Calculated properties of the commensurate monolayers of helium and hydrogen on graphite

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Calculations of the mean-square lateral displacements and of the Brillouin-zone-center frequency gap are reported for the $\sqrt{3}R30°$ lattices of helium adsorbed on the basal plane surface of graphite. Results, which depend strongly on the value adopted for the corrugation amplitude in the holding potential, are in good agreement with experimental data. Correction and extension of calculations reported by the authors in Phys. Rev. B **40**, 148 (1989) bring the results for hydrogen also into good agreement with experimental data.

Commensurate monolayer solids of helium and of hydrogen adsorbed on the basal plane surface of graphite have a gap in the in-plane frequency spectra at zero wave vector, the Brillouin-zone-center frequency gap, which is directly related to the leading amplitude V_g in the Fourier expansion of the lateral periodicity of the admolecule-substrate holding potential. The amplitude V_g also has a major effect in determining the mean-square lateral displacements in the ground state of the commensurate solid. Both the frequency gap and the mean-square displacement are probed in recent neutron-scattering experiments[1-4] on adsorbed helium and on adsorbed molecular hydrogen. We report here calculations for the $\sqrt{3}R30°$ commensurate lattice of helium on graphite and a correction and extension of our results[5] for the hydrogen case.

The major components of the interactions for the helium/graphite system are quite well determined. The helium-helium isolated pair potential has been the subject of many studies; we adopt here the HFDHE2 potential of Aziz et al.[6] The lateral average of the helium-graphite potential was constructed[7] from selective adsorption resonances in atom-surface scattering. Those experiments also give a value $\bar{V}_g = -0.28$ meV ($= -3.25$ K) for the average, in the ground state of perpendicular (z) motion, of the amplitude for wave vector $g_0 = 2.95$ Å^{-1}. Therefore, one may anticipate good agreement between model calculations based on these interactions and the new data which are sensitive to $\bar{V}_g$. This is accomplished in our calculations using the two-dimensional quantum monolayer solid formalism of previous papers:[5,8] The helium calculations are now refined to include the periodic potential terms $\bar{V}_g$ when optimizing the parameters in the Jastrow trial function.

It is necessary to distinguish several stages in the development of the calculations before making comparisons to experimental data. The Hartree approximation[8] has a self-consistent treatment of noncorrelated atomic motions in the solid and is less detailed than the Jastrow variational treatment which includes correlation effects. For two-dimensional quantum solids on a smooth substrate, the mean-square displacements about average lattice sites are much larger[8] in the Jastrow ground state than in the Hartree ground state. The larger values are supported by Green's-function Monte Carlo calculations[9] for helium, which have a more complete treatment of the correlations

than in the Jastrow trial function. However, when the Jastrow function is optimized for a model which includes the $\bar{V}_g$ terms, the atoms are much more localized about the average lattice sites and the mean-square displacements are reduced and numerically become closer to the initial Hartree estimates.[8]

Similarly, the first excitation energy calculated[8] with the Hartree ground-state wave function for an effective field for single-particle motion represents an average excitation frequency of the adlayer. A much better estimate[5] of the zone-center frequency gap is based on an adiabatic approximation for the restoring force for small lateral displacements of the center of mass. The resulting approximation for the angular frequency Ω of oscillations of molecules of mass M about the honeycomb centers on the graphite is

$$\Omega = g_0[-3\bar{V}_g\langle\exp(i\mathbf{g}\cdot\mathbf{r})\rangle/M]^{0.5}, \qquad (1)$$

where $\bar{V}_g$ denotes the z-averaged energy amplitude and the second expectation value denotes an average in the ground state of the lateral motion for a primitive substrate reciprocal lattice vector ($|\mathbf{g}| = g_0 = 2.95$ Å^{-1} here). Equation (1) is formally the same as the zone-center frequency calculated in the self-consistent phonon theory[10] of the adlayer; the new Jastrow calculations lead to larger values for the expectation value, because of the tighter localization about lattice sizes.

The mean-square lateral displacement for D_2/graphite has been estimated[2] from the ratio of the structure factors (intensities) of the (10) and (11) Bragg reflections of the adlayer, using the Debye-Waller expression:

$$S_{(11)}/S_{(10)} = \exp(-\tau_0^2\langle u^2\rangle_{DW}), \qquad (2)$$

where τ_0 is the magnitude of the (10) wave vector (1.70 Å^{-1} here). Implicit in the use of Eq. (2) is a neglect of anharmonic effects and of some multiphonon processes. We have calculated $\langle u^2\rangle_{DW}$ from structure-factor averages with the Jastrow trial function; as shown in Table I the values agree to 10% with the direct calculation of the mean-square displacements for the same trial functions.

Our results for the zone-center frequency gap, calculated with Eq. (1), and for the mean-square lateral displacements, calculated directly and derived from calculated structure-factor ratios using Eq. (2), are collected in

TABLE I. Properties of commensurate lattices on graphite. For helium, the Jastrow calculations are for two-dimensional solids with the HFDHE2 potential and $\bar{V}_g = -3.25$ K. For hydrogen, the results are for the Silvera-Goldman potential without substrate-mediated interactions [case (a) of Ref. 5] and $\bar{V}_g = -6.4$ K.

	³He	⁴He	H₂	D₂
Ω [a]				
Eq. (1)	16	16	39.1	31.2
Expt.	13[b]		47.3[c]	40.2[c]
$\langle r^2 \rangle$ [d]	0.76	0.63	0.446	0.334
$\langle u^2 \rangle_{DW}$	0.71	0.61	0.436	0.328
Expt.	0.58[e]			0.25[f]

[a]Zone-center frequency gap in K, with Jastrow expectation values in Eq. (1).
[b]Reference 3.
[c]References 4 and 1.
[d]Mean-square displacements in Å^2, calculated directly from the Jastrow expectation value $\langle r^2 \rangle$ and derived from the Jastrow calculations of the structure factors by Eq. (2), $\langle u^2 \rangle_{DW}$.
[e]Estimate in Ref. 3 based on the measured zone-center gap.
[f]Derived in Ref. 2 from the observed (11) and (10) diffraction intensities, using Eq. (2).

Table I. The values for helium have a firmer grounding than the values for hydrogen, because the helium value of $\bar{V}_g$ is directly based on atomic scattering data; for hydrogen the value of $\bar{V}_g$ is derived from modeling of the lateral average of the holding potential and is more uncertain.[8,10] Our results for the monolayer solids are based on a two-dimensional quantum theory; Novaco[10] showed for hydrogen that a three-dimensional theory may lead to 25% changes in the effective value for V_g in the solid.

The helium calculations also have relevance for the self-binding of the monolayer. Both ³He and ⁴He show a condensation transition from a dilute two-dimensional (2D) gas to commensurate monolayer solid, indicating that the solid is self-bound. The 2D ground-state energy for the commensurate lattice of ⁴He/graphite is -2.5 K/atom with the present model, more tightly bound than estimates for the binding energy of 2D liquids of ⁴He. The 2D ground-state energy of the commensurate lattice of ³He/graphite is $+0.8$ K/atom with this model, i.e., not self-bound; however a 20% increase in the value of V_g is sufficient to achieve self-binding with an energy of -0.03 K/atom. These values are indicative that small adjustments to the present model will suffice to reproduce the observed self-binding of the ³He monolayer; the three-dimensional character of the adsorbed layer and sub-strate-mediated interactions must be included before this conclusion is firmly established.

The zone-center frequency gap should lead to an apparent Einstein oscillator term in the specific heat of the commensurate monolayer. It is observed for the commensurate H₂/graphite,[11] but there is no temperature range for the commensurate He/graphite where an exponential activation process clearly dominates the experimental data. Motteler's reanalysis[12] of the He/graphite data in terms of several energy modes shows evidence for peaks in the spectral density at excitation energies of 11 K (⁴He) and 12 K (³He), but there are also spectral peaks at energies of 1–3 K which have no explanation thus far.

The level of agreement between the modeling and observations for the commensurate lattices of helium and of hydrogen is important in establishing cases where the corrugation amplitude has some confirmation in experimental data. It sharpens the contradictions which arise in attempts to model the zone-center gap for commensurate lattices of anisotropic molecular adsorbates.

[1]V. L. P. Frank, H. J. Lauter, and P. Leiderer, Phys. Rev. Lett. 61, 436 (1988).
[2]H. Freimuth, H. Wiechert, H. P. Schildberg, and H. J. Lauter (unpublished).
[3]V. L. P. Frank, H. J. Lauter, H. Godfrin, and P. Leiderer (unpublished).
[4]H. J. Lauter, Phonons 89 (World Scientific, Singapore, in press).
[5]J. M. Gottlieb and L. W. Bruch, Phys. Rev. B 40, 148 (1989). The mean-square displacements on p. 153 are to be divided by 2, to correct for a programming error; the energies and structure factors are not affected by this error.

[6]R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, J. Chem. Phys. 70, 4330 (1979).
[7]M. W. Cole, D. R. Frankl, and D. L. Goodstein, Rev. Mod. Phys. 53, 199 (1981), and references therein.
[8]X.-Z. Ni and L. W. Bruch, Phys. Rev. B 33, 4584 (1986).
[9]P. A. Whitlock, G. V. Chester, and M. H. Kalos, Phys. Rev. B 38, 2418 (1988).
[10]A. D. Novaco, Phys. Rev. Lett. 60, 2058 (1988).
[11]F. A. Chaves, M. E. B. P. Cortez, R. E. Rapp, and E. Lerner, Surf. Sci. 150, 80 (1985).
[12]F. C. Motteler, Ph.D. thesis, University of Washington, 1986.