Zone-center frequency gap of a commensurate quantum monolayer solid

L. W. Bruch
Department of Physics, University of Wisconsin–Madison, Madison, Wisconsin 53706
(Received 4 October 1993)

Identities and approximations are developed for the first and second moments of the spectral density of center-of-mass oscillations of a commensurate quantum monolayer solid. This corresponds to the one-phonon approximation for inelastic scattering at a reciprocal lattice vector. The results are applied with parameters for monolayers of helium/graphite and hydrogen/graphite. Estimates of the zone-center gap with averages in an optimized Jastrow trial function are internally consistent to better than 10%. There is a marginal level of agreement between the zone-center gap for helium/graphite observed with inelastic neutron scattering and the gap calculated with the Fourier component of the helium/graphite potential derived from atom-surface scattering. The application for hydrogen/graphite amounts to a reanalysis of previous calculations and is in good agreement with them.

I. INTRODUCTION

There is only a small body[1] of empirical data for the leading Fourier component, or corrugation amplitude, in the adatom-substrate potential energy; thus, an instance with two fairly direct measures of the amplitude merits further examination of the consistency of the results. For the helium/graphite system the corrugation amplitude at the potential minimum was derived[2–4] from band-structure splittings of selective adsorption resonances in atom-surface scattering. Recently, the frequency gap[5,6] at the Brillouin zone center of the commensurate helium/graphite monolayer was observed with inelastic neutron scattering for a wave-vector transfer equal to a reciprocal lattice vector. An improved method of relating the zone-center gap to the corrugation amplitude is informative for the energy topography of an adsorbing surface and for analysis[7] on the relative stability of commensurate and incommensurate monolayer solids.

Here, identities and approximations are developed for the frequency moments and spectral density[8,9] at the Brillouin zone center of a quantum monolayer solid. At the zone center of a lattice with one atom per unit cell, the adatom motions are in phase and the collective coordinate is the center-of-mass displacement vector, enabling a more complete account of the response[8] than at a general point in the Brillouin zone. The spectral density of center-of-mass oscillations is also the response function corresponding to the one-phonon approximation[9] for inelastic scattering at a reciprocal lattice vector.

The response is estimated three ways: (i) with an approximation introduced by Feynman[10] for the spectrum of density oscillations in three-dimensional superfluid ^{4}He, (ii) with an approximation[11] for the restoring force constant similar to the Born-Oppenheimer approximation, and (iii) from the first and second moments of the spectral density.[8,9] The estimates are formulated first as averages in the ground state of the quantum solid, which may be accessible with developments of nominally exact solutions.[12] Then approximate relations among these quantities are derived by evaluating the averages with optimized Jastrow variational trial functions for a planar monolayer. Numerical illustrations are given for models used[7,13,14] for helium/graphite and hydrogen/graphite.

The organization of this paper is as follows: Section II contains the derivation of identities and approximations for the frequency moments and the excitation energy at the Brillouin zone center. Section III contains results of applications to monolayer quantum solids and a discussion of the consistency of helium-graphite scattering data and inelastic neutron-scattering data. Section IV contains concluding remarks.

II. FORMULATION

Let the average lattice positions be specified by $R_{j\alpha}$ and the actual position by $r_{j\alpha}$, where the index j enumerates the atom (1 to N) and the index α denotes the Cartesian component. The center-of-mass vector η_α is defined in terms of displacements from the average lattice positions by

$$\eta_\alpha=(1/N)\sum_{j=1}^{N}(r_{j\alpha}-R_{j\alpha})\ . \tag{2.1}$$

Components $\alpha=x$ and $\alpha=y$ refer to displacements in the plane of the monolayer, and the y axis is taken to be parallel to a primitive reciprocal lattice vector of the commensurate monolayer.

The spectral function of center-of-mass motions is defined[8,9] by an average in the ground state

$$S_\alpha(\omega)=(1/2\pi)\int_{-\infty}^{\infty}\langle\eta_\alpha(t)\eta_\alpha(0)\rangle e^{i\omega t}dt\ , \tag{2.2}$$

where the time dependence is governed by a Hamiltonian with pair-potential interactions among the adatoms and a spatially periodic external potential from the substrate

$$H=\sum_j(p_j^2/2m)+\sum_{i<j}\phi(|r_j-r_i|)+\sum_j v_{\rm ext}(r_j)\ . \tag{2.3}$$

A. Identities

The zeroth, first, and second moments of the spectral function S_α are given by[15]

$$\int_{-\infty}^{\infty} S_\alpha(\omega)d\omega=\langle \eta_\alpha(0)^2\rangle \ , \tag{2.4}$$

$$\hbar\overline{\omega_\alpha}=\int \hbar\omega\, S_\alpha(\omega)d\omega \Big/ \int S_\alpha(\omega)d\omega=\hbar^2/(2mN\langle \eta_\alpha^2\rangle) \ , \tag{2.5}$$

$$\hbar^2\overline{\omega_\alpha^2}=(\hbar^2/mN)\left\langle \eta_\alpha \sum_j \partial_{j\alpha} v_{\rm ext}(r_j)\right\rangle \Big/ \langle \eta_\alpha^2\rangle \ . \tag{2.6}$$

The virial theorem is derived[16] by evaluating the ground-state expectation value of the commutator of the center-of-mass virial operator and the Hamiltonian

$$\langle [\eta_\alpha P_{c\alpha}, H]_-\rangle=0 \ , \tag{2.7}$$

where $P_{c\alpha}$ denotes the α component of the total (center-of-mass) momentum. Thus, the center-of-mass kinetic energy and the virial of the total force acting on the center of mass are related by

$$\langle P_{c\alpha}^2/mN\rangle=\left\langle \eta_\alpha \sum_j \partial_{j\alpha} v_{\rm ext}(r_j)\right\rangle \ . \tag{2.8}$$

An approximate excited state wave function, orthogonal to the exact ground state Ψ_0, is $\eta_\alpha\Psi_0$. As in a similar construction by Feynman,[10] it leads to an upper bound for the excitation energy

$$E_{\rm exc}\le \hbar^2/(2mN\langle \eta_\alpha^2\rangle)=\hbar\overline{\omega_\alpha} \ . \tag{2.9}$$

If the center-of-mass motion is a harmonic oscillation, the inequality becomes an equality and the excitation energy is equal to the first frequency moment of S_α.

The uncertainty principle gives an inequality

$$\langle \eta_\alpha^2\rangle \ge \hbar^2/(4\langle P_{c\alpha}^2\rangle) \ . \tag{2.10}$$

When combined with Eq. (2.6) for the second moment and the virial theorem, Eq. (2.8), it leads to the result

$$\overline{\omega_\alpha^2}\ge(\overline{\omega_\alpha})^2 \ . \tag{2.11}$$

Of course, this is also a direct consequence of the definitions of the moments.

The Born-Oppenheimer approximation to the zone-center frequency is derived from the force constant for lateral displacements of the adlayer and is[11]

$$\hbar^2\omega_{\rm BO}^2|_\alpha=(\hbar^2/mN)\left\langle \sum_j \partial_{j\alpha}^2 v_{\rm ext}(r_j)\right\rangle \ . \tag{2.12}$$

A similar construction has been used[17] for a classical molecular monolayer with a potential energy which was optimized with respect to eight of the ten molecular coordinates in the unit cell. There, within the context of the quasiharmonic approximation, it can be shown that the lowest frequency of the Born-Oppenheimer approximation is an upper bound to the lowest frequency (the "gap") of the full lattice dynamics theory.

The ground-state expectation values are accessible in nominally exact solutions, such as with the Green's-function Monte Carlo Method.[12] Explicit reductions of the expectation values occur when approximate forms for the ground-state function are used; then Eqs. (2.8) and (2.11) give measures of the internal consistency of the approximation.

B. Relations based on the Jastrow trial function

The Jastrow function $\Psi_{\rm JS}$ is a variational approximation[7] to the ground-state wave function Ψ_0; as used here it is

$$\Psi_{\rm JS}=\exp(-S/2) \tag{2.13a}$$

with

$$S=\sum_{i<j}(b/r_{ij})^5+A\sum_j (r_j-R_j)^2 \ , \tag{2.13b}$$

where b and A are parameters selected to minimize the trial ground-state energy. The center of mass is localized for $\Psi_{\rm JS}$, a feature which is a nuisance in the nuclear many-body problem,[18] but which is a physical aspect of the commensurate monolayer. In this section, the vectors r_j and R_j are in a two-dimensional (x-y) plane and there is an implicit factorization[13] of the average over motions perpendicular to the plane. This trial function incorporates the small-mass effects of a quantum solid, but it does not include exchange terms.

Identities for expectation values $\langle \ldots \rangle_J$ with respect to $\Psi_{\rm JS}$ are derived from derivatives of the generating function

$$F(\xi)=\langle \exp(-i\xi P_{c\alpha}/\hbar)F\exp(i\xi P_{c\alpha}/\hbar)\rangle_J \tag{2.14}$$

using the relation

$$\exp(i\xi P_{c\alpha}/\hbar)\exp[-S(r_1,\ldots,r_n)/2] = \exp[-S(r_1+\xi n_\alpha,\ldots,r_N+\xi n_\alpha)/2] \ , \tag{2.15}$$

where n_α denotes a unit vector along the α-Cartesian axis and ξ is a parameter. The fact that the center-of-mass displacement has a Gaussian distribution is proved by examining the moments obtained by evaluating the derivative $dF(\xi)/d\xi$ at $\xi=0$ for $F=\eta_\alpha^k$, with $k=1,2,3,\ldots$.

Components of the mean-square displacement thus are related to the parameter A in the trial function by

$$\langle \eta_\alpha^2\rangle_J=1/(2NA) \ . \tag{2.16}$$

Similarly, the choice

$$F=\sum_j \partial_{j\alpha} v_{\rm ext}(r_j) \tag{2.17}$$

leads to a relation between the virial and the force constant in the Born-Oppenheimer approximation for the frequency

$$\left\langle \sum_j \partial_{j\alpha}^2 v_{\rm ext}\right\rangle_J=(2NA)\left\langle \eta_\alpha \sum_j \partial_{j\alpha} v_{\rm ext}\right\rangle_J \ . \tag{2.18}$$

Thus, the Born-Oppenheimer frequency is identical to the root-mean-square frequency, for the Jastrow trial function

$$\omega_{\rm BO}^2|_{J\alpha}=\overline{\omega_{J\alpha}^2} \ . \tag{2.19}$$

Equation (2.9) is a bound for the excitation energy relative to the (unknown) exact ground-state energy. A leading approximation, used in Sec. III is to evaluate an energy $\hbar\omega_\alpha(J)=\hbar^2 A/m$ for the optimized Jastrow trial function by using Eq. (2.16) in Eq. (2.5). Another estimate for

the excitation energy is the difference of the expectation value of the Hamiltonian H in the optimized states Ψ_{JS} and $\eta_\alpha\Psi_{JS}$:

$$E_{exc}(JS)=\hbar\omega_\alpha(J)+\Delta\epsilon(JS) \tag{2.20}$$

with

$$\Delta\epsilon(JS)=[\langle\eta_\alpha^2 H\rangle_J-\langle H\rangle_J\langle\eta_\alpha^2\rangle_J]/\langle\eta_\alpha^2\rangle_J \ . \tag{2.21}$$

A further relation involving $\Delta\epsilon(JS)$ arises in the generalization[16] of the virial theorem, Eqs. (2.7) and (2.8), to the Jastrow trial states. The form valid for variational calculations with optimized length scales does not apply but calculus with the virial operator for the center of mass leads to

$$\left\langle\eta_\alpha\sum_j\partial_{j\alpha}v_{ext}\right\rangle_J-(\langle P_{c\alpha}^2\rangle_J/Nm)=\Delta\epsilon(JS) \ . \tag{2.22}$$

An explicit form of Eq. (2.22) for v_{ext} which is simply periodic is given in Eq. (3.3).

Direct evaluation yields the mean-square total momentum in terms of the mean-square displacement

$$\langle P_{c\alpha}^2\rangle_J=(NA\hbar)^2\langle\eta_\alpha^2\rangle_J \ . \tag{2.23}$$

Combining Eqs. (2.16), (2.22), and (2.23) with Eq. (2.6) yields

$$[\hbar^2\overline{\omega_{J\alpha}^2}-(\hbar\overline{\omega_{J\alpha}})^2]/(\hbar\overline{\omega_{J\alpha}})^2=\Delta\epsilon(JS)/(\langle P_{c\alpha}^2\rangle_J/Nm) \ . \tag{2.24}$$

Thus, the dispersion of the Jastrow approximation to the spectral function $S_\alpha(\omega)$ is proportional to the remainder $\Delta\epsilon(JS)$ in the generalized virial theorem, Eq. (2.22). As noted in Sec. III, the remainder is sometimes negative, and then Eq. (2.11) is violated for the moments evaluated with the Jastrow trial function. That is, if the expectation value in Eq. (2.2) is taken in a Jastrow state, the resulting spectral function may become negative.

III. APPLICATIONS

The formalism of Sec. II is applied to the calculation of the Brillouin zone-center frequency gap of the commensurate $(\sqrt{3}\times\sqrt{3})\ R30°$ lattice of quantum monolayer solids adsorbed on the basal plane surface of graphite. For H_2 and D_2 the application amounts to a reanalysis of previous calculations[13,14] with the Silvera-Goldman intermolecular potential. For ^{3}He and ^{4}He, recent work[7] with the Aziz-McLachlan effective interaction is extended and the consistency of two measures[4,6] of the corrugation amplitude is discussed.

The monolayer motions are assumed[1,7] to be in a plane determined by the laterally averaged adatom/graphite potential. The external potential of Eq. (2.3),

$$v_{ext}(r_j)=\sum_g\overline{V_g}\exp(i\mathbf{g}\cdot\mathbf{r}_j) \ , \tag{3.1}$$

has a sum over the (six) shortest reciprocal lattice vectors of the graphite surface. The amplitude $\overline{V_g}$ is the result of an average over perpendicular (out-of-plane) motions of the adatom; this separation of out-of-plane motions is also present in Novaco's treatment[13] of the dynamics of monolayers of molecular hydrogen. The averaging over perpendicular motions is different for a single atom under the conditions of the selective adsorption resonances and for an adatom in a commensurate monolayer. In calculations for adsorbed molecular hydrogen that effect leads[13] to a significant increase in the magnitude of the effective amplitude for the commensurate lattice.

The results for H_2 and D_2 in Sec. III B are for the choice[14] $\overline{V}_g=-6.4$ K, which is based on an isotropic atom-atom model for the hydrogen/graphite interaction. Novaco[13] has a similar interaction model, but with commensurate lattice effective amplitudes of -7.7 and -8.1 K for H_2 and D_2, respectively. For helium, the value $\overline{V}_g=-3.25$ K has been used[7] as the best estimate, based on helium-graphite scattering data.[4] For ^{4}He/graphite, the enhancement in the commensurate lattice is estimated to be 5–10 %, using matrix elements and energy levels from the scattering data for the adatom/graphite potential.[4] The tests in Sec. III A explore trends for values in the range -1.5 to -3.8 K.

A. Tests

A consequence of Eqs. (2.16) and (2.18) is that the first and second frequency moments for the Jastrow function can be evaluated with information collected[7,14] in variational calculations of the ground-state energy, namely, the optimal value of the parameter A and the expectation value of v_{ext}. These results of operator calculus on the generating function, Eq. (2.14), are tested by Monte Carlo evaluations of the averages for both x and y components of the center-of-mass displacement. The equalities in Eqs. (2.16) and (2.18) are verified to within 3% from Monte Carlo averages over 2×10^6 configurations of a periodically repeated cell of 100 atoms for the helium case. Moments of $S_x(\omega)$ and $S_y(\omega)$ on the hexagonal lattice should be equal for the Jastrow function, Eq. (2.13); the equality is verified to 5% in the computations.

The magnitude and sign of the remainder in the generalized virial theorem, Eq. (2.22), are examined by Monte Carlo evaluation of the terms in the ratio

$$TV_\alpha=\left\langle\eta_\alpha\sum_j\partial_{j\alpha}v_{ext}(r_j)\right\rangle_J\Big/(\langle P_{c\alpha}^2\rangle_J/Nm) \tag{3.2}$$

for the helium/graphite model.[7] The ratio increases from 0.9 to 1.2 for ^{4}He as the parameters A and b are optimized for $\overline{V}_g$ decreasing from -1.5 to -3.8 K. The corresponding variation of TV_α for ^{3}He is from 0.7 to 1.1. The fluctuations in TV_α for averages over 2×10^6 to 4×10^6 Monte Carlo configurations of 100 particles are on the scale of 0.1.

Attempts to calculate $\Delta\epsilon(JS)$ directly from the covariance, Eq. (2.21), were unsuccessful, due to large fluctuations in the averages and sensitivity to the range of configurations selected in a simulation of up to 4×10^6 Monte Carlo configurations. Much more stable answers were obtained from the expression

$$\Delta\epsilon(JS)=-(A\hbar^2/2m)-(g^2/4NA)\left\langle\sum_j v_{ext}(r_j)\right\rangle_J \tag{3.3}$$

which is derived from Eq. (2.22) by using Eqs. (2.18) and

(2.23) and (3.1) for the external potential.

The interpolation and smoothing procedures for the Monte Carlo expectation values are also a source of uncertainty. In the helium case, a grid of approximately 100 (A,b) pairs is available;[7] the optimal value of A appears to be determined to within 2–4 %, depending on the isotope and the value of $\bar{V}_g$.

B. Zone-center frequency gap

Results for the zone-center frequency gap are shown in Tables I and II for models of hydrogen/graphite and helium/graphite, respectively. The energy $\hbar\omega(J)$ is $\hbar^2 A/m$. The root-mean-square energy, from Eqs. (2.19) and (3.1), is

$$\hbar\omega_{\rm rms}=\sqrt{(\hbar^2\overline{\omega_J^2})} = \left[(-\hbar^2 g^2/2Nm)\left\langle \sum_j v_{\rm ext}\right\rangle_J\right]^{1/2} . \quad (3.4)$$

The energy $E_{\rm exc}$(JS) is the Jastrow excitation energy, Eq. (2.20), and the scaled energy $\Delta\epsilon$(JS) gives the departure from unity of the virial test ratio Eq. (3.2).

The results in Table I are based on previous Monte Carlo calculations[14] for monolayer solids of the molecular hydrogen isotopes. The entry for $\omega_{\rm rms}$ had been reported[11] as the Born-Oppenheimer approximation to the zone-center frequency, Eq. (2.19). The results illustrate the discussion of Eq. (2.24): the ratio TV_α, Eq. (3.2), may be either larger or smaller than 1 and Eq. (2.11) may be violated for the Jastrow expectation values. There is a remarkable internal consistency of the estimates for a given case. In particular, the values $E_{\rm exc}$ (JS) are scarcely distinguishable from the rms energy values; this is a surprise in the light of conventional caution about forming an excitation energy from the energy difference between an approximate excited state and approximate ground state.

The inelastic neutron-scattering results[5] for the zone-center gap are 47 K for H_2/graphite and 40 K for D_2/graphite. Specific-heat data[19] for commensurate H_2/graphite are fit to an Einstein oscillator excitation of ca. 55 K. The values in Table I are rather far from these. Novaco's initial values[13] with $\bar{V}_g=-6$ K are close to the values in Table I, but his final values, with an effective $\bar{V}_g$, are 47 and 37 K, respectively. The agreement among the values $E_{\rm exc}$(JS), $\omega_{\rm rms}$, and the self-consistent phonon result[13] indicates that the zone-center frequency gap for the commensurate hydrogen monolayers may be evaluated to 5% for a given model. However, the input value for the corrugation amplitude remains uncertain[13] because of the lack of relevant[4] molecule-graphite scattering data.

TABLE I. Zone-center gap for hydrogen/graphite. [The zone-center gap, in K, for the commensurate $\sqrt{3}$ monolayer of hydrogen/graphite and of deuterium/graphite. The experimental values from inelastic neutron scattering (Ref. 5) are 47 and 40 K, respectively. The energy estimates are defined in Sec. III B of the text.]

Case[a]	$\hbar\omega(J)$	$E_{\rm exc}$(JS)	$\hbar\omega_{\rm rms}$	$\Delta\epsilon$(JS)/($\langle P_{c\alpha}^2\rangle_J/Nm$)
H_2(a)	39.2	39.0	39.0	−0.007
H_2(b)	40.8	39.8	39.8	−0.049
D_2(a)	28.0	31.4	31.2	+0.24
D_2(b)	29.0	31.7	31.6	+0.19

[a]The interaction models are based on the Silvera-Goldman intermolecular potential, as in Ref. 14, and cases (a) and (b) have values 12.14 and 9.94 a.u., respectively, for the coefficient C_6. The corrugation amplitude is $\bar{V}_g=-6.4$ K.

TABLE II. Zone-center gap for helium/graphite. [Zone-center gap, in K, for the commensurate $\sqrt{3}$ monolayer of ^{3}He/graphite and ^{4}He/graphite. The experimental values, from inelastic neutron scattering (Ref. 6) are 11 K for both isotopes. The energy estimates are defined in Sec. III B of the text.]

Model[a]	$\bar{V}_g$	$\hbar\omega(J)$	$E_{\rm exc}$(JS)	$\hbar\omega_{\rm rms}$	$\Delta\epsilon$(JS)/($\langle P_{c\alpha}^2\rangle_J/Nm$)
^{4}He Aziz	−3.25	15.2	16.2	16.2	+0.13
	−2.6	12.4	13.1	13.1	0.12
	−2.0	9.7	10.0	10.0	0.06
	−1.5	8.4	7.9	7.9	−0.11
Aziz+McL	−3.25	15.5	16.4	16.4	+0.12
	−2.6	12.9	13.3	13.3	0.07
	−2.0	10.1	10.4	10.4	0.05
^{3}He Aziz	−3.25	15.4	16.0	16.0	0.08
	−2.6	13.1	13.1	13.1	0.004
	−2.0	11.4	10.5	10.4	−0.16
	−1.5	10.2	8.6	8.5	−0.32
Aziz+McL	−3.25	16.0	16.4	16.4	+0.08
	−2.6	13.5	13.4	13.4	−0.02
	−2.0	11.7	10.7	10.7	−0.17

[a]Corrugation amplitude $\bar{V}_g$ of Eq. (3.1) and effective pair potential among the adatoms as in Ref. 7. The Aziz model is a good approximation to the interaction of a pair of isolated helium atoms; the Aziz+McL (McLachlan) model includes substrate-mediated van der Waals forces between adsorbed helium atoms.

Table II contains results for the zone-center gap of commensurate monolayers of helium/graphite for two interaction models and for a range of values for the corrugation amplitude. The Aziz model is used in many calculations of 3D gaseous and condensed helium. The second model incorporates the McLachlan substrate-mediated dispersion energy, as in a recent calculation[7] of the relative stability of the two-dimensional (2D) liquid and commensurate monolayer solid phases of ^{4}He/graphite. The values for $\omega_{\rm rms}$ for the Aziz model and $\bar{V}_g=-3.25$ K had been reported[11] as the results of a Born-Oppenheimer approximation. As in Table I, the entries for $E_{\rm exc}$(JS) and $\omega_{\rm rms}$ are in good agreement; most of the entries for $\omega(J)$ deviate from these by less than 10%.

There are experimental data for both the leading Fourier amplitude (corrugation amplitude) in the ground state of the helium/graphite potential, from atom-surface scattering resonances,[2,3] and for the zone-center gap, from inelastic neutron scattering.[6] For ^{4}He/graphite Boato *et al.*[2] find $\bar{V}_g=-0.28\pm0.01$ meV (-3.25 ± 0.1 K), while Derry *et al.*[3] find $\bar{V}_g=-0.25\pm0.03$ meV (-2.9 ± 0.3 K). Lauter, Godfrin, and Leiderer[6] report the value of the zone-center gap for both commensurate ^{3}He/graphite and ^{4}He/graphite to be 11 K; an earlier

value[6] for ^{3}He/graphite, without a correction for instrumental resolution, was 13 K. Greywall[20] analyzes his specific-heat data for commensurate ^{4}He/graphite as including an Einstein oscillator excitation of 10.5 K.

The calculations for the zone-center gap of helium/graphite appear to be reliable to about 10%. If so, the effective value for the corrugation amplitude necessary to fit the gap derived from the neutron-scattering data[6] is -2 to -2.6 K, 20–40 % below the value based on the Boato *et al.*[2] experiment; the enhancement[13] of the amplitude in the commensurate lattice is estimated to be 5–10 %. The deviation from the value reported by Derry *et al.*[3] is somewhat smaller. Thus, there is only a marginal consistency between the neutron data for the zone-center gap and the values calculated from the atom-scattering corrugation amplitude.[2–4] The parameters of the Jastrow trial function are optimized for the total energy, so it is possible that the center-of-mass motion is given badly in the estimates in Table II. An evaluation of the frequency moments of Sec. II A using a nominally exact ground state[12] could resolve this question.

Thus, calculations with parameters considered plausible in other contexts[4] lead to zone-center gap significantly larger than the neutron-scattering value[6] for helium/graphite. It is difficult at this stage to identify defects in the experiments. If the corrugation amplitude for ^{4}He/graphite is indeed in the range -2 to -2.6 K, a tentative conclusion[7,20] that the ground state of the monolayer is a 2D liquid is strengthened. However, the agreement[4] between calculated and measured band-structure effects in the low coverage specific heat of helium/graphite is somewhat degraded then.

IV. CONCLUDING REMARKS

There has been extensive modeling of the zone-center frequency gap for three commensurate monolayer systems: helium/graphite, hydrogen/graphite,[13] and nitrogen/graphite.[17] For nitrogen/graphite, the calculated gap was significantly smaller than the neutron-scattering value until an additional mechanism for corrugation was identified.[17] For hydrogen/graphite, the calculated values[13] are close to the data for a model which does not include dielectric anisotropy[4] of the graphite. For helium/graphite the calculated values are significantly larger than the data,[6] for a corrugation amplitude believed to have a good basis[4] from atomic-scattering data. This trend does not appear to follow from difficulty in calculating the zone-center gap for a quantum solid: the results in Tables I and II indicate that the gap can be evaluated to within 10% for a given model. There remains a possibility that the discrepancy is indeed a problem of the quantum solid arising from the use of the Jastrow trial function to evaluate the frequency moments. That may be tested by using the formalism of Sec. II A in a nominally exact solution[12] for the ground state of the quantum solid; the formalism may also be generalized to finite-temperature averages.

There is an artifact of Ψ_{JS} which so far has not given difficulty. The trial function incorporates a broken symmetry, with a localized center of mass.[18] The parameter A is nonzero even in calculations for an uncorrugated surface ($\bar{V}_g=0$), although translational invariance for the center of mass then implies a vanishing zone-center gap. That is, the approximation $\omega(J)$ for the zone-center gap must fail for sufficiently small corrugation. There are indications of this in Table II for the smaller magnitudes of $\bar{V}_g$, where the entries violate Eq. (2.11) and the calculated mean-square displacement of the center of mass apparently is nonphysically small. The root-mean-square energy $\omega_{\rm rms}$ calculated with Ψ_{JS} maintains a qualitatively correct trend for small corrugation.

ACKNOWLEDGMENTS

I thank Professor S. T. Epstein for an instructive conversation on the quantum-mechanical virial theorem. This work is supported in part by the National Science Foundation through Grant No. DIR-9120199.

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