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Rare-gas monolayers on graphite: Study of anharmonic effects

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A lattice-dynamical study of the inert-gas monolayers of Xe, Kr, Ar, and Ne, in epitaxy with the (0001) graphite surface has been made at different temperatures. The calculation considers an extended version of the anharmonic theory of Dobrzynski and Maradudin for a Bravais lattice. We observe only a small relaxation of monolayer away from the graphite surface in the temperature range 0 K to the melting temperature of the rare-gas solid. The mean-square displacement (MSD) of the inert-gas atoms lying in the plane of the monolayer are, in general, an order of magnitude larger than that of the carbon atoms. The value of the in-plane component of MSD is greater than the out-of-plane component and their difference increases with a decrease in the mass of the adsorbed atom. The calculated values of the MSD's are in reasonable agreement with the available experimental data. No soft phonon appears.

I. INTRODUCTION

Atomic or molecular films physisorbed on uniform solid surfaces form well-defined monolayers.[1,2] Many efforts have been made to understand the types of phase transitions taking place in these films, the nature of the phase involved, and the possible relationship between weakly bound surface monolayers and the idealized two-dimensional (2D) systems of the theory. The adsorbed atoms or molecules can exist in a variety of thermodynamic phases; in particular, in the submonolayer region, 2D gas, liquid, and solid phases have been detected. Also, the solid phase may be either commensurate or incommensurate with the substrate surface. In a commensurate phase, one notes the lattice parameter of the 2D physisorbed layer as a multiple or submultiple of that of a normal plane of the substrate in bulk.

Inert-gas atoms like Xe, Kr, Ar, etc., physisorbed on the basal plane (0001) of graphite have been studied extensively, partly because of simplicity of their being monatomic, reducing thus the complexities associated with the extra intramolecular degrees of freedom, and partly because of the commercial availability of Grafoil (a form of graphite) having large specific areas and surfaces of exceptional uniformity and homogeneity. All three phases, i.e., gas, liquid, and solid have been identified. In particular, the solid-liquid transition is interesting as it may, in principle, be second order at high coverages representing a 2D analog of the usual melting process which is of first order in three-dimensional systems. Both commensurate and incommensurate solid phases have been detected. In some systems, by a variation of temperature and the pressure of the inert gas, one may observe an apparently second- (or higher-)order phase transition from a commensurate (in-registry) $(\sqrt{3}\times\sqrt{3})$ 30° superstructure to an incommensurate (out-of-registry) compressed or expanded monolayer structure. Very recently, rotation of the adsorbed layer in the incommensurate phase with respect to the graphite substrate has been reported in the literature.[3,4]

Near the surface one may observe relaxation bigger than in the bulk and the distance between an adsorbed monolayer and the substrate might increase with temperature. The two-dimensional order inside the monolayer may then overcome the three-dimensional order imposed by the substrate. This may enable a phonon to become soft at a certain temperature.[5] In earlier studies[6,7] we investigated the stability as a function of temperature of (001) and (111) monolayers of the rare-gas atoms adsorbed on surfaces of the other rare-gas crystals. It was observed that the soft phonons could exist in the adsorbate-substrate system of the rare-gas solids.

A few theoretical attempts have been made to study the atomic motions of the physisorbed monolayer.[8-12] In the inert-gas layers on graphite, it has been pointed out that the magnitude of the mean-square displacement of the adsorbed atoms parallel to the substrate surface is higher than the component perpendicular to the surface. One may thus hope for the appearance of a soft phonon responsible for a second-order phase transition. The present work was motivated by this. Using the anharmonic theory of Dobrzynski and Maradudin[13] we determine first the distance between the monolayer and the graphite surface with increasing temperature, then we obtain the renormalized interatomic forces. We present here also the results for the mean-square displacements (MSD) of the adsorbed atoms at different temperatures and compare them with the available experimental data.

The organization of the paper is as follows: In Sec. II we discuss the graphite (0001) surface having the physisorbed monolayers of the rare-gas atoms such as Xe, Kr, Ar and Ne. Numerical calculations for the thermal expansion, mean-square displacements and soft phonons have been performed by taking Mie–Lennard-Jones pair potentials for the adatom-adatom and the adatom-carbon atom interactions. The conclusions are contained in Sec. III.

II. INERT-GAS MONOLAYERS ON GRAPHITE SURFACE

The anharmonic theory of Dobrzynski and Maradudin[13] for a Bravais crystal may easily be extended to a non-Bravais crystal after replacing the unit cell index (l) by the pair index (l, κ) with κ as a type of atom in the unit cell. For the details of the theory and the calculation of the thermal expansion we refer to earlier papers.[13,7]

We make here a study of the thermal expansion and the mean-square displacements of the inert-gas, Xe, Kr, Ar, and Ne monolayers in epitaxy with the (0001) graphite surface (Fig. 1), and thereafter investigate the possibility of soft phonons in these systems.

The graphite crystal possesses a hexagonal structure (Fig. 2). The unit cell contains four atoms. For a simpler calculation we use here a simple lattice-dynamical model discussed earlier by Champier *et al.*[14] and used by others.[9,15,16] This force-constant model allows us to make analytical calculations for the phonon dispersion relations. In this model one considers a central force constant β and the two noncentral force constants (α, γ) between the two nearest-neighbor atoms lying in a layer (0001). The interactions between the two adjacent layers are described in the same manner by the central force constant (γ') and the noncentral force constant (α').

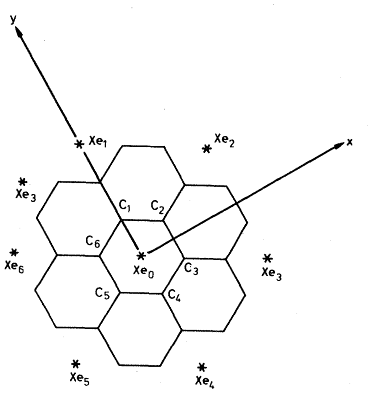

FIG. 1. Commensurate phase of rare-gas atom monolayer on graphite basal (0001) plane. Atomic positions: Xe_l and C_l denote the rare-gas and carbon atoms, respectively.

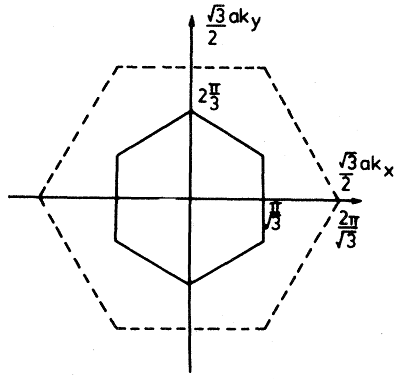

FIG. 2. Two-dimensional first Brillouin zone for the graphite basal plane. The inner small zone is for the rare-gas monolayer.

The first two-dimensional Brillouin zone for the graphite surface (0001) has been depicted in Fig. 2 which also contains the first Brillouin zone for the inert-gas monolayer in epitaxy with the substrate surface lattice. The allowed values of the wave vectors $\phi_x = \frac{1}{2}\sqrt{3}ak_x$ and $\phi_y = \frac{1}{2}\sqrt{3}ak_y$ are

$$-\pi/\sqrt{3} \leqslant \phi_x \leqslant \pi/\sqrt{3}, \quad -\tfrac{2}{3}\pi \leqslant \phi_y \leqslant \tfrac{2}{3}\pi . \tag{1}$$

The necessary dynamical matrix elements and the values of the force constants have been given by Albinet *et al.*[15] as

$$\begin{aligned} &\beta = 913 \times 10^3 \text{ dyn/cm}, \quad \alpha' = 10 \times 10^3 \text{ dyn/cm}, \\ &\alpha = 194 \times 10^3 \text{ dyn/cm}, \quad \gamma' = 5.67 \times 10^3 \text{ dyn/cm}, \\ &\gamma = 53 \times 10^3 \text{ dyn/cm}. \end{aligned} \tag{2}$$

A. Mie-Lennard-Jones potential (MLJ)

The rare-gas-atom monolayer has a $\sqrt{3} \times \sqrt{3}$ structure and its Brillouin zone is rotated by an angle of 30° with respect to that of graphite surface. One describes this superstructure of the surface as $(\sqrt{3} \times \sqrt{3})\, 30°$.

Let a and c be the lattice constants of the graphite in bulk. The six nearest neighbors of an inert-gas atom in the monolayer are situated at a distance of $3a$. For describing the nearest-neighbor adatom-adatom interactions and also the nearest-neighbor adatom-substrate interactions we use here the Mie–Lennard-Jones (MLJ) pair potentials $\phi_{a-a}(r)$ and $\phi_{a-s}(r)$, respectively, (a denotes adsorbed atom and s the substrate atom). The MLJ potential is given as

$$\phi(r) = \epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^{6}\right], \tag{3}$$

where r denotes the separation of two atoms and the values of the potential parameters σ and ϵ are obtained by using the measured values of the virial coefficients of inert gases.[17] The values of the two parameters ϵ and σ for the graphite and the inert-gas atoms Xe, Kr, Ar, and Ne are contained in Table I.

For determining the values of the parameters ϵ and σ for the adatom-substrate interaction potential, we utilize the following prescription:

$$\epsilon_{as} = (\epsilon_a \epsilon_s)^{1/2} \text{ and } \sigma_{as} = \tfrac{1}{2}(\sigma_a + \sigma_s) . \tag{4}$$

As stated earlier, the thermal expansion for graphite both parallel and perpendicular to the basal plane (0001) is quite small (~10^{-6} K); we therefore do not determine any numerical values for the thermal expansion in bulk, but instead use the values given in standard tables.[18] However, the contribution of the homogeneous deformation is negligible.

In the absence of any experimental information about the monolayer-substrate surface separation c, the static equilibrium condition is utilized to determine it. The condition for a net force on an Xe atom along normal to the surface is given by

$$\left(\frac{d\phi_{as}(r)}{dr}\right)_{\text{eq}} = 0 , \tag{5}$$

where r is the distance between an Xe atom and its neighbor and $\phi_{as}(r)$ is the MLJ potential for the adatom-substrate atom interactions. Price[19] has determined the values of c for these systems after summing up interactions to all the neighbors. The values are reproduced in Table I.

In the evaluation of the thermal expansion near the surface we take the values of the correlation functions $\langle U_\alpha(l\kappa)U_\beta(l'\kappa')\rangle$ in the Einstein approximation. The approximation is quite good for the atomic displacements normal to the surface. In the harmonic approximation, Coulomb *et al.*[9] has shown that for the Xe monolayers the correction due to the second-order terms in the expansion of the correlation functions is only ~0.7% of the value in Einstein's approximation. However, for the mean-square displacement parallel to the surface the convergence is a little slower.

TABLE I. Parameters of Mie–Lennard-Jones potential (MLJ 6–12) and the monolayer-substrate separation c. The values of ϵ and σ are in K and Å, respectively. The melting temperature T_M of solid rare gas is in K and c is in Å.

Sample number	Atom	ϵ	σ	T_M	c
1	carbon (graphite)	27.0	3.871		(Ref. 19)
2	Xe	332.0	4.318	155	3.69
3	Kr	182.9	4.020	116	3.54
4	Ar	125.2	3.810	84	3.42
5	Ne	35.6	3.080	24.5	3.13

During the course of calculation, we find that the numerical values of the mean-square displacements for the inert-gas atom are larger compared to that of graphite atoms at all temperatures and one may work in a frozen-substrate approximation. However, we present here our results for the thermal expansion for a graphite surface where the carbon atoms are vibrating.

B. Thermal expansion near the surface

The thermal expansion of the monolayer-substrate separation is defined as

$$\frac{\Delta c(T)}{c(0)} = \frac{\delta c(T) - \delta c(0)}{c(0)} , \tag{6}$$

where $\delta c(T)$ is the relaxation of the monolayer at temperature T. $c(0)$ is the monolayer-substrate separation at $T = 0$ K given in Table I. In fact, one observes a small relaxation near 0 K causing $\delta c(0)$ to be nontrivial.

The percentage relative relaxation for the rare-gas monolayers has been depicted in Figs. 3–6. For Xe, in a temperature interval of 150 K, one observes a relaxation of ~3.5%. It arises because of a comparatively large initial monolayer-substrate separation (3.69 Å). It may be recalled that the separation between the basal planes in bulk graphite is 3.35 Å. For krypton and argon, the relaxation is about 0.8% in a temperature interval of ~100 K, and for neon, the corresponding relaxation is 0.15% in the temperature interval of 25 K.

C. Soft phonons

In the calculation of the temperature-dependent phonons we employ a frozen-substrate approxima-

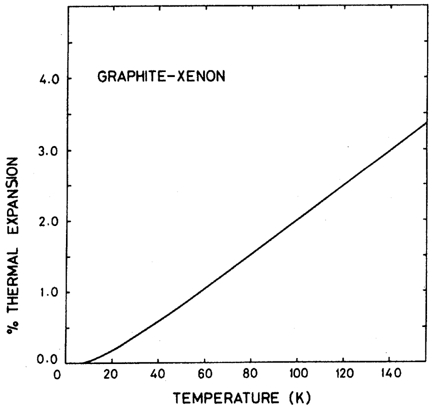

FIG. 3. Percentage relative relaxation for Xe monolayer.

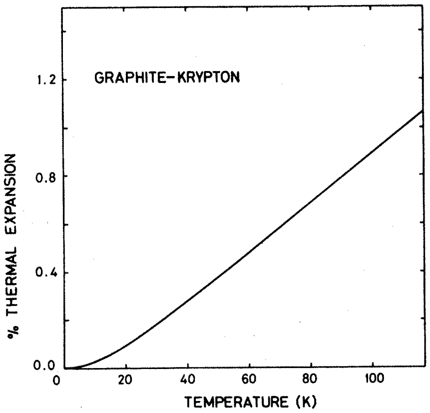

FIG. 4. Percentage relative relaxation for Kr monolayer.

tion. The equations of motion for the y and z components of the displacement of an inert-gas atom in the y direction get decoupled as[20]

$$[-Mw^2+3a_{22}+F(3-\cos 2\phi_y-2\cos\phi_y)]U_y^{(a)}=0\,, \tag{7}$$

$$(-Mw^2+6a_{33})U_z^{(a)}=0\,. \tag{8}$$

Here M is the mass of inert gas atom; F, a_{22}, and a_{33} are the nearest-neighbor central adatom-adatom force constant and adatom-substrate force constant, respectively. Their explicit forms are

$$F=\phi''_{aa}(3a)+\phi'_{aa}(3a)/3a\,, \tag{9}$$

$$a_{22}=a^2D^2\phi_{as}(r_0)+2D\phi_{as}(r_0)\,,$$

$$a_{33}=c^2D^2\phi_{as}(r_0)+D\phi_{as}(r_0)\,, \tag{10}$$

with $D\phi(r)=\phi'(r)/r$, $D^2\phi(r)=\phi''(r)/r^2-\phi'(r)/r^3$, and $\phi'(r)$ and $\phi''(r)$ as the first and second space derivatives of the pair potential $\phi(r)$; r_0 is the nearest-neighbor distance between the rare gas and carbon atoms.

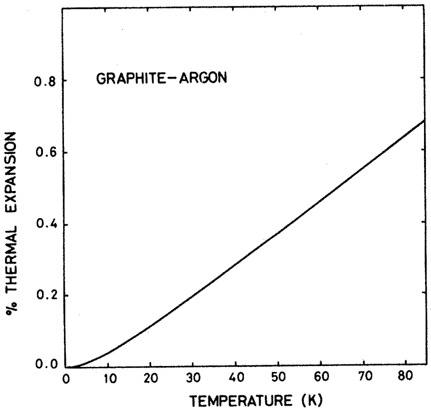

FIG. 5. Percentage relative relaxation for Ar monolayer.

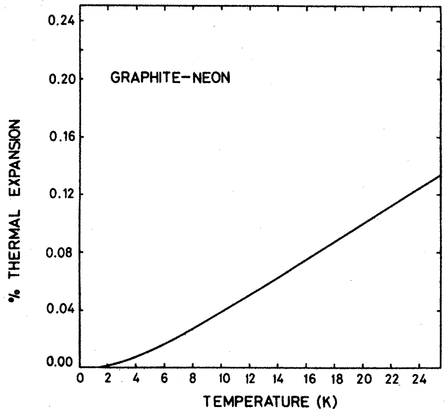

FIG. 6. Percentage relative relaxation for Ne monolayer.

From Eq. (7) it is evident that a phonon may become soft if $a_{22}=0$ at a certain temperature before the melting temperature of the inert-gas solid is reached. We look into this possibility and find that no soft phonon appears in any inert-atom monolayer physisorbed on (0001) graphite.

D. Mean-square displacements (MSD)

The variations of the out-of-plane component U_z^2 of the mean-square displacement with temperature for monolayers of Xe, Kr, Ar, and Ne in epitaxy with the (0001) surface of graphite are shown in Figs. 7–11. Some measured values of the out-of-plane component available in the literature are also shown in these figures. The

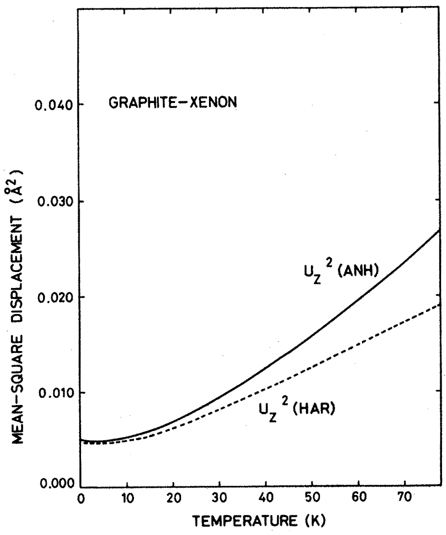

FIG. 7. Temperature variation of the out-of-plane $\langle U_z^2\rangle$ mean-square displacements for Xe monolayer in harmonic and anharmonic approximations.

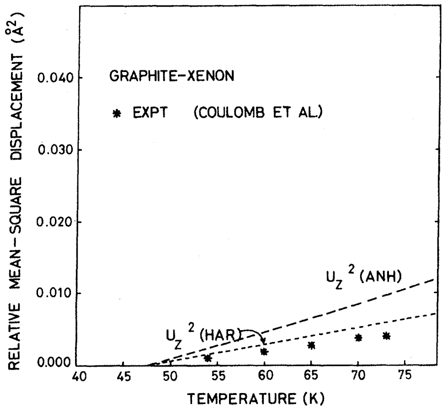

FIG. 8. Comparison of the calculated and the experimental relative out-of-plane mean-square displacement in Xe monolayer. The experimental results of Coulomb *et al.* (Ref. 9) are shown by asterisks.

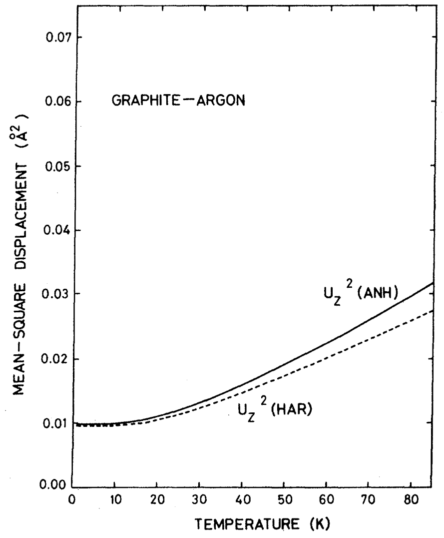

FIG. 10. Same as Fig. 7 but for argon.

calculations have also been performed for the in-plane component of MSD for all the systems. In general, the parallel component of the mean-square displacement is greater than the normal component. It is due to the fact that the adatom-adatom interactions are weaker than the adatom-substrate interactions.

We now turn towards a discussion of individual rare-gas monolayer. For the Xe monolayer (Fig. 7) the effect of anharmonicity is apparent in the out-of-plane component. It arises due to a comparatively larger monolayer-substrate separation (3.69 Å) compared to a separation of 3.35 Å between the successive planes of the bulk graphite. Coulomb *et al.*[9] have measured the out-of-plane component of the MSD in the temperature range 48–73 K by low-energy-electron diffraction and have seen a good agreement with the results of a lattice-dynamical calculation of MSD in harmonic approximation with $c = 3.63$ Å. Our results for $c = 3.69$ Å in harmonic approximation tally with their results. In fact, Coulomb *et al.* have measured the variation of MSD of an Xe atom with respect to that at 48 K. A comparison of this variation has been made in Fig. 8. We observe a steeper rise in the MSD in the anharmonic theory.

For the Kr monolayer (Fig. 9), our values of the in-plane component are somewhat lower than the experimental values of Horn *et al.*[21] available at two temperatures $T = 30$ and 90 K. At $T = 30$ and 100 K, the calculated values are 0.04 and

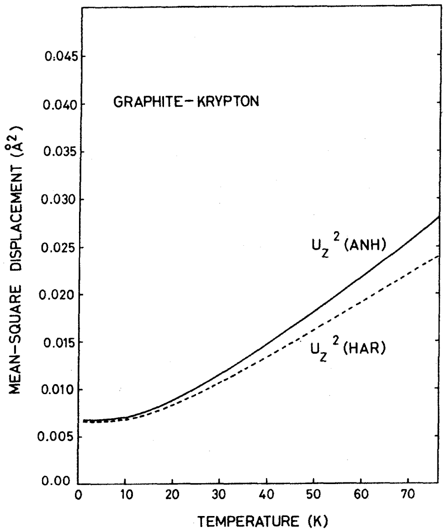

FIG. 9. Same as Fig. 7 but for krypton.

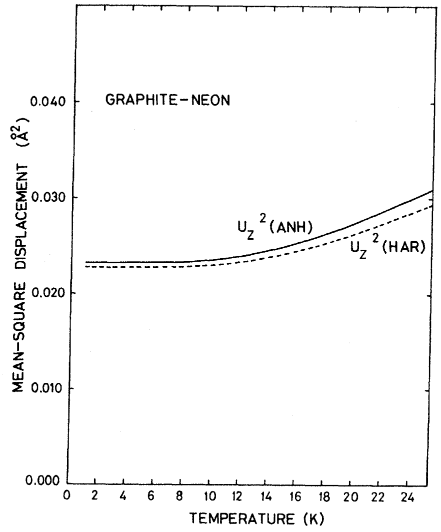

FIG. 11. Same as Fig. 7 but for neon.

0.12 Å^2, respectively, as compared to the experimental values 0.055 and 0.17 Å^2, respectively. The results seem to be reasonable as the contributions of the neglected higher-order terms in the expansion of the correlation functions may be significant for the in-plane component.

For the Ar monolayer (Fig. 10) the values for the in-plane component are quite high compared to those of out-of-plane component. For the Ar monolayer, some experimental and theoretical results for the phonons and the mean-square displacement for a two-dimensional lattice have recently been reported in the literature.[10-12] Taub *et al.*[10] have reported an out-of-plane Einstein oscillator frequency of ~5.6 meV. For this phonon mode having vibration normal to the plane of monolayer we obtain a value of 5.4 meV, quite in agreement with the neutron scattering data of these authors. Further, our value of the in-plane component of MSD is 0.043 Å^2 which is in very good agreement with their value of 0.04 Å^2 from the analysis of neutron data. An estimate of the in-plane component of MSD has been made by Tsang[12] using a modified-cell theory for a two-dimensional Ar monolayer having a nearest-neighbor distance of 3.86 Å, in contrast to the present value of 4.26 Å corresponding to a commensurate $\sqrt{3}\times\sqrt{3}$ 30° phase. Tsang's values are ~3 times smaller than our values.

For the Ne monolayer, the in-plane component is quite large compared to the out-of-plane component. This is again indicative of a quite strong coupling of the monolayer to the substrate. The author is not aware of any experimental data for the phonon or mean-square displacement for Ne monolayer on graphite.

III. CONCLUSIONS

We have studied the lattice-dynamical aspects of the inert-gas monolayers in epitaxy with the (0001) graphite surface using an anharmonic theory. Only a small relaxation of ~1% of the monolayer over a temperature interval of 100 K has been observed for Kr, Ar and Ne monolayers. For the Xe monolayer the corresponding relaxation is ~2%. No soft phonon has been detected. The mean-square displacements of all the monolayers are an order of magnitude larger than those of the carbon atoms in graphite surface and one may safely work in the frozen-substrate approximation. The mean-square displacements of inert-gas atoms parallel to the surface are, in general, greater than those perpendicular to the surface. The differences in the two components increase with increased coupling with the substrate surface and decrease with the mass of the adsorbed atom. The variation of the mean-square displacements for the monolayers with temperature has been determined. The calculated values of the mean-square displacements in Xe, Kr, and Ar monolayers are in good agreement with the available experimental data. It may be noted that the present theory considers only the cubic anharmonic term to lowest order in perturbation formalism. The inclusion of higher-order terms such as the quartic anharmonic one or those in the perturbation formulation may affect the results at higher temperatures. Thus, the results at high temperatures should be taken with caution in the theory.

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