Dynamics of rare-gas floating monolayers in the self-consistent phonon theory

L. K. Moleko* and B. Joos

Ottawa-Carleton Institute of Physics, University of Ottawa Campus, Ottawa, Ontario, Canada K1N 9B4

T. M. Hakim and H. R. Glyde

Department of Physics, University of Delaware, Newark, Delaware 19716

S. T. Chui

Bartol Research Foundation of the Franklin Institute, University of Delaware, Newark, Delaware 19711

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The dynamics of floating two-dimensional (2D) monolayers of Xe, Kr, Ar, and Ne are explored over a range of lattice spacings and temperature using the self-consistent phonon theory. Phonon dispersion curves and the zero-point energy are calculated and appropriate Debye temperatures and rms vibrational amplitudes \( \langle u^2 \rangle \) estimated at \( T = 0 \) K. The results show that floating monolayers of Ar and Xe represent their physisorbed counterparts well. They also show that Xe and Kr are effectively harmonic at \( T \leq 25 \) K while Ne is a strongly anharmonic 2D crystal at all \( T \). The self-consistent harmonic frequencies in Ne at \( T = 0 \) K are nearly twice the harmonic values. Ar is an intermediate case. The effective Debye temperature is \( \Theta_D \approx 65 \) K in all cases and the Lindemann ratio \( \gamma = \langle u^2 \rangle / R \) varies from 3\% in Xe to 9\% in Ne at \( T = 0 \) K, similar to 3D crystal values. The phonon frequencies depend sensitively on lattice parameter and temperature, more so than in 3D crystals.

I. INTRODUCTION

Rare-gas monolayers form some of the most important realizations of two-dimensional (2D) systems. Even when physisorbed on graphite or other substrates such as Ag(111), Pd(100), Cu(100), or Pt(111), they can be regarded as essentially 2D in character.\(^1,2\) So far only dispersion curves for vibrational modes perpendicular to the substrate have been obtained experimentally in these systems.\(^3\) These modes are nearly dispersionless and are fairly decoupled from the in-plane modes. The in-plane modes, though they are more difficult to probe experimentally,\(^4,5\) play an important role in the thermodynamics of the 2D solid. This paper presents an extensive study of the in-plane modes within the self-consistent phonon theory. The advantage of this technique is that it allows a direct estimate of anharmonicity and quantum effects. We do not in this work take into account the modulations in the rare-gas–substrate interaction, hence the designation floating monolayers. It is well known that these modulations alter significantly the properties of the Kr monolayer physisorbed on graphite.\(^6,7\) But many other physisorbed systems are expected to be similar to their floating counterparts in particular at high temperature or when the equilibrium lattice parameters are very different from the nearest commensurate structure favored by the substrate. This is the case for Ar and Ne on graphite. Also, when compressed, a physisorbed monolayer such as Xe on graphite tends to preserve many of its floating characteristics.\(^6,7\) Although the floating limit has not yet been realized experimentally, there is evidence that the Ag(111) surface exerts an absorptive potential which is nearly free of corrugation.\(^8\) We do not either take into account the coupling between adsorbate and substrate motion.\(^9,10\) The effect of this coupling on the in-plane modes is expected to be significant only for very long wavelengths.\(^9\) Apart from serving as a starting point for the understanding of physisorbed structures, the floating systems are of intrinsic interest as model 2D solids. It is interesting to see how the properties of rare-gas solids are affected by the reduction in dimension. In the text below, Sec. II describes the self-consistent phonon theory in 2D and Sec. III its application to rare-gas monolayers. In Sec. IV we present our results and we conclude with some comments.

II. THE SELF-CONSISTENT PHONON THEORY IN TWO DIMENSIONS

The self-consistent phonon (SCP) theory\(^11\) has been used successfully to evaluate the dynamical properties of three-dimensional (3D) crystals.\(^12–15\) This is both for the phonon frequencies and lifetimes\(^12–13\) and for the thermodynamic properties\(^13\) of the rare-gas crystals and simple metals.\(^15\) The SCP theory can be applied in a straightforward manner to 2D systems.\(^16\) As is now well known,\(^17–20\) the mean-square vibrational amplitude \( \langle u_i^2 \rangle \) of an atom in a 2D crystal diverges logarithmically with the size of the crystal. However, the relative vibrational amplitude of two atoms, \( \langle (u_0 - u_i)^2 \rangle \), does not diverge and it is \( u_{0f} = u_0 - u_i \) which enters the SCP theory.\(^21\) Here, we restrict ourselves to the self-consistent harmonic (SCH) approximation in which the phonons have infinite lifetime.

In the SCH theory, the frequency of a phonon having wave vectors \( q \) and branch \( \lambda \) is given by the usual harmonic relation,
\[
\omega_{\alpha \lambda}^2 = \sum_{\alpha, \beta = 1}^2 \epsilon_\alpha(q, \lambda) \epsilon_\beta(q, \lambda) \frac{1}{M} \sum_l (1 - e^{-i q \cdot R_{0l}}) \Phi_{\alpha \beta}(0, l) .
\]

Here \( \epsilon_\alpha(q, \lambda) \) is the polarization vector of the phonon, \( M \) is the atomic mass, and \( R_{0l} \) is a Bravais lattice vector. The SCH force constant is

\[
\Phi_{\alpha \beta}(0, l) = \left\langle \frac{\partial^2 \nu(r_{0l})}{\partial u_\alpha \partial u_\beta} \right\rangle ,
\]

where \( \nu(r) \) is the pair interatomic potential, \( r_{0l} = u + R_{0l} \), and \( u \equiv u_{0l} \) defined above. The average in (2) is an average over the relative vibrational distribution of the atom pair about their lattice points. For harmonic vibration this distribution is a Gaussian and

\[
\Phi_{\alpha \beta}(0, l) = \left[ (2\pi)^2 \left| \tilde{\Lambda}_{\alpha \beta} \right| \right]^{-1/2} \times \int d^2 u e^{-1/2u^2} \frac{\partial^2 \nu(u + R_{0l})}{\partial u_\alpha \partial u_\beta} .
\]

Here \( \tilde{\Lambda}_{\alpha \beta} \) is a \( 2 \times 2 \) matrix of the relative amplitudes of atoms 0 and \( l \),

\[
\Lambda_{\alpha \beta}(0, l) \equiv \left\langle u_\alpha(0, l) u_\beta(0, l) \right\rangle = \frac{\hbar}{2NM} \sum_{q, \lambda} (1 - e^{-i q \cdot R_{0l}}) \epsilon_\alpha(q, \lambda) \epsilon_\beta(q, \lambda)
\]

\[
\times \coth \left( \frac{1}{2} \beta \hbar \omega_{q \lambda} \right) / \omega_{q \lambda} ,
\]

where \( \beta = (k_B T)^{-1} \) and \( N \) is the number of atoms in the crystal.

In the quasiharmonic (QH) approximation, the vibrational amplitude in (4) is assumed to be zero (\( \Lambda_{\alpha \beta} = 0 \)). The second derivative in (2) and (3) is then evaluated with the atoms fixed at their lattice points (\( u_{0l} = 0 \)). In the SCH theory \( \Lambda_{\alpha \beta} \) and \( \omega_{q \lambda} \) are evaluated iteratively until consistent. For example, we may begin with the QH frequencies, evaluate \( \Lambda_{\alpha \beta} \) in (4), evaluate \( \Phi_{\alpha \beta}(0, l) \) in (3) and evaluate the new \( \omega_{q \lambda} \)'s from (1). The calculation proceeds by iterating (4), (3), and (1) until consistent.

In terms of anharmonic perturbation theory, the SCH theory includes the even anharmonic terms that appear as first-order corrections to the QH theory. For a potential having a steep repulsive core, as is the case for the rare gases, the even anharmonic terms generally increase the phonon frequencies. Thus we expect the SCH frequencies to lie above the QH values and that the difference will increase with temperature as anharmonic contributions become more important. Equally, if \( \nu(r) \) has a repulsive core, the \( \Phi_{\alpha \beta}(0, l) \) in (2) increases when the vibrational amplitude increases and the atoms sample more of the strongly repulsive core region of \( \nu(r) \). As noted above, the relative amplitude \( \left\langle (u_0 - u_l) (u_0 - u_l) / \beta \right\rangle = \Lambda_{\alpha \beta}(0, l) \) is well defined for the periodic, infinite 2D crystals investigated here. This is because \( \Lambda_{\alpha \beta}(0, l) \) in (4) contains the factor \( (1 - e^{-i q \cdot R_{0l}}) \). As \( q \to 0 \) this factor is \( \sim q^2 \) and it is this \( q^2 \) which prevents \( \Lambda_{\alpha \beta} \) from diverging as \( q \to 0 \) for large crystals. By contrast the mean-square amplitude \( \left\langle u_0^2 \right\rangle \) for a single atom does diverge for infinite 2D crystals for \( T \neq 0 \). Since we impose periodic symmetry here, this means that the whole model crystal can translate in time while the relative amplitudes \( \left\langle (u_0 - u_l)^2 \right\rangle \) of the atoms remain finite.

III. MODEL

In our model the rare-gas atoms (Ne, Ar, Kr, and Xe) form an isotropic triangular lattice and interact via pairwise central forces. We note that in our calculations there is no underlying substrate. The pair potentials between the atoms Ne-Ne, Ar-Ar, Kr-Kr, and Xe-Xe have been chosen to follow the Hartree-Fock HFD Aziz form, 

\[ V(r) = \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \]

which consists of a short-range closed-shell repulsion derived from a self-consistent Hartree-Fock calculation together with an empirical inverse power-law term with coefficients fitted to second virial, viscosity and thermal conductivity data. The functional form is given by

\[ V(r) = \frac{1}{r} \frac{e^{-ax} - F(x)}{x} \]

where \( A = \frac{C_6}{C_8} \) and \( B = \frac{C_8}{C_{10}} \).

The parameters for the Ne-Ne, Ar-Ar, and Kr-Kr potentials were determined by Aziz et al. 

In the case of the Xe-Xe interaction we used the Kr-Kr potential \( \frac{1}{r} \) to an appropriate well depth \( \epsilon/k_B = 282 \) K and length parameter \( R_m = 4.36 \) Å as in Ref. 26. We have also investigated the Lennard-Jones 12-6 potential for argon with \( \epsilon/k_B = 119.8 \) K and \( \sigma = 3.4 \) Å (Ref. 27) so as to compare with the only known SCH calculation in 2D, that by Novaco.

With the theory developed above we have constructed the dispersion curves in the irreducible \( \frac{1}{2} \text{th} \) sector of the Brillouin zone. We found that it was sufficient to sum out to five neighbor shells to evaluate (1) fully and to use 5000 \( q \) points in the full Brillouin zone to evaluate (4). The integral (3) was done using standard Gauss-Hermite methods. (The values quoted are for 20 roots).

IV. RESULTS

A. Dispersion curves

In Fig. 1 we show the phonon frequency dispersion curves for 2D Xe having nearest-neighbor separation \( R = 4.26 \) Å at \( T = 0 \) K. This is the spacing the atoms physisorbed on graphite would assume in the \( \sqrt{3} \times \sqrt{3} \) commensurate configuration. A monolayer of Xe would seem not to form a commensurate phase on graphite; \( 4.26 \) Å is a lower bound on the nearest-neighbor separation. From Fig. 1 we see that the SCH frequencies lie 3–5% above the QH values showing that anharmonic effects are small.

In Fig. 2 we display the same curves for Xe at \( T = 21 \) K compared with the multidimensional (MD) calculations of Marchese, Jacucci, and Klein who included the interaction with a graphite substrate. Marchese et al. and Cardini and O'Shea also present QH frequencies for Xe at
TABLE I. Parameters for the interatomic potentials.

<table>
<thead>
<tr>
<th></th>
<th>Ne-Ne</th>
<th>Ar-Ar</th>
<th>Kr-Kr</th>
<th>Xe-Xe</th>
</tr>
</thead>
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<tr>
<td>$\epsilon / k_B$ (K)</td>
<td>42.250</td>
<td>143.224</td>
<td>199.9</td>
<td>282</td>
</tr>
<tr>
<td>$r_m$ (Å)</td>
<td>3.087</td>
<td>3.759</td>
<td>4.012</td>
<td>4.36</td>
</tr>
<tr>
<td>$B$</td>
<td>0.2111998$\times 10^7$</td>
<td>0.950272.0$\times 10^7$</td>
<td>0.1215312$\times 10^9$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>14.879416</td>
<td>16.345655</td>
<td>16.496763</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.50</td>
<td>2.00</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td>$C_6$</td>
<td>1.3057606</td>
<td>1.0914254</td>
<td>1.1561739</td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>0.3999415</td>
<td>0.6002595</td>
<td>0.5414923</td>
<td></td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>0.1641572</td>
<td>0.3700113</td>
<td>0.2839735</td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td>1.28</td>
<td>1.40</td>
<td>1.28</td>
<td></td>
</tr>
</tbody>
</table>

*Aziz, Meath, Allnatt (Ref. 23).

*Aziz and Chen (Ref. 24).

*Aziz (Ref. 25).

$R=4.26$ Å. Without a substrate, we find QH frequencies in Fig. 2 of 1.33 THZ and 0.75 THZ at the $M$ point and 1.15 THZ at the $K$ point. Marchese et al.\textsuperscript{20} find corresponding QH frequencies of 1.39 THZ, 0.77 THZ, and 1.17 THZ at these points. This comparison shows that the interaction with the substrate lattice increases the QH frequencies near the Brillouin-zone edge. The chief effect of the substrate interaction is to introduce a gap of approximately 0.2 THZ in the dispersion curves at $q=0$ (the $\Gamma$ point). It is interesting that the MD and SCH frequencies in Fig. 2 agree well except at $q=0$. This is partly fortuitous because the increase in the SCH $\omega_{\alpha k}$ above the QH values is approximately equal to the contribution to the MD values due to the interaction with the substrate.

To illustrate the effects of temperature, we display dispersion curves for Xe at $T=50$ K in Fig. 3. There we see that the SCH curves lie $\sim 10\%$ above the QH values. Thus anharmonic effects have increased due to thermal vibration, but are still small. We find (see Sec. IV B) the Debye temperature of Xe to be 65 K so that Xe is quite classical at $T=50$ K.

Figure 4 shows the dispersion curves of 2D Xe at $T=0$ K and $R=4.36$ Å. This $R$ is a typical spacing Xe would assume on a weakly modulated substrate. Comparing Fig. 1 and Fig. 4 we see that the frequencies drop by $\sim 20\%$ as $R$ is increased from 4.26 to 4.36 Å showing that the QH and SCH $\omega_{\alpha k}$ depend greatly on the area.

Figure 5 displays the dispersion curves for Ar at $T=0$ K and $R=3.86$ Å, the nearest-neighbor separation observed in neutron scattering experiments\textsuperscript{14} on monolayers of Ar on graphite. The equilibrium $R$ found by Phillips and Bruch\textsuperscript{31} for 2D Ar is $R=3.85$ Å. In Fig. 5 the SCH $\omega_{\alpha k}$ lie $15-20\%$ above the QH values showing that the lighter Ar atom has significant zero-point vibration which increases the anharmonic contributions to the $\omega_{\alpha k}$. We also evaluated the SCH frequencies for 2D Ar interacting

![FIG. 1](image1.png)

**FIG. 1.** Phonon frequency dispersion curves for a Xe monolayer for a lattice parameter $R=4.26$ Å at a temperature $T=0$ K. Both the self-consistent harmonic (SCH) and quasiharmonic (QH) predictions are shown. (We plot $\nu=\omega/2\pi$.)

![FIG. 2](image2.png)

**FIG. 2.** Same as Fig. 1 but at $T=21$ K. The dotted circles are the results of the molecular dynamics (MD) calculations of Marchese, Jacucci, and Klein (Ref. 12).
via the Lennard-Jones potential to compare with Novaco's values\textsuperscript{16} and found agreement to within 1\%. The dispersion curves for Ne at $T=0$ K and $R=3.25$ Å was selected since this is the value found for coverages up to half a completed monolayer for Ne on graphite\textsuperscript{33} at $T=1.5$ K. For Neon the SCH $\omega_{q\lambda}$ are almost twice the QH values showing that Ne forms a highly anharmonic 2D crystal having substantial zero-point vibration. As mentioned in the discussion, we expect the cubic anharmonic term, not included here, to reduce the Ne $\omega_{q\lambda}$ to somewhere between the SCH and QH curves. However, it is clear from Fig. 6 that Ne is extremely anharmonic and that the complete description of its dynamics must include anharmonic contributions at all $T$ and quantum effects for $T \leq 65$ K.

Finally, in Fig. 7 we show the dispersion curves for Kr at $T=0$ K and $R=4.02$ Å, the equilibrium spacing for 2D Kr. The difference between the SCH and QH frequencies is 4--5% at the Brillouin-zone edge so that Kr, like Xe, is essentially harmonic\textsuperscript{32} at low $T$. Anharmonic contributions will be significant only for $T \geq \Theta_D = 65$ K in Kr as is the case in Xe.

### B. Zero-point energy

The importance of quantum effects may be assessed by evaluating the zero-point energy and introducing a corresponding Debye temperature $\Theta_D$. The zero-point energy per atom ($E_z$) is

$$E_z = \frac{1}{2N} \sum_{q,\lambda} \hbar \omega_{q\lambda}.$$  \hspace{1cm} (6)

In a Debye approximation this is

$$E_z = \frac{1}{2N} \int_0^{\omega_D} g(\omega) \hbar \omega d\omega,$$

where in 2D $g(\omega) = 4N\omega/\omega_D^2$ giving

$$E_z = \frac{1}{2} \hbar \omega_D = \frac{1}{2} k_B \Theta_D.$$

(7)

The relations (6) and (7) serve to define $\Theta_D = \hbar \omega_D / k_B$ appropriate to the zero-point energy. We have calculated
\( E_z \) in (6) using the SCH \( \omega_{qk} \) on a grid of approximately 5000 \( q \) points and obtained \( \Theta_D \) from (7).

The values of \( E_z \) are given in Table II. Also given in the table is a quantity \( \lambda = |E_z/E_p| \) where \( E_p \) is the static potential energy. This essentially determines the importance of quantum effects. In bulk rare-gas crystals the ratios decrease from 0.25 in neon to about 0.03 in Xe. We find that for monolayers the ratios decrease from 0.39 to 0.05 being higher than the corresponding 3D values in all cases. The small \( \lambda \) found in Xe again confirms that the system is classical. The large ratio \( \lambda \) in Ne indicates that for this system quantum-mechanical effects are dominant.

Also listed in Table II are the Debye temperatures for the rare-gas monolayers. Bruch et al.\textsuperscript{34} in their cell model with a Lennard-Jones (LJ) potential and a lattice spacing of 3.30 Å find a Debye temperature of \( \Theta_D = 40 \) K in Ne. Here with the Aziz, Meath, and Allnatt potential at a 3.31 Å lattice separation we find a Debye temperature of 63.61 K. The LJ value for the SCH approximation is also expected to be much higher than 40 K. The definitions of \( \Theta_D \) in the two cases are not the same, neither are the models of the dynamics so that a difference in \( \Theta_D \) values is expected. Experimentally from heat-capacity measurements Huff and Dash\textsuperscript{35} estimate \( \Theta_D \) for Ne to be approximately 50 K. Similar measurements by Chung\textsuperscript{36} yield for Ar a \( \Theta_D \) of about 70 K. Both are in agreement with neutron scattering estimates.\textsuperscript{4,33} Our SCH result for Ar is 68 K.

### C. Mean-square vibrational amplitudes

In a 2D solid at \( T=0 \) K the mean-square vibrational amplitude is given by

\[
\langle u^2 \rangle = \frac{1}{N} \sum_{q,\lambda} \frac{h}{2M \omega_{qk}} .
\]  

(8)

In the Debye approximation of Sec. II above this is

\[
\langle u^2 \rangle = \frac{2\hbar^2}{MK_B \Theta_D} .
\]  

(9)

We may use the \( \Theta_D \) values listed in Table II obtained from \( E_z \) to estimate \( \langle u^2 \rangle \). These estimates are very close to the values calculated from Eq. (8). Our value for Xe is nearly identical to the value obtained by de Wette \textit{et al.}\textsuperscript{37} from a different model (they plot \( \langle u^2 \rangle = \frac{1}{3} \langle u^2 \rangle \)). They have done a full dynamical calculation within the harmonic approximation for a graphite slab covered with a registered Xe monolayer (\( R=4.26 \) Å).\textsuperscript{9} The agreement between the results of the two models is an indication that the compressed physisorbed Xe monolayer is very similar to its floating counterpart as other considerations also show.\textsuperscript{6,7} The Lindemann ratios \( \gamma^2 = \langle u^2 \rangle / R^2 \) for the 2D-rare-gas crystals (RGC's) at zero temperature are listed in Table II. It is interesting to observe that for Ne the rms vibrational amplitude is close to 10% of the interatomic spacing. The ratios decrease as the mass increases. The large ratio in neon is further testament of the importance of anharmonic effects. Xe is again observed to be essentially a classical system. We observe that the ratios are almost similar to the same for 3D rare-gas crystals.\textsuperscript{38}

A different Lindemann's ratio, the rms relative displacement between nearest neighbors divided by the nearest-neighbor distance can be defined at finite temperature.\textsuperscript{39} This turned out to work quite well as a melting criterion. Our results for Ne at different temperatures are shown in Table III. As expected, this is quite large (about 10%) at zero temperature and increases as the temperature is increased.

### D. Effects of temperature

We also study the temperature dependence of the phonon frequencies. We choose three different phonon modes, \( M, K, \) and \( \frac{1}{2} k_{F} \). The results are presented graphically in Figs. 8–10 for Xe, Ar, and Ne, respectively. In Xe (Fig. 8) it is clear that thermal effects start to

![](image-url)

**FIG. 7.** Same as Fig. 1 but for a Kr monolayer with \( R=4.02 \) Å and \( T=0 \) K.

### TABLE II. Debye temperatures (\( \Theta_D \)), zero-point energies (\( E_z \)), mean-square vibrational amplitudes (\( \langle u^2 \rangle^{1/2} \)) and \( \lambda = (E_z/E_p) \) where \( E_p \) is the average potential energy for the four rare-gas monolayers at \( T=0 \) at the equilibrium lattice parameters \( R=R_m \).

<table>
<thead>
<tr>
<th></th>
<th>( R ) (Å)</th>
<th>( \Theta_D ) (K)</th>
<th>( E_z/k_B ) (K)</th>
<th>( \langle u^2 \rangle^{1/2} ) (Å)</th>
<th>( \langle u^2 \rangle^{1/2}/R )</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>3.253</td>
<td>63.61</td>
<td>42.41</td>
<td>0.28</td>
<td>0.086</td>
<td>0.39</td>
</tr>
<tr>
<td>Ar</td>
<td>3.86</td>
<td>68.02</td>
<td>45.35</td>
<td>0.19</td>
<td>0.049</td>
<td>0.11</td>
</tr>
<tr>
<td>Kr</td>
<td>4.02</td>
<td>61.24</td>
<td>40.83</td>
<td>0.14</td>
<td>0.034</td>
<td>0.065</td>
</tr>
<tr>
<td>Xe</td>
<td>4.26</td>
<td>65.73</td>
<td>43.82</td>
<td>0.11</td>
<td>0.025</td>
<td>0.050</td>
</tr>
</tbody>
</table>
TABLE III. The Lindemann ratio as defined by Ramakrishnan (Ref. 39) for the same lattice parameters as in Table II.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>0</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.1023</td>
<td>0.1057</td>
<td>0.1328</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0596</td>
<td>0.0676</td>
<td>0.0816</td>
</tr>
<tr>
<td>Kr</td>
<td>0.0418</td>
<td>0.0490</td>
<td>0.0614</td>
</tr>
<tr>
<td>Xe</td>
<td>0.0305</td>
<td>0.0354</td>
<td>0.0446</td>
</tr>
</tbody>
</table>

dominate as soon as the temperature is turned on. In Fig. 9 for Ar the frequency rises slowly up to about \( \frac{1}{3} \)th of the Debye temperature and then rises more sharply. This shows that below about 10 K, the zero-point energy is still dominant in Ar, and above this thermal effects become more dominant. In the case of Ne in Fig. 10 the zero-point energy is dominant up to about \( \frac{1}{3} \) of the Debye temperature, after this thermal effects show more prominently. These are further signals that quantum-mechanical effects are large in Ne, and that Xe is a classical system.

E. Volume dependence

Finally we studied the volume dependence of some chosen phonons in Ne, Ar, and Xe. These results are presented in Table IV. We also calculated a quantity

\[
\gamma_{\phi\lambda} = \frac{\partial \ln (\gamma_{\phi\lambda})}{\partial \ln A}
\]  

(10)
equivalent to the 3D Grüneisen parameter. These 2D Grüneisen parameters are given in Table V. For bulk solids the Grüneisen parameters range from 2.5 to 3.40,41

We see that the QH \( \gamma_{\phi\lambda} \) are generally larger than the SCH \( \gamma_{\phi\lambda} \), and they are all larger than the observed 3D

FIG. 8. Temperature dependence of the phonon frequencies of Xe at selected points in the Brillouin zone for the longitudinal (\( L \)) and transverse (\( T \)) modes in Xe with a lattice parameter \( R=4.26 \) Å. (We plot \( \nu=\omega/2\pi \).)
TABLE IV. Dependence of phonon frequencies (in THZ) on the lattice parameter at \( T=0 \) K at selected points in the Brillouin zone. For each phonon the smaller number is the quasiharmonic frequency. (To convert to cm\(^{-1}\) units divide by 0.03 and to meV multiply by 4.136 (\( \omega = 2\pi v \)).

<table>
<thead>
<tr>
<th>( R ) (Å)</th>
<th>( v_L ) (K) = ( v_T ) (K)</th>
<th>( v_L ) (M)</th>
<th>( v_T ) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>3.087</td>
<td>1.292</td>
<td>1.492</td>
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<tr>
<td></td>
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<td>1.676</td>
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<td>0.970</td>
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Grüneisen parameters. It is noteworthy that the 3D Grüneisen parameters have been quoted at zero pressure, whereas the parameters above have been calculated for lattice parameters requiring an external pressurizing fluid.

V. DISCUSSION

As noted in the text, the mean-square vibrational amplitude \( \langle u^2 \rangle \) of any atom in an infinite 2D solid diverges at a finite temperature. A periodic crystal can be supposed to exist in practice when pinned by a substrate. In this event the substrate introduces a gap in \( \omega_{q\lambda} \) at \( q=0 \) and this removes the divergence in \( \langle u^2 \rangle \).

By comparing the SCH and QH dispersion curves, we have seen that anharmonic contributions to the dynamics of inert-gas monolayers are very important, especially in Ar and Ne. However, in terms of a complete anharmonic theory, the SCH theory is an unbalanced approximation. It includes the even anharmonic terms (to first order) which generally shift the frequencies to higher values. It omits notably the cubic anharmonic terms which always shift the frequencies to lower values. In the 3D alkali-halide crystals the upward shift due to the quartic term is nearly completely canceled by the downward shift due to the cubic term. In the 3D inert-gas crystals the cubic shift to the \( \omega_{q\lambda} \) is generally one-half the value \(^5\) of the QH to SCH shift. On this basis we expect the phonon frequencies including the cubic anharmonic term in Figs. 1—7 to lie approximately one-half way between the QH and SCH values. It would be most interesting to include the cubic term and particularly to investigate phonon lifetimes. The cubic terms will also be necessary to study the stability of expanded monolayers and the effects of temperature on such systems. An extreme case is the Kr monolayer adsorbed on graphite which can be considerably expanded often beyond the lattice parameter at which the vacancy energy of the floating monolayer goes negative.\(^6\) It is a soft monolayer and the density modulations brought about by the substrate make it very anharmonic and quite unlike its floating counterpart.\(^6\) The lowest vibrational modes are associated with domain-wall motion.\(^42\)

A comparison of dynamics in 2D and 3D is interesting. Firstly, the ZPE for the 2D RGC's listed in Table II is roughly 42 K in each case. This is one-half of the 3D values, approximately.\(^38\) Thus the 2D crystals are less-tightly bound which is expected on dimensional grounds.

TABLE V. Grüneisen parameters \( \gamma \) at selected points in the Brillouin zone for all phonon branches for the SCP and QH calculations.

<table>
<thead>
<tr>
<th>( \gamma_L ) (1 / ( \gamma_T )</th>
<th>( \gamma_T ) (1 / ( \gamma_T ))</th>
<th>( \gamma_L ) (K) = ( \gamma_T ) (K)</th>
<th>( \gamma_L ) (M)</th>
<th>( \gamma_T ) (M)</th>
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<tbody>
<tr>
<td>Xe (( R=4.26 ) Å)</td>
<td>QH</td>
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<td>3.93</td>
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<td>SCH</td>
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<td>3.82</td>
<td>4.31</td>
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<tr>
<td>Ar (( R=3.86 ) Å)</td>
<td>QH</td>
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<td>4.10</td>
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<tr>
<td>Ne (( R=3.25 ) Å)</td>
<td>QH</td>
<td>7.82</td>
<td>6.26</td>
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</tr>
<tr>
<td></td>
<td>SCH</td>
<td>3.90</td>
<td>3.71</td>
<td>3.85</td>
</tr>
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</table>
The ratio of the $E_z$ to $E_p$ is comparable in 2D and 3D. The $\Theta_D$ in 2D is roughly 65 K for all the RGC’s. In 3D there is a much wider variation of $\Theta_D$ from Ne to Xe. The rms vibrational amplitudes are comparable\textsuperscript{38} in 2D and 3D at $T=0$ K. The anharmonic contributions are larger in 2D than in 3D (and the $\omega_{q\lambda}$ in the SCH approximation at least. Similarly, the SCH $\omega_{q\lambda}$ are more sensitive functions of temperature and volume in 2D than in 3D. In particular the Grüneisen constants $\gamma_{q\lambda}$ are approximately 50% larger in 2D.

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\*Present address: Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7.
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