

Zone-center gap in the frequency spectrum of a commensurate monolayer

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The gap at the Brillouin-zone center in the frequency spectrum of small-amplitude vibrations of a commensurate-monolayer solid is expressed in terms of the leading Fourier amplitudes of the atom-substrate potential. Cases with one atom per unit cell, e.g., a commensurate lattice of krypton on graphite, and with four atoms per unit cell, e.g., a commensurate lattice of neon on graphite, are treated.

I. INTRODUCTION

A commensurate-monolayer solid has a placement relative to the underlying substrate which is determined by the periodic components of the adatom-substrate potential. The invariance under lateral translations of the monolayer center of mass which exists for floating incommensurate monolayers, and which leads to normal modes with vanishing frequency at the Brillouin-zone center, is absent. The normal mode frequencies near the zone center of the commensurate monolayer have a nonzero minimum value which should be manifest in the low-temperature specific heat of the monolayer. The gap is shown in model calculations by Cardini and O'Shea¹ for a monolayer of nitrogen adsorbed on the basal plane surface of graphite, N₂/graphite, and there is evidence for the gap in specific-heat data² for neon on graphite, Ne/graphite. For a monatomic adsorbate the gap is directly related to the amplitudes V_g of the periodic components of the adatom-substrate potential.³ The amplitudes V_g also enter in determining the stability⁴ of commensurate monolayers and the modulation structures in slightly incommensurate monolayers, but there are few experimental values for them.⁵ The purpose of this paper is to develop the small-amplitude-vibration theory of the zone-center (zero wave vector) frequency gap and to analyze the contributions to the gap for a commensurate lattice of Ne/graphite.

The simplest case is the triangular commensurate lattice of a monatomic solid with one atom per unit cell. Results are presented in Sec. II. However, a quantitative determination of the gap for the $\sqrt{3}R$ 30° commensurate solid of H₂/graphite, in which vibrations are not of small amplitude, requires a self-consistent treatment of anharmonicities.⁶

The case of a coincidence superlattice, a commensurate lattice with several atoms in the unit cell, is treated in Sec. III. The $\sqrt{7}$ lattice⁷ of Ne/graphite, with four atoms in the basis, is used as an example. It has a mixing of terms of nominally different magnitudes; harmonic theory is only semiquantitative for the dilated anharmonic neon lattice.⁸

Steele's Fourier decomposition of the adatom-substrate potential is³

$$V(\mathbf{r}, z) = V_0(z) + \sum_{\mathbf{g}} V_{\mathbf{g}}(z) \exp(i\mathbf{g} \cdot \mathbf{r}), \quad (1.1)$$

where z is measured perpendicular to the substrate surface, \mathbf{r} is a vector in the plane of the surface, and the vectors \mathbf{g} are reciprocal-lattice vectors of the substrate surface lattice. For inert gases adsorbed on the basal plane surface of graphite, model calculations show that the amplitude $V_{\mathbf{g}}$ evaluated at the height z_0 which minimizes V_0 decreases rapidly as $|\mathbf{g}|$ increases. Associated with the z dependence of the amplitudes in Eq. (1.1) is a modulation of the height of a monolayer which is observed in atomic scattering experiments.⁹

When an explicit model for the interatomic potential is needed in this work, the Lennard-Jones (12,6) form is used:

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (1.2)$$

More general forms are easily incorporated in the theory.

Previous calculations^{10,11} of the Novaco-McTague orientational alignment of Ne/graphite were for mathematical two dimensions. The theory¹² includes modulations in the z coordinate and, in light of the results of Sec. III, the Ne/graphite calculations are repeated including this effect. The results are presented in the Appendix: the energies are increased markedly, but the optimal orientation angles remain nearly the same.

II. FREQUENCY GAP FOR THE $\sqrt{3}R$ 30° MONOLAYER

Two examples of a commensurate triangular monolayer with one adatom per unit cell are shown in Fig. 1. The case of Kr/graphite is shown in Fig. 1(a), with the location of the surface carbon atoms in the unit cell; the height z_0 for Steele's parameters³ is 3.48 Å, and the first three distinct amplitudes are $V_{g_0} = -4.4$ K, $V_{\sqrt{3}g_0} = 0.045$ K, and $V_{2g_0} = -0.003$ K ($g_0 = 2.95 \text{ \AA}^{-1}$). The likely case for Xe/Pt(111) is shown in Fig. 1(b), with adatoms in threefold coordination to surface Pt atoms; an estimate¹³ of the leading amplitude based on energetic stability relative to a floating monolayer is $V_{g_0} \sim 20$ K ($g_0 = 2.62 \text{ \AA}^{-1}$).

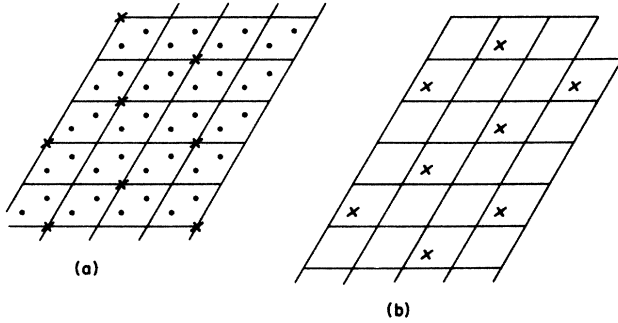


FIG. 1. Two examples of the $\sqrt{3}R30^\circ$ commensurate monolayer. The solid lines outline several unit cells of the triangular substrate Bravais lattice. (a) Adsorption on the basal plane surface of graphite, with the dots marking carbon atom positions and the \times marking sites of the triangular adlayer lattice. (b) Adsorption on the (111) face of a fcc solid, with substrate atoms at the unit-cell vertices and adatoms in threefold sites marked by \times .

The phases of the amplitudes are linked to the choice of the origin of the planar coordinates; the cited values have the origin at the sites of the surface Bravais lattice shown in Fig. 1. The preferred adsorption site for $V_{g_0} < 0$ is at the Bravais lattice site and for $V_{g_0} > 0$ is at the threefold site shown in Fig. 1(b). The activation energy (at constant z_0) from the adsorption site to the saddle (or "bridge site") is approximately $-8V_{g_0}$ in the first case and V_{g_0} in the second. Similarly the detailed forms of the angular frequencies of perpendicular motion (ω_z) and of in-plane motion (ω_{\parallel}) at the zone center differ in the two cases. In the limit of zero wave vector, there are no relative displacements of atoms in different Bravais unit cells. Here, for one atom in the unit cell, the restoring force arises entirely from the holding potential. The results for an adatom of mass m are, retaining only the leading Fourier amplitude and with V'' denoting the second derivative of V with respect to z ,

$$\begin{aligned}\omega_z &= [(V_0'' + 6V_{g_0}'')/m]^{1/2}, \\ \omega_{\parallel} &= g_0(-3V_{g_0}/m)^{1/2}, \quad V_{g_0} < 0\end{aligned}\quad (2.1)$$

and

$$\begin{aligned}\omega_z &= [(V_0'' - 3V_{g_0}'')/m]^{1/2}, \\ \omega_{\parallel} &= g_0(1.5V_{g_0}/m)^{1/2}, \quad V_{g_0} > 0.\end{aligned}\quad (2.2)$$

The frequency gap for the Kr/graphite lattice, with $V_{g_0} = -4.4$ K, is $\omega_{\parallel} \sim 8$ K; for the Xe/Pt(111) lattice, with $V_{g_0} = 20$ K, it is $\omega_{\parallel} \sim 9$ K. The harmonic vibration approximation for H_2 /graphite with $V_{g_0} = -6.4$ K gives $\omega_{\parallel} \sim 63$ K, much larger than the 43 K obtained by Novaco⁶ with a self-consistent phonon approximation. The gap for the Kr/graphite lattice should lead to observable effects in the monolayer specific heat at temperatures less than 10 K.

III. GAP FOR A COMMENSURATE LATTICE WITH A BASIS

Higher-order coincidence lattices of a monolayer solid with a substrate, where the ratio of the lattice constant of the monolayer to that of the substrate surface is a rational number, are sometimes proposed.⁹ If the Fourier amplitudes V_g decrease rapidly with increasing wave number g , such lattices are stabilized more by a modulation energy associated with the leading terms of Eq. (1.1) than by the contribution of higher terms to the registry energy of the average lattice. The coincidence adlayer lattices are then viewed as Bravais lattices with many atoms (a large basis) in the unit cell.

The particular case of the $\sqrt{7} \times \sqrt{7}$ lattice of Ne/graphite oriented at 10.9° relative to the 30° axis of the graphite basal plane, Fig. 2, is treated here to display several terms in the theory of the commensurate lattice with a basis. Specific-heat data² show an energy gap of around 3.5 K for this system and there is a model for the adatom-substrate potential constructed¹⁴ from gas-surface virial data. For this model, the values of the first three V_g amplitudes in the series of Eq. (1.1), evaluated at the minimum of V_0 ($z_0 = 2.99$ Å), are -3.0 , 0.08 , and -0.0066 K. Terms of nominally different orders of magnitude mix in this example: the third amplitude contrib-

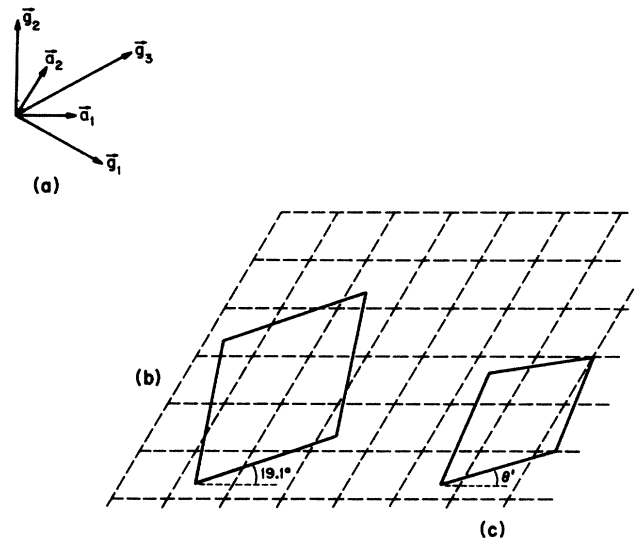


FIG. 2. Geometry of lattices of neon adsorbed on the basal plane surface of graphite. (a) The primitive vectors \mathbf{a}_1 and \mathbf{a}_2 of the substrate Bravais lattice and three reciprocal lattice vectors \mathbf{g}_1 , \mathbf{g}_2 , and \mathbf{g}_3 (of length $g_0 = 2.95 \text{ \AA}^{-1}$) used in the formulation of the first shell registry potential V_1 , Eq. (3.2). (b) Relation of the Bravais lattice unit cells of the adlayer (solid lines) and substrate (dashed lines) for the $\sqrt{7}$ commensurate lattice. The two-atom basis of the graphite surface and the four-atom neon basis are not shown. The lateral position of the neon cell is only schematic; the 19.1° angle between the Bravais cell axes is set by the coincidence lattice condition. (c) Schematic diagram of the orientational alignment of an incommensurate monolayer, with an angle θ' between the Bravais cell axes of adlayer and substrate; the angle usually cited as the Novaco-McTague angle is $\theta = 30^\circ - \theta'$.

utes appreciably to the frequency gap. The energy of the modulation perpendicular to the adsorption plane is also an important contribution, acting to reduce the frequency gap.

The calculation is formulated in second order of a perturbation theory by first approximating the adatom-adatom potential energy as a sum of an energy for an unmodulated average lattice and a distortion energy Φ for the change in the potential energy resulting from displacements ρ_j from positions \mathbf{R}_j in the average lattice:

$$\Phi = \frac{1}{4} \sum_{\substack{i,j \\ i \neq j}} \nabla \nabla \phi: (\rho_i - \rho_j)(\rho_i - \rho_j). \quad (3.1)$$

The first shell of reciprocal lattice vectors in Eq. (1.1) leads to a registry potential

$$V_1 = 2 \sum_j V_{g_0}(z_j) \sum_{k=1}^3 \cos(\mathbf{g}_k \cdot \mathbf{r}_j) \quad (3.2)$$

which depends on the lateral positioning $\mathbf{r}_j = \mathbf{R}_j + \rho_j$ of the adatom relative to the substrate; the vectors \mathbf{g}_1 , \mathbf{g}_2 , and \mathbf{g}_3 are identified in Fig. 2.

For the $\sqrt{7}$ lattice, the displacements ρ_j are expressed in terms of four amplitudes \mathbf{A}_k by

$$\rho_j = \mathbf{A}_0 + \sum_{k=1}^3 \mathbf{A}_k \exp(i \mathbf{g}_k \cdot \mathbf{R}_j). \quad (3.3)$$

Determining the amplitudes \mathbf{A}_k is equivalent to determining the positions of the four-atom basis in this example.

The lateral distortion energy has a simple form with these amplitudes:

$$\Phi = (N/2) \sum_{k=1}^3 \underline{D}(k): \mathbf{A}_k \mathbf{A}_k, \quad (3.4)$$

where N is the number of atoms in the monolayer and the dynamical matrix is

$$\underline{D}(k) = \sum_{\substack{\mathbf{R}_j \\ \mathbf{R}_j \neq 0}} \nabla \nabla \phi(\mathbf{R}_j) [1 - \cos(\mathbf{g}_k \cdot \mathbf{R}_j)]. \quad (3.5)$$

Expansion of V_1 to first order in the amplitudes \mathbf{A}_k ($k \neq 0$) gives

$$V_1 = -2NV_{g_0}(z_0) \sum_{k=1}^3 \sin(\mathbf{g}_k \cdot \mathbf{A}_0) \mathbf{g}_k \cdot \mathbf{A}_k + 2NV'_{g_0} \sum_{k=1}^3 \cos(\mathbf{g}_k \cdot \mathbf{A}_0) A_{kz}, \quad (3.6)$$

where the prime denotes differentiation and A_{kz} is the z component of \mathbf{A}_k . \mathbf{A}_0 is treated distinctly because it sets the overall position of the adlayer relative to the substrate and need not be small compared to the adatom spacings. Finally, the expansion of the laterally averaged holding potential at a height z not necessarily equal to z_0 is

$$V_{h_0} = NV_0(z) + NA_{0z} V'_0 + (N/2) V''_0 \sum_{k=0}^3 A_{kz}^2. \quad (3.7)$$

The expansions in Eq. (3.3)–(3.7) lead to an explicit

form for the ground-state energy as a function of the lateral position \mathbf{A}_0 . The minimization of the quadratic form

$$E = \Phi + V_1 + V_{h_0} \quad (3.8)$$

with respect to A_{0z} and \mathbf{A}_k leads to

$$A_{0z} = -V'_0 / V''_0$$

and

$$A_{kz} = -2V'_{g_0} \cos(\mathbf{g}_k \cdot \mathbf{A}_0) / [V''_0 + D_{zz}(k)], \quad (3.9)$$

$$A_{k\alpha} = 2V_{g_0} \sin(\mathbf{g}_k \cdot \mathbf{A}_0) [\underline{D}(k)^{-1} \cdot \mathbf{g}_k]_{\alpha}$$

for $k \neq 0$ and $\alpha = x, y$. The final form for the energy per atom as a function of the lateral position \mathbf{A}_0 is then

$$E/N = -(V_0'^2 / 2V_0'') - \frac{3}{2}(e_{\parallel} + e_z) + \frac{1}{2}(e_{\parallel} + 4V_{2g_0} - \bar{e}_z) \sum_{k=1}^3 \cos(2\mathbf{g}_k \cdot \mathbf{A}_0) \quad (3.10)$$

where the first-order contribution of the third amplitude V_{2g_0} of Eq. (1.1) is included, e_{\parallel} and e_z are second-order energies in terms of the first amplitude V_{g_0} :

$$e_{\parallel} = 2V_{g_0}^2 \mathbf{g}_1 \cdot \underline{D}(1)^{-1} \cdot \mathbf{g}_1, \quad (3.11)$$

$$e_z = 2(V'_{g_0})^2 / [D_{zz}(1) + V''_0], \quad (3.12)$$

and \bar{e}_z includes a correction from the second shell of reciprocal lattice vectors:

$$\bar{e}_z = e_z [1 + 4(V'_{\sqrt{3}g_0} / V'_{g_0})]. \quad (3.13)$$

Equation (3.10) displays the “phase locking” in the energy of superlattices described by Theodorou and Rice.¹⁵

The sign of the coefficient

$$C = \frac{1}{2}(e_{\parallel} + 4V_{2g_0} - \bar{e}_z) \quad (3.14)$$

determines the lateral position of the minimum energy commensurate monolayer. For $C < 0$, the energy is minimized at $\mathbf{A}_{0\parallel} = 0$ and is

$$E_0/N = -V_0'^2 / 2V_0'' - \frac{3}{2}(e_{\parallel} + e_z - 2C) \quad (C < 0). \quad (3.15)$$

For $C > 0$, the energy is minimized at $\mathbf{A}_{0\parallel} = (\mathbf{a}_1 + \mathbf{a}_2)/6$, where the \mathbf{a}_i are primitive vectors of the substrate surface shown in Fig. 2(a), and is

$$E_0/N = -V_0'^2 / 2V_0'' - \frac{3}{2}(e_{\parallel} + e_z + C) \quad (C > 0). \quad (3.16)$$

The angular frequency of the zone-center gap is obtained from the second derivative of the energy E , Eq. (3.10), with respect to lateral displacements \mathbf{A}_0 of the Bravais cell, to follow the center-of-mass motion of the adlayer. The positions of atoms in the basis also relax through the dependence of \mathbf{A}_k on \mathbf{A}_0 shown in Eq. (3.9), but the corresponding kinetic energy terms are higher order in the corrugation and are omitted. As with Eqs. (2.1) and (2.2), the detailed expression depends on the

sign of C :

$$\begin{aligned}\omega_{\parallel} &= g_0(-6C/m)^{1/2} \quad (C < 0), \\ \omega_{\parallel} &= g_0(3C/m)^{1/2} \quad (C > 0),\end{aligned}\quad (3.17)$$

where g_0 is the length of the primitive reciprocal-lattice vectors of the substrate.

For a quantitative estimate in the Ne/graphite case, the pair potential ϕ is approximated by the Lennard-Jones (12,6) potential Eq. (1.2) with Hansen's parameters¹⁶ $\epsilon = 36.76$ K and $\sigma = 2.786$ Å. Then at $z_0 = 2.99$ Å the second-order perturbation energies from the leading amplitude V_{g_0} are $e_{\parallel} = 0.429$ K and $e_z = 0.334$ K. The contribution $4V_{2g_0} = -0.026$ K in C is 25% of the difference $e_{\parallel} - e_z$, but it is offset by the correction $\bar{e}_z/e_z = 0.864$. The coefficient $C (= 0.057$ K) is positive and Eq. (3.16) applies. The gap in the frequency spectrum at the zone center from Eq. (3.17) is then 1.9 K, considerably smaller than the 3.5 K identified in the specific-heat data.² The calculated modulation, peak to valley, of the heights z in the four-atom basis is 0.04 Å.

The values for Ne/graphite depend on subtractions involving four parameters from the atom-substrate potential, $V_{g_0}(z_0)$, dV_{g_0}/dz , $dV_{\sqrt{3}g_0}/dz$, and V_{2g_0} , so that a comparison of the calculated and experimental values of ω_{\parallel} does not directly test a single feature of the corrugation energy. The fact that the calculated value is much smaller than the measured one is in accord with estimates of the corrugation of the holding potential of other inert gases on graphite. For helium, the corrugation derived from atom scattering is larger than that obtained from the atom-atom sums with central pair potentials.⁵ For krypton, calculations of the corrugation energy to stabilize the $\sqrt{3}R30^\circ$ lattice as the monolayer ground state show⁴ that V_{g_0} must also have larger magnitude than the value from the atom-atom sum modeling of the gas-surface virial data.³

The perpendicular and parallel modulation energies are similar in magnitude for the Ne/graphite case, in part because the wave vectors of the modulation are at the Brillouin-zone boundary and not near the zone center as for a nearly commensurate layer with one adatom per cell. The Ne/graphite monolayer solid has⁸ large effects of anharmonicity and the calculation of the zone-center frequency gap given here is based on derivatives of the ground-state energy rather than on the long-wavelength limit of a lattice-dynamics theory.

IV. CONCLUDING REMARKS

Working with derivatives of the ground-state energy leads directly to compact expressions for the gap in the

harmonic frequency spectrum at zero wave vector. A consideration of anharmonic processes in the neon monolayer may be necessary.

There are two other relevant issues which have not been treated here. The analysis is for exactly commensurate adlayers; what the results would be for an adlayer with very small misfit is not known. Second, the substrate has been treated as a static external potential for the monolayer without consideration of dynamical coupling of the adlayer to the substrate for wave vectors near the Brillouin-zone center. If measurements of the frequency gap are to be used to give precise values for the corrugation amplitudes V_g , these issues will have to be addressed.

APPENDIX: ORIENTATIONAL EPITAXY OF THE Ne/GRAPHITE MONOLAYER

The second-order perturbation theory of Novaco and McTague¹² leads to an orientational alignment energy per adatom of

$$e_{NM} = - \sum_{k=1}^3 (e'_{\parallel} + e'_z) \quad (A1)$$

where

$$e'_z = (dV_{g_0}/dz)^2 / [D_{zz}(k) + V''_0] \quad (A2)$$

and

$$e'_{\parallel} = V_{g_0}^2 \mathbf{g}_k \cdot \underline{D}(k)^{-1} \cdot \mathbf{g}_k, \quad (A3)$$

using the notation of Sec. III. The dependence of e_{NM} on the angle θ' between the axes of the adlayer and substrate Bravais cells, Fig. 2(c), enters through the $\cos(\mathbf{g}_k \cdot \mathbf{R}_j)$ term in the dynamical matrix \underline{D} , Eq. (3.5).

The energy e'_z is frequently omitted in determinations of the angle $\theta (= 30^\circ - \theta')$ which minimizes e_{NM} because the denominator in Eq. (A2) is dominated by the dispersionless term V''_0 . However, in the total energy of Ne/graphite it is similar in magnitude to e'_{\parallel} .

Using the Ne/graphite parameters^{14,16} of Sec. III and triangular Ne lattices with nearest-neighbor spacing L , the angle θ which minimizes e_{NM} differs from that¹⁰ which minimizes e_{\parallel} by at most 0.3° for L from 3.27 to 3.09 Å. Some values are $e_{NM} = -1.09$ K, $\theta = 12.7^\circ$, and $e_{\parallel} = -0.63$ K at 3.27 Å, $e_{NM} = -0.82$ K, $\theta = 15.2^\circ$, and $e_{\parallel} = -0.35$ K at 3.19 Å, and $e_{NM} = -0.72$ K, $\theta = 17.1^\circ$, and $e_{\parallel} = -0.24$ K at 3.09 Å.

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