experiments¹⁹ only an "Einstein mode" could be detected in the commensurate phase and no phonon dispersion measured. More recent work, performed with higher resolution³, could assign the zone center phonon gap and the transverse and longitudinal zone boundary phonons. In figure 1 are shown the results for D₂, HD and H₂. Deuterium, which has a coherent neutron cross section, allows a separate measurement of the transverse and longitudinal phonons using the technique described in the paragraph above (see insert in fig. 1). HD and H₂, on the other hand, possess a large

Figure 1

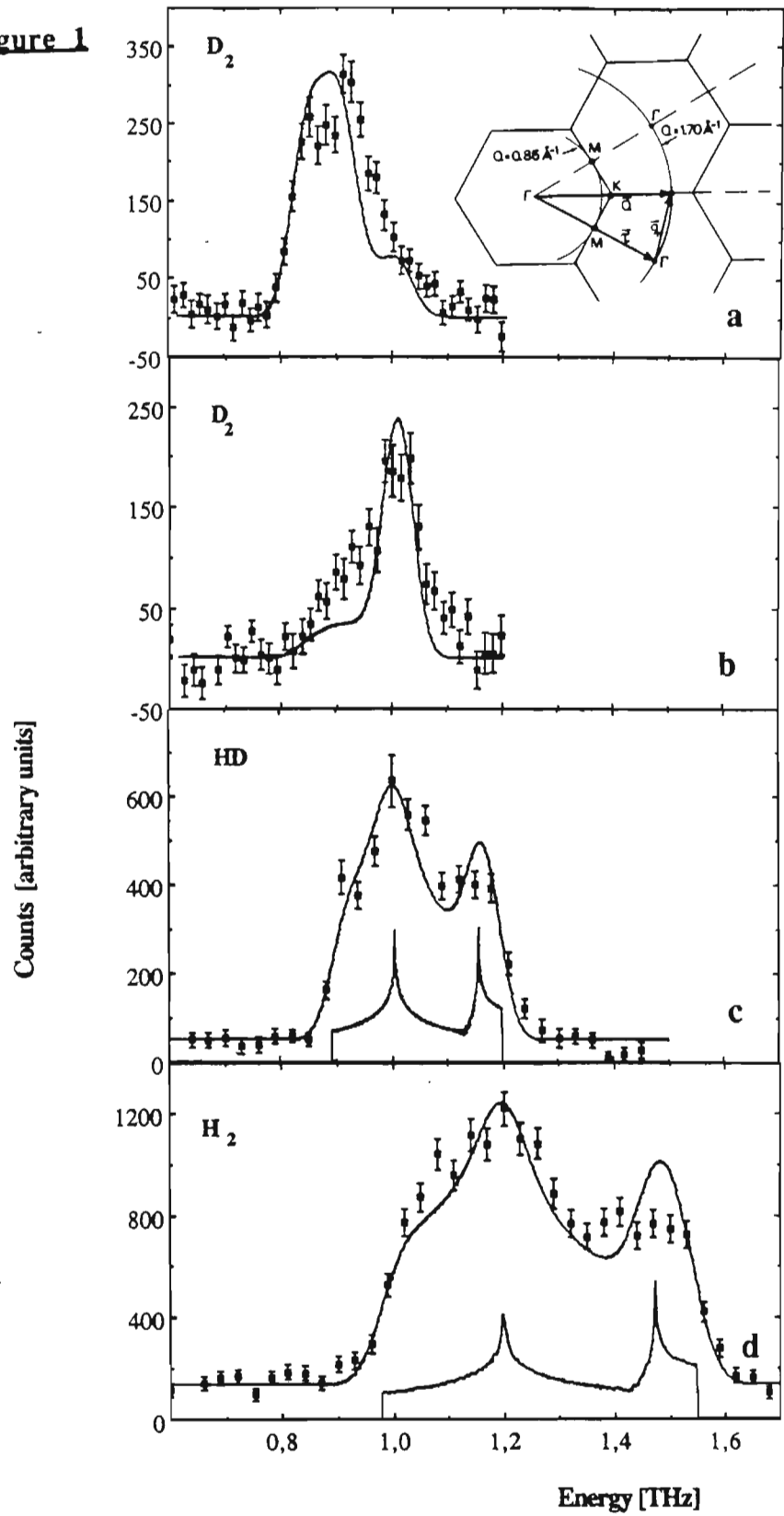


Figure 1: Neutron inelastic data of the hydrogen isotopes adsorbed on graphite in the commensurate phase (the background has already been subtracted). At the top are the deuterium (D₂) spectra for $Q=1.70\text{\AA}^{-1}$ (a) and $Q=0.85\text{\AA}^{-1}$ (b), the full line is the fit to the data as explained in Refs. 3 and 4. The insert shows the region of reciprocal space covered by these two scans. One example of a scattering triangle is sketched: it corresponds to the excitation of a transverse zone boundary phonon (Q is the total momentum transfer, τ is a reciprocal lattice vector and q is the phonon momentum). The deuterated hydrogen (HD) and the hydrogen (H₂) spectra taken at $Q=1.70\text{\AA}^{-1}$ are shown in parts (c) and (d), respectively. The curve through the experimental points is the fit with the phonon density of states convoluted with the energy resolution of the spectrometer. The unconvoluted density of states is drawn beneath it.

incoherent neutron cross section and thus, only the density of states can be measured. Nevertheless, the main features of the phonon spectrum could be identified and they are listed in Table I together with the theoretical results.

The zone center frequencies, which are a measure of the hydrogen-graphite corrugation, are in reasonable agreement with the calculations, but the width of the DOS is overestimated by theory. The interaction between the adsorbed molecules is weaker than expected and more theoretical work would be welcome. The mass dependence of the phonon spectrum cannot be explained with an isotopic effect only. This aspect will be discussed after the experimental results for the He isotopes have been presented.

Table I

Parameters characterizing the phonon density of states for the in-plane modes of the commensurate phase of the hydrogen isotopes adsorbed on graphite (the uncertainty of the experimental values is estimated to be ≈ 2 K).

	H ₂	HD	D ₂
Zone center gap ⁴ (neutron scattering)	47.3 K	43.2 K	40.0 K
calculations from reference 20	39.1 K	-	31.2 K
calculations from reference 21	46.6 K	-	36.9 K
DOS width ⁴ (neutron scattering)	27.5 K	14.7 K	9.5 K
calculations from reference 21	42.1 K	-	14.8 K

At higher coverages (around $\rho=1.15$) a striped domain wall phase could be identified using neutron diffraction and LEED²². Inelastic neutron spectra performed on D₂/graphite, show the appearance of a new excitation with an energy ≈ 29 K, lower than the phonon gap of the C phase²³. The fact that the energy of this excitation does not change when modifying the coverage (in the limits of the DW phase) suggests that it corresponds to the excitation of a single domain wall. If it were due to the interaction of domain walls it should shift in energy as the distance between domain walls is changed. The peak corresponding to the commensurate structure remains, but is reduced in intensity and begins to broaden due to lifetime effects. A very interesting aspect of these excitations is that they exist with a well defined shape in the domain wall liquid phase, where the diffraction data only show the signal of a liquid²³.

The inelastic spectra obtained for the IC phase of D₂ (with $\rho > 1.3$) show that the frequency of the modes increases linearly with coverage up to monolayer completion, indicating a gradual stiffening of the lattice. They can be fitted assuming a homogeneous triangular lattice, where, in first approximation, the effect of the substrate has been ignored. Such a fit is shown in figure 2 for $\rho=1.48$. The sound velocities obtained from this model are $c_L=2200$ m/s for the longitudinal modes and $c_T=1280$ m/s for the transverse ones. The nearest neighbor distance at this coverage is 3.50\AA . This is comparable to solid hcp D₂ at 279 bar²⁴ ($a=3.526\text{\AA}$, $c=5.750\text{\AA}$), where the sound velocities in the hexagonal planes are $c_L=2160$ m/s and $c_T=1130$ m/s.

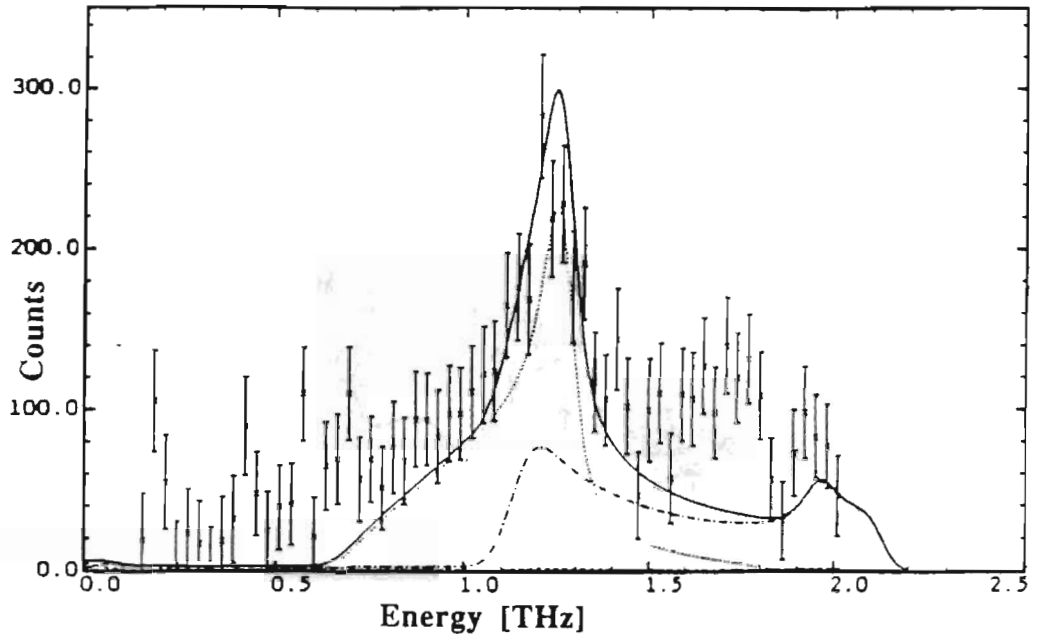


Figure 2: Inelastic spectra taken at $Q=1.70\text{\AA}^{-1}$ of D_2 adsorbed on graphite in the incommensurate phase ($\rho=1.48$, $T=4$ K). The full line is the fit to the data. The model considers a triangular lattice interacting through central harmonic forces, taking into account the mosaicity of the sample, the powder average and the resolution of the spectrometer as described in ref.3. The dotted line and the dashed-dotted line are the contribution of the transverse and longitudinal phonon branches, respectively. The fitted force constant between adjacent adsorbed molecules is 0.2 N/m, the corresponding longitudinal and transverse sound velocities are 2200 m/s and 1280 m/s, respectively.

The Helium isotopes

Only recently the zone center phonon gap of the commensurate phase of the He isotopes has been measured^{5, 25}. The large neutron absorption cross section of ^3He makes it extremely difficult to obtain reliable data. As discussed above, a corrected background has to be subtracted. ^4He , on the other hand, has a very small coherent neutron cross section which makes its measurement very difficult.

In figure 3a are shown the INS data obtained for a $\rho=0.9$ ^3He coverage at $T=0.85$ K. A clear peak can be seen at 0.27 THz which has been identified as the phonon gap. The dashed line is the background corrected for the large neutron absorption cross section of ^3He . Figure 3b depicts the same data with the background subtracted. The full line is a fit with a model that considers a triangular array of interacting helium atoms. Each atom also interacts with the graphite through a restoring force to its equilibrium position, the center of the graphite hexagon. All the forces are assumed to be central harmonic forces. The mosaicity and powder averages were performed as described in ref. 3.

The origin of the extra intensity at frequencies up to 0.7 THz is not yet clear. It can be ascribed to two possible origins: it is either the signal of the transverse zone boundary phonon or it is related to the out-of-plane bouncing mode. This out-of-plane mode has been found at 1.5 THz for a single He atom²⁷. It seems unlikely that the presence of adjacent He atoms should modify substantially this value. On the other hand, if the transverse phonon is at ≈ 0.65 THz, as suggested by the data, then the phonon dispersion relation of ^3He would be the largest measured for the quantum gases. This would imply that the effective interaction between the ^3He atoms is very strong, much stronger indeed than for the hydrogen isotopes.

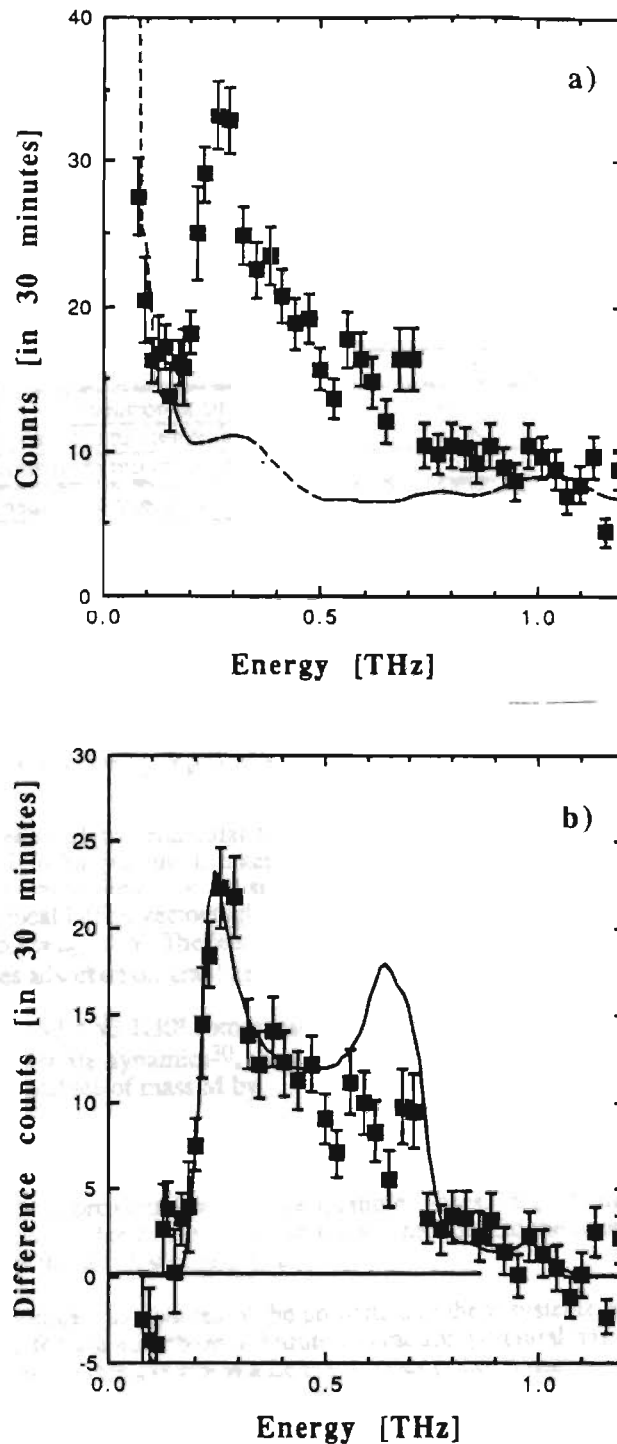


Figure 3: a) Neutron inelastic spectra for ^3He ($Q=1.70\text{\AA}^{-1}$, $\rho=0.9$ and $T=0.85\text{K}$). The dashed line is the background corrected for absorption as described in the text. b) The same data with the background subtracted. The full line is the fit with a model that considers a triangular array of ^3He atoms and takes account of the mosaicity and powder averages of the sample, as well as the spectrometer resolution.

If this feature is confirmed by further experiments, then the picture of the domain wall phase for ^3He will be completely different from that of hydrogen. The sharp superheavy domain walls found in the DW phase of the hydrogen isotopes is a result of the weak adatom-adatom interaction potential compared with the adatom-substrate one. In the case of ^3He the DW would consist of very broad domain walls (a rough calculation suggest that they would be ≈ 7 commensurate lines wide), since it would be energetically more favorable for the system to loose commensurability keeping the adatom-adatom separation as large as possible.

Table I

Parameters characterizing the phonon density of states for the in-plane modes of the commensurate phase of the helium isotopes adsorbed on graphite (the uncertainty of the experimental values is estimated to be ≈ 2 K).

	^3He	^4He
Zone center gap ^{5, 25} (neutron scattering)	11 K	11 K
calculations from reference 26	35 K	28 K
calculations from reference 20	16 K	16 K
DOS width ⁵ (neutron scattering)	(?)38 K	-

DISCUSSION

Usually, when modelling the adsorbate-substrate potential Steele's²⁸ Fourier decomposition has been used

$$V(\vec{r}, z) = V_0(z) + \sum_{\vec{g}} V_{\vec{g}}(z) \exp(i\vec{g} \cdot \vec{r})$$

where z is measured perpendicular to the substrate surface, \vec{r} is a vector in the plane of the surface (its origin for graphite is taken at the center of the honeycomb cell), and the vectors \vec{g} are reciprocal lattice vectors of the substrate surface lattice. This sum is truncated at the first shell of reciprocal lattice vectors $|\vec{g}| = g_0$ and the functions $V_0(z)$ and $V_{g_0}(z)$ are treated near the minimum ($z=z_0$) of V . The leading amplitude of the corrugation V_{g_0} is negative for the quantum gases adsorbed on graphite and the minimum adsorption energy is found²⁹ at $r=0$.

For the $(\sqrt{3} * \sqrt{3})R30^\circ$ commensurate lattice, ignoring a possible hybridization of the adlayer and substrate dynamics³⁰, the frequency for the in-plane zone center phonon gap is given for an adsorbate of mass M by

$$\Delta = g_0 [- 3 V_{g_0} / M]^{0.5}$$

in an harmonic approximation. For the quantum gases, large deviations from this simple formula is expected due to their large zero point motion and the strong anharmonicity of the in-plane part of the adsorption potential.

In theoretical calculations of the properties of these systems, a form for the adsorbate-adsorbate and for the adsorbate-substrate interaction potential has to be assumed. For the interaction between rare gas atoms a Lennard-Jones (12,6) form:

$$\varphi(r) = 4 \epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$$

seems quite reasonable, but also more accurate potentials have been proposed³¹. For the hydrogen isotopes calculations Novaco²¹ used the Silvera-Goldmann³² potential.

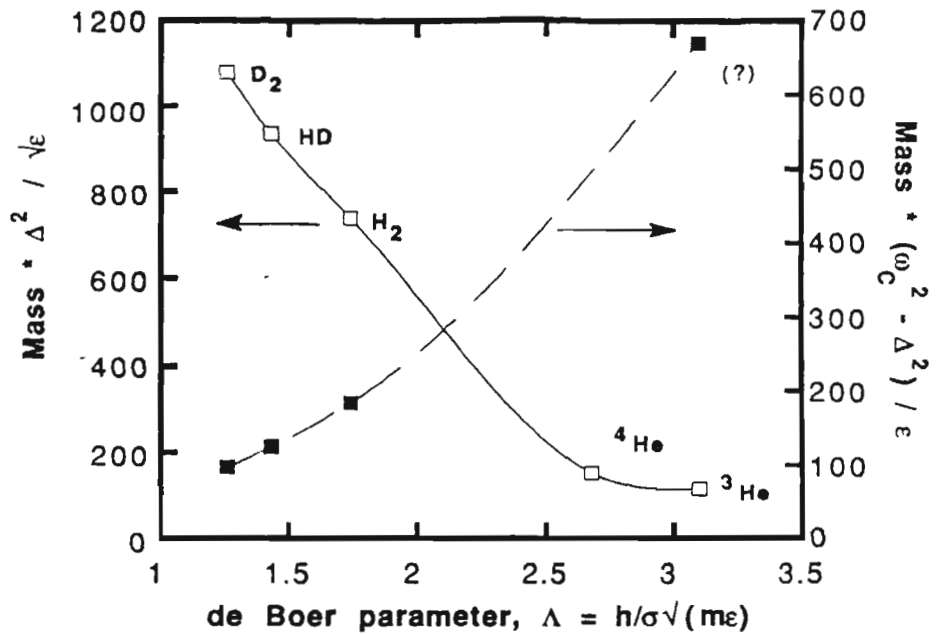


Figure 4: Gap values and DOS width plotted vs. the de Boer parameter Λ for the quantum gases (Λ is the ratio between the de Broglie wavelength of the relative motion of two atoms with energy ϵ and the minimum in the LJ potential). The values plotted are reduced quantities and are explained in the text.

For the interaction with the substrate the Lorentz-Berthelot rules for unlike interactions have been generally accepted:

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB}) / 2$$

$$\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{0.5}$$

combining the Lennard-Jones parameter of both systems. This practice is questionable, since it is known that the geometric mean often overestimates ϵ_{AB} and other combining rules have been suggested^{33,34}. To circumvent this problem, a set of Lennard-Jones parameters have been constructed that match the values of the bound state energies as determined by selective adsorption experiments^{21,35,36}. The results of these calculations, as shown in Tables I and II, are quite encouraging and reproduce very well the experimental gap values. An excellent review on the substrate corrugation problem for rare gases and also more complicated molecules has been presented recently by Bruch³⁷.

Figure 4 presents the gap and DOS width values for the quantum gases. Assuming the Lorentz-Berthelot combination rule, V_{go} is proportional to $(\epsilon_{AA} \epsilon_{BB})^{0.5}$, where ϵ_{AA} corresponds to the adsorbate and ϵ_{BB} to graphite. The quantity $M \Delta^2 / \epsilon_{AA}^{0.5}$ should always be a constant. There is still a dependence on σ that is left, but it should not modify dramatically the result, since it changes only slightly between He and H₂. The strong departure of a constant seen in figure 4, is an evidence of the importance of the quantum character of these molecules. The large zero point motion, increasing with the de Boer parameter, averages the surface corrugation producing a lower effective corrugation.

The DOS width is a measure of the interaction between adsorbed molecules. All the quantum gases adsorbed in the C phase are diluted respect to their bulk value. A larger zero point motion increases the overlap of the wave functions and produces a stronger effective interaction. The quantity $M (\omega_C^2 - \Delta^2) / \epsilon_{AA}$, where ω_C is the upper cutoff frequency of the DOS, should also be constant. A clear increasing tendency is displayed by the hydrogen isotopes⁴, unfortunately the ³He value is still only a guess.

CONCLUSIONS

The agreement between theoretical calculations for the commensurate phase and experimental values for the phonon gap is reasonable, but the interaction between adatoms is still overestimated. The measurements performed in the C and IC phases allow the determination of elastic constants which are comparable to bulk systems under large positive and negative pressures. An adequate analysis of these data permit the determination of the interaction potential at distances that are hard to reach in 3D matter. A precise knowledge of the graphite surface has an intrinsic interest that goes beyond the adsorbate monolayer regime.

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