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Phonon Contribution to the Free Energy of Interacting Adatom Pairs

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The free energy ΔF due to the interaction through the crystal phonon field of two identical atoms adsorbed on a (100) surface of a simple cubic monatomic lattice is studied within the framework of the Montroll–Potts model. The zero-point energy of interaction, ΔE_0, is found analytically in the limit of large separation distances, and numerical results are presented for small separation distances. The leading temperature-dependent terms in the expansion of ΔF are given in closed form in both the low- and high-temperature limits. The results are given as a function of the mass and separation distance of the adsorbed atoms and as a function of the force constant binding the adsorbed atoms to the surface. For all values of the model parameters, it is found that the free energy decreases with the separation distance. Thus, two adatoms on a surface are attracted toward each other.

I. INTRODUCTION

Recently, chemisorption, and to a lesser degree physisorption, has been extensively studied in several laboratories. The well-defined patterns within the surface adlayer are often different in structure from the surface layer of the absorbate.[1] Of fundamental importance in understanding these various patterns is an understanding of the interaction energy between pairs of adatoms.

Recently, Einstein and Schrieffer[2] have studied the electronic contribution to the energy of interaction at 0 °K (the zero-point energy) of two adatoms on the (001) surface of a simple cubic monoatomic solid within the tight-binding approximation. Their simple non-self-consistent first approach applies mainly to the case of chemisorption of simple gases on transition metals.

In this paper we consider the energy of interaction of two adatoms through the crystal phonon field. It is of interest to know the magnitude of the phonon contribution to the interaction free energy relative to the magnitude of the electronic contribution. Whereas one might expect the phonon contribution to be negligible compared to the electronic contribution, such a conclusion has not been demonstrated.[3] It seems possible, for example, that there might be cases in physisorption of rare-gas atoms on rare-gas crystals where the phonon contribution may be expected to be the major contribution to the free energy of interacting adatom pairs. In addition, Einstein and Schrieffer have found that the interaction energy in the electronic case may vanish depending upon the location of the Fermi level in the band. It should be noted that, like Einstein and Schrieffer, we do not consider direct interactions between the adatoms.

In Sec. II we introduce the phonon model and present the general expressions which enable us to calculate the free energy as a function of temperature. In Sec. III we consider the interaction free energy at 0 °K. For a general separation distance, this zero-point energy ΔE_0 must be calculated numerically. We present results showing how this zero-point energy depends upon separation distance, the mass of the adatoms, and the strength of the force constant binding the adatoms to the surface. In addition, an analytic expression is obtained for ΔE_0 in the limit of weak binding and large separation distances. In Sec. IV, we consider the

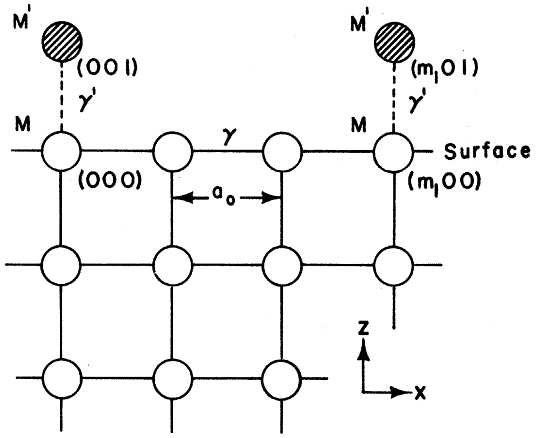

FIG. 1. Model geometry showing two adatoms of mass M' bound in the "on-site" configuration to a surface atom of mass M by a force constant γ'. The force constant in the simple cubic monatomic crystal is γ.

temperature dependence of the interaction free energy. In both the high- and low-temperature limits, the leading terms can be determined analytically.

II. FORMALISM

In this section we first describe the very simple model[4] we have chosen to represent the phonon field of the semi-infinite crystal. Then we give the perturbation due to the introduction of one or two adatoms. Finally, we assemble the relevant equations for calculating the change in the free energy due to the interaction of two adatoms. The formalism which we have used for this last step is well known[5] in the related study of the influence of point defects on the bulk vibrational properties of infinite crystals.

A. Equations of Motion

First we confine our attention to the semi-infinite crystal without the adatoms. We assume the crystal to be a monatomic simple cubic crystal with a (001) surface (see Fig. 1). The lattice vibrations are described by the model introduced by Rosenstock and Newell and popularized by Montroll and Potts.[6,7] Let $u_\alpha(l)$ denote the α component of the displacement from equilibrium of the atom at site $\vec{x}(l)=a_0(l_1\hat{x}+l_2\hat{y}+l_3\hat{z})$, where a_0 is the lattice parameter. The potential energy Φ associated with the lattice vibrations has the simple form

$$\Phi=\tfrac{1}{4}\gamma\sum_{l}\sum_{\delta}\sum_{\alpha}[u_\alpha(l)-u_\alpha(l+\delta)]^2 \times\Theta(-l_3)\,\Theta(-l_3-\delta_3). \tag{1}$$

Here, γ is the nearest-neighbor force constant, the sum over δ is restricted to first neighbors, and the Heaviside step functions $\Theta(-l_3)$ and $\Theta(-l_3-\delta_3)$ ensure that all the counted bonds occur only in the negative half-space $l_3\leq 0$.

By assuming a sinusoidal time dependence for the displacements, we obtain the equation of motion

$$M\omega^2u_\alpha(l)=\gamma\sum_{\delta}[u_\alpha(l)-u_\alpha(l+\delta)] \times\Theta(-l_3)\,\Theta(-l_3-\delta_3), \tag{2}$$

where M is the mass of the atoms in the bulk. In matrix notation, Eq. (2) can be written as

$$\underline{\mathrm{L}}\,\underline{\mathrm{u}}=0, \tag{3}$$

where

$$L_{\alpha\beta}(ll',\omega^2)=\left((M\omega^2-6\gamma+\gamma\delta_{l_30})\,\delta_{ll'}+\sum_{\delta}\gamma\delta_{ll'+\delta}\right) \times\delta_{\alpha\beta}\Theta(-l_3)\,\Theta(-l_3-\delta_3). \tag{4}$$

We now want to modify the model by adding two identical adatoms of mass M' (see Fig. 1). The adatoms are assumed to be located in the "on-site" configuration. The mathematics for other adatom configurations is notably more complex for this problem. Einstein and Schrieffer[2] have shown that for the electronic problem, the results are of the same order of magnitude for various adatom configurations, and we expect similar behavior in our problem. Thus, we assume each adatom is bound to one surface atom by a force constant γ'. Let $\xi_\alpha(m_1m_2 1)$ denote the α component of the displacement from equilibrium of the adatom absorbed at the surface site $m_1m_2 0$. The equation of motion for each adatom is

$$M'\omega^2\xi_\alpha(m_1m_2 1)=\gamma'[\xi_\alpha(m_1m_2 1)-u_\alpha(m_1m_2 0)]. \tag{5}$$

This can be rearranged as

$$\xi_\alpha(m_1m_2 1)=\frac{\omega_0^2}{\omega_0^2-\omega^2}\,u_\alpha(m_1m_2 0), \tag{6}$$

where

$$\omega_0^2=\gamma'/M'. \tag{7}$$

The equation of motion for the entire system, which now consists of the semi-infinite crystal with two absorbed atoms located at the lattice sites 000 and $m_1m_2 0$, is

$$M\omega^2u_\alpha(l)=\gamma\sum_{\delta}[u_\alpha(l)-u_\alpha(l+\delta)\cdot\Theta(-l_3)\,\Theta(-l_3-\delta) +\gamma'[u_\alpha(l_1l_2 0)-\xi_\alpha(l_1l_2 1)] \times[\delta_{l_10}\delta_{l_20}+\delta_{l_1m_1}\delta_{l_2m_2}]. \tag{8}$$

By substituting the adatom displacements of Eq. (6) into Eq. (8) we obtain

$$M\omega^2u_\alpha(l)=\gamma\sum_{\delta}[u_\alpha(l)-u_\alpha(l+\delta)]\,\Theta(-l_3)\,\Theta(-l_3-\delta_3)$$

$$+\frac{\gamma' \omega^2}{\omega^2 - \omega_0^2}\, u_\alpha(l)\, \delta_{l_3 0}[\delta_{l_1 0}\delta_{l_2 0} + \delta_{l_1 m_1}\delta_{l_2 m_2}]. \tag{9}$$

In matrix form this equation becomes

$$(\underline{L} - \underline{D})\underline{u} = 0, \tag{10}$$

where $\underline{L}$ is given by Eq. (4) and $\underline{D}$ is

$$D_{\alpha\beta}(ll') = \frac{\gamma' \omega^2}{\omega^2 - \omega_0^2}\, \delta_{\alpha\beta}\, \delta_{ll'}\, \delta_{l_3 0} \times (\delta_{l_1 0}\delta_{l_2 0} + \delta_{l_1 m_1}\delta_{l_2 m_2}). \tag{11}$$

For the case of a single adatom on the surface at site 000, the perturbation matrix $\underline{D}$ becomes

$$D_{\alpha\beta}(ll') = \frac{\gamma' \omega^2}{\omega^2 - \omega_0^2}\, \delta_{\alpha\beta}\delta_{ll'}\delta_{l0}. \tag{12}$$

B. Green's Function

The Green's function for the semi-infinite crystal with a free surface can be formally written as

$$\underline{G} \equiv \underline{L}^{-1}$$

or

$$G_{\alpha\beta}(l, l'; \omega^2) = L^{-1}_{\alpha\beta}(l, l', \omega^2). \tag{13}$$

The virtue of using the Montroll–Potts model is that the Green's function, even for the case of the crystal with a surface, is of a rather simple form. It has been shown previously[8] that

$$G_{\alpha\beta}(l, l'; \omega^2) = \delta_{\alpha\beta} G(l, l'; \omega^2), \tag{14a}$$

and

$$G(l, l'; \omega^2) = G^0(l_1 - l_1', l_2 - l_2', l_3 - l_3'; \omega^2) + G^0(l_1 - l_1', l_2 - l_2', l_3 + l_3' - 1; \omega^2). \tag{14b}$$

Here we have introduced the Green's function for the infinite crystal $G^0(l; \omega^2)$, which for the Montroll–Potts model can be written as

$$G^0(l; \omega^2) = \frac{1}{\pi^3}\iiint_0^\pi \frac{\cos l_1\varphi_1 \cos l_2\varphi_2 \cos l_3\varphi_3\, d\varphi_1\, d\varphi_2\, d\varphi_3}{M\omega^2 - 2\gamma(3 - \cos\varphi_1 - \cos\varphi_2 - \cos\varphi_3) + i\epsilon}. \tag{15}$$

In this expression, ϵ is a positive infinitesimal and the integration is over the entire Brillouin zone. For general ω^2 and l, the value of this Green's function must be found by numerical methods.[9,10] However, the asymptotic behavior for large values of $|l|$ and for large and small values of ω^2 has been studied elsewhere,[5,9] and it is this behavior that will be exploited in obtaining the analytic results in Secs. III and IV.

The reason for introducing the Green's function is that for any arbitrary additive function of the normal-mode frequencies (such as the free energy), the information needed to find the change in the additive function due to a perturbation is contained in the determinant[6]

$$\Delta(\omega^2) \equiv |\underline{I} - \underline{G}\underline{D}|, \tag{16}$$

where $\underline{I}$ is the unit matrix. For the case that the perturbation is a single adsorbed atom at site a or site b, using Eq. (12) with Eq. (16), we have

$$\Delta_a(\omega^2) = \Delta_b(\omega^2) = 1 - \frac{\gamma' \omega^2}{\omega^2 - \omega_0^2} G(000, 000; \omega^2). \tag{17}$$

For the case of two adsorbed atoms located at 000 and $m_1 m_2 0$, we have

$$\Delta_{ab}(\omega^2) = \begin{vmatrix} \Delta_a(\omega^2) & \chi(\omega^2) \\ \chi(\omega^2) & \Delta_a(\omega^2) \end{vmatrix}, \tag{18}$$

where

$$\chi(\omega^2) = \frac{-\gamma' \omega^2}{\omega^2 - \omega_0^2} G(000, m_1 m_2 0; \omega^2). \tag{19}$$

To obtain the interaction free energy of the adatom pair, we must subtract the free energy of infinitely separated adatoms from the free energy when they are separated by the distance $a_0|l|$. For reasons that will soon become apparent, this can be done by forming the ratio of the respective Δ's. Therefore, we define

$$\Delta(\omega^2) \equiv \frac{\Delta_{ab}(\omega^2)}{\Delta_a(\omega^2)\,\Delta_b(\omega^2)} = 1 - \frac{(\gamma'\omega^2)^2 G^2(000, m_1 m_2 0; \omega^2)}{[\omega^2 - \omega_0^2 - \gamma'\omega^2 G(000, 000; \omega^2)]^2}. \tag{20}$$

C. Interaction Free Energy

The general formalism for calculating the change in additive functions of the normal-mode frequencies due to the introduction of defects into a perfect crystal has been fully developed elsewhere.[5] The method requires knowledge of the perfect-crystal Green's function and the perturbation matrix due to the defect. For our problem, the same approach can be used if we replace everywhere in the formalism the perfect-crystal Green's function by the semi-infinite crystal Green's function and the defect perturbation by the perturbation due to the adatom pair.

The interaction free energy as a function of temperature T can be written as

$$\Delta F(T)=\Delta E_0-k_BT\sum_{n=1}^{\infty}\frac{\Delta I_n(T)}{n}, \tag{21}$$

with

$$\Delta E_0=\frac{-3\hbar\omega_L}{2\pi}\int_0^{\infty}f\,\Omega(f)\,df \tag{22}$$

and

$$\Delta I_n(T)=\frac{3}{\pi}\int_0^{\infty}\Omega(f)\sin(\alpha_n f)\,df\,. \tag{23}$$

Here, the factor 3 arises from the fact that the phonon branch is threefold degenerate. In writing these equations, we have used the notation

$$\omega_L^2=12\gamma/M, \tag{24}$$

$$f=\omega/\omega_L, \tag{25}$$

$$\alpha_n=n\hbar\omega_L/k_BT, \tag{26}$$

and the function $\Omega(f)$ is

$$\Omega(f)=\frac{d}{df}\ln\Delta(-\omega_L^2f^2). \tag{27}$$

It is the fact that the function $\Delta(\omega^2)$ occurs in a logarithm that allows us to calculate the difference in two free-energy expressions by forming a ratio as we did in Eq. (20).

At low temperatures when α_n is very large, the change in the free energy can be written as[5]

$$\Delta F(T)=\Delta E_0-\frac{3k_BT}{\pi}\left[\frac{\pi^2}{6}\left(\frac{k_BT}{\hbar\omega_L}\right)\Omega(0)-\frac{\pi^4}{90}\left(\frac{k_BT}{\hbar\omega_L}\right)^3\times\Omega^{(ii)}(0)+\frac{\pi^6}{945}\left(\frac{k_BT}{\hbar\omega_L}\right)^5\Omega^{(iv)}(0)-\cdots\right], \tag{28}$$

where $\Omega^{(ii)}(0)$ is the second derivative of $\Omega(f)$ evaluated at zero frequency. In the high-temperature limit, a different form for the free energy is particularly useful[5]:

$$\Delta F(T)=3k_BT\sum_{n=1}^{\infty}\ln\Delta(-a_n^2T^2), \tag{29}$$

where

$$a_n=2\pi nk_B/\hbar\,. \tag{30}$$

In the next section, we present the results of numerical calculations of the zero-point energy of interaction ΔE_0 for adatoms that are fairly close together on the surface. In addition, an expression for ΔE_0 valid in the limit of large separation distance is obtained in closed form. In Sec. IV, the low- and high-temperature expansions in Eqs. (28)–(30) are considered separately and analytic results are obtained for the change in the free energy in these temperature regions.

III. ZERO-POINT ENERGY OF INTERACTION

The interaction free energy at 0 °K is given by ΔE_0 in Eq. (22). Upon integrating by parts, we obtain

$$\Delta E_0=-\frac{3\hbar\omega_L}{2\pi}\left(f\ln\Delta(-\omega_L^2f^2)\Big|_0^{\infty}-\int_0^{\infty}\ln\Delta(-\omega_L^2f^2)\,df\right). \tag{31}$$

As will become apparent in Sec. IV, the first term vanishes at both limits. Thus we have

$$\Delta E_0=\frac{3\hbar\omega_L}{2\pi}\int_0^{\infty}\ln\Delta(-\omega_L^2f^2)\,df, \tag{32}$$

where, from Eq. (20), we have

$$\Delta(-\omega_L^2f^2)=1-\frac{(\gamma'f^2)^2G^2(000,m_1m_20;-\omega_L^2f^2)}{\{f_0^2+f^2[1-\gamma'G(000,000,-\omega_L^2f^2)]\}^2}, \tag{33}$$

and where we have introduced

$$f_0^2=\frac{\omega_0^2}{\omega_L^2}=\frac{\gamma'M}{12\gamma M'}\,. \tag{34}$$

A. Analytic Results

An analytic expression for the zero-point energy can be obtained in the limit of weak binding and large separation distance. In the limit as

$$|\gamma'G(000,000;-\omega_L^2f^2)|\ll 1, \tag{35}$$

Eq. (33) can be written

$$\Delta(-\omega_L^2f^2)=1-\frac{(\gamma'f^2)^2G^2(000,m_1m_20;-\omega_L^2f^2)}{(f_0^2+f^2)^2}\,. \tag{36}$$

The magnitude of the Green's function in Eq. (35) is a maximum when $f=0$ and is very nearly equal to $-(3\gamma)^{-1}$. Thus, condition (35) translates to

$$\gamma'/\gamma\ll 3. \tag{37}$$

In the region of large separation distance where $m=(m_1^2+m_2^2)^{1/2}\gg 1$, an expansion for the perfect-crystal Green's function has been given previously.[5] The leading term is

$$G^0(m_1m_20;-\omega_L^2f^2)=\frac{-\exp(-12^{1/2}mf)}{4\pi\gamma m}\,. \tag{38}$$

From Eq. (14b), the leading term for the surface Green's function is simply

$$G(000,m_1m_20;-\omega_L^2f^2)=\frac{-\exp(-12^{1/2}mf)}{2\pi\gamma m}\,. \tag{39}$$

By substituting Eq. (39) into Eq. (36), we obtain

$$\Delta(-\omega_L^2f^2)=1-\frac{1}{4\pi^2}\left(\frac{\gamma'}{\gamma}\right)^2\frac{f^4}{(f_0^2+f^2)^2}$$

$$\times \frac{\exp(-48^{1/2}mf)}{m^2} . \qquad (40)$$

The second term in this expression is small compared to the first in the limits we are considering. Therefore the logarithm in Eq. (32) can be expanded, and we obtain

$$\Delta E_0 = -\frac{3\hbar\omega_L}{8\pi^3 m^2}\left(\frac{\gamma'}{\gamma}\right)^2 \int_0^\infty \frac{df f^4 \exp(-48^{1/2}mf)}{(f_0^2+f^2)^2} . \qquad (41)$$

If we confine our attention to the region where m is large such that

$$48^{1/2} m f_0 \gg 1, \qquad (42)$$

then the important contribution to the integral in Eq. (41) comes from values of f less than f_0. Hence, the denominator of the integral can be expanded about f_0 and the lowest-order term in the zero-point energy expression becomes

$$\Delta E_0 = -\frac{3\hbar\omega_L}{8\pi^3 m^2 f_0^4}\left(\frac{\gamma'}{\gamma}\right)^2 \int_0^\infty f^4 \exp(-48^{1/2}mf)\, df . \qquad (43)$$

Evaluating the integral and substituting for f_0 gives, finally,

$$\Delta E_0 = -\frac{(27)^{1/2}}{64\pi^3}\left(\frac{M'}{M}\right)^2 \frac{1}{m^7}\hbar\omega_L . \qquad (44)$$

The condition in Eq. (42) can be rewritten as

$$m \gg \tfrac{1}{2}(M'\gamma/M\gamma')^{1/2} . \qquad (45)$$

Thus, in the weak defect limit and for large separation distances [Eqs. (37) and (45), respectively], the zero-point energy (a) is independent of γ', (b) is proportional to the square of the relative mass of the defect, and (c) varies inversely as the seventh power of the separation distance. This behavior is similar to that found for the zero-point interaction energy of a pair of isotopic impurities in the bulk of the crystal.[5] This similarity is not surprising, since the Green's function for the crystal with a surface is the sum (not the difference) of two infinite crystal Green's functions.

B. Numerical Results

In practice, the result in Eq. (44) is only good if the two adatoms are separated by more than about eight lattice sites (i.e., $m \geq 8$). For separation distances smaller than this, numerical methods must be used in evaluating Eq. (32). The most difficult step in the numerical calculation is obtaining good values for the Green's function in Eq. (15). This problem is simplified somewhat by the fact that only negative values of ω^2 are needed for the integration in Eq. (32). These frequencies fall outside of the phonon bands and, consequently, the Green's function is totally real.

Values of the Green's function $G^0(l; -\omega_L^2 f^2)$ have been tabulated by Maradudin *et al.*[9] in the energy region of interest and for values of $|l|^2 < 15$. With the use of recursion relations, all of the Green's functions for the bulk can be obtained for which $l_1 + l_2 + l_3 \leq 5$. The accuracy of the tabulated functions is better than one part in 10^4. The recursion relations, however, are unstable to small errors, and the Green's functions calculated by means of the recursion relations decrease in accuracy as the magnitudes of $|l|$ and f^2 become larger. Fortunately this is the region where the magnitude of the Green's function is very small. In the numerical calculation, the integration was truncated at a value $f^2 = f_T^2$. The value of f_T^2 was chosen large enough such that the contribution to the integral from values of f^2 larger than f_T^2 was negligible and was chosen small enough such that the Green's function determined by the recursion relations was still accurate. The value of f_T^2 varied depending upon the separation distance of the adatoms. We believe the numerical results presented are accurate to within 1%.

In Fig. 2 we show the dependence of the zero-point energy upon separation distance of the adatom pairs for two values of the coupling constant γ and for separation distances less than $4a_0$. Al-

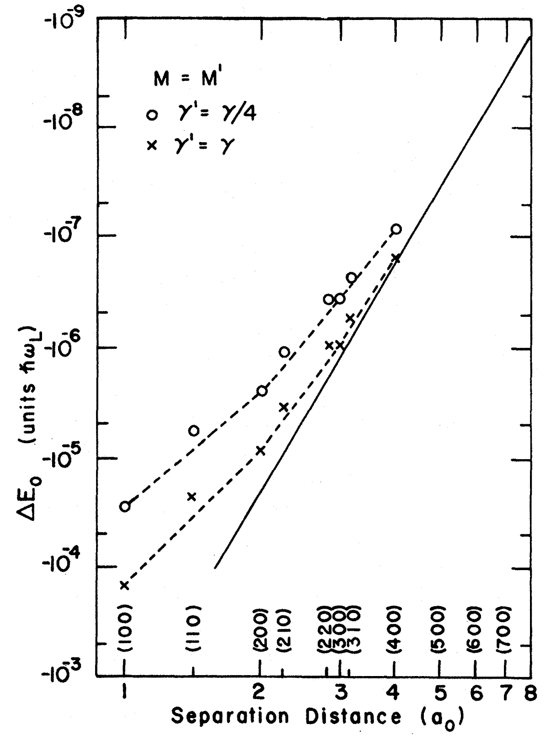

FIG. 2. Zero-point energy as a function of separation distance for two values of the force-constant ratio γ'/γ. The solid line is the asymptotic limit for large distances, and the points are results of the numeric calculations. The adatom mass is set equal to the crystal atom mass in this figure. Note that ΔE_0 is negative.

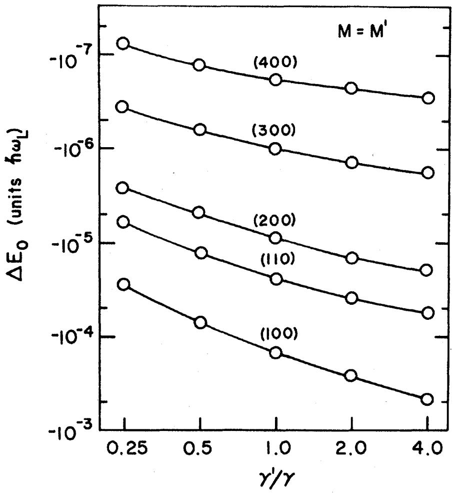

FIG. 3. Zero-point energy as a function of the force-constant ratio γ'/γ for various near-neighbor adatom configurations. These points are the result of the numeric calculation with the adatom mass set equal to the crystal atom mass.

so shown is the asymptotic limit of Eq. (44). The fact that the numerically calculated points do not fall on a smooth curve indicates that the correction terms for smaller separation distances are anisotropic. These correction terms also depend upon the relative value of γ' and γ. Since the zero-point energy always decreases as the adatoms become closer together, the force between adatoms at 0 °K due to the indirect interaction through the phonon field is always attractive.

In Fig. 3 we show the family of curves for various separation distances of the zero-point energy as a function of the coupling constant γ'. As the separation distance becomes larger, the dependence on γ' becomes weaker. In the asymptotic limit, ΔE_0 is independent of γ'.

In Fig. 4 we present the dependence of the zero-point energy on the mass of the adatoms M' for various separation distances. As the separation distance becomes larger, the dependence changes from nearly linear to quadratic in M'/M.

In every case, the magnitude of ΔE_0 is given in units of $\hbar\omega_L$, the maximum phonon energy for the model. Even for the most favorable case, the zero-point energy of interaction is very small. However, the results of Einstein and Schrieffer[2] indicate that in some cases, depending upon the position of the Fermi surface in the band, the indirect interaction of adatoms through the electronic states may vanish. Thus, in such cases the effect we have calculated may be the most important indirect contribution to the interaction energy.

IV. TEMPERATURE DEPENDENCE OF FREE ENERGY

In order to find the leading temperature-dependent term in both the high- and low-temperature limits, we need the Green's function $G^0(m_1m_2m_3; -\omega_L^2 f^2)$ in the limit as $f \to 0$ and $f \to \infty$. It can be easily shown from previous results[9] that

$$\lim_{f\to 0} G^0(m_1m_2m_3; -\omega_L^2 f^2) = \gamma^{-1}[A_0(m_1m_2m_3) + A_1(m_1m_2m_3)\,|f\,| + \cdots] \quad (46)$$

and

$$\lim_{f\to\infty} G^0(m_1m_2m_3; -\omega_L^2 f^2) = -\frac{(m_1+m_2+m_3)!}{\gamma m_1!m_2!m_3!} \times \left(\frac{1}{12f^2}\right)^{m_1+m_2+m_3+1}. \quad (47)$$

In Eq. (46), $A_0(m_1m_2m_3)$ and $A_1(m_1m_2m_3)$ are numerical constants whose values depend upon the separation distance of the bulk atoms. It is due to the fact that the Green's function has a finite value at $f = 0$ and decays rapidly for large values of f that the first term in Eq. (31) vanishes.

A. Low-Temperature Limit

To evaluate the lowest-order temperature-dependent term in Eq. (28) we must determine up to the fifth derivative of the natural logarithm of Eq. (33). In the region where $f \ll f_0$, we may write this logarithm as

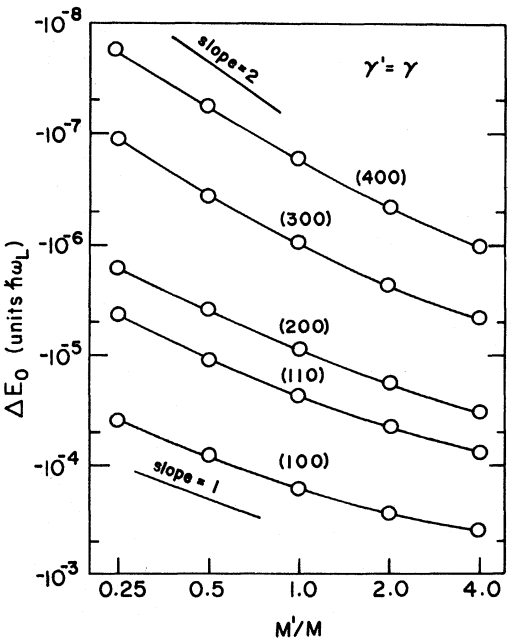

FIG. 4. Numerically calculated zero-point energy as a function of the mass ratio M'/M for near-neighbor adatom configurations. The dependence varies from nearly linear for the (100) configuration to quadratic for large separation distances. The force-constant ratio $\gamma'/\gamma = 1$.

$$\ln\Delta(-\omega_L^2 f^2) = -\left(\frac{\gamma' f^2}{\gamma f_0^2}\right)^2 [B_0^2(m_1 m_2) + 2|f| B_0(m_1 m_2) B_1(m_1 m_2) + \cdots], \tag{48}$$

where we have written the surface Green's function as

$$G(000, m_1 m_2 0; -\omega_L^2 f^2) = \gamma^{-1}[B_0(m_1 m_2) + B_1(m_1 m_2)\,|f| + \cdots], \tag{49}$$

and where

$$B_0(m_1 m_2) = A_0(m_1 m_2 0) + A_0(m_1 m_2 1) \tag{50}$$

and

$$B_1(m_1 m_2) = A_1(m_1 m_2 0) + A_1(m_1 m_2 1). \tag{51}$$

The derivatives of Eq. (48) are easily found to be

$$\Omega(0) = 0, \tag{52}$$

$$\Omega^{(ii)}(0) = 0, \tag{53}$$

$$\Omega^{(iv)}(0) = -240(\gamma'/\gamma f_0^2)^2 B_0(m_1 m_2) B_1(m_1 m_2). \tag{54}$$

Hence, the free energy in the low-temperature region becomes

$$\Delta F(T) = \Delta E_0 + \frac{16\pi^5}{21}\left(\frac{\gamma'}{\gamma}\right)^2 \frac{\omega_0}{\omega_L} \times B_0(m_1 m_2) B_1(m_1 m_2) \frac{(k_B T)^6}{(\hbar\omega_0)^5}. \tag{55}$$

For the bulk Green's function,[9]

$$A_0(m_1 m_2 m_3) < 0 \tag{56}$$

and

$$A_1(m_1 m_2 m_3) > 0 \tag{57}$$

for all values of m_1, m_2, and m_3. Thus,

$$B_0(m_1 m_2) < 0 \tag{58}$$

and

$$B_1(m_1 m_2) > 0. \tag{59}$$

The leading temperature-dependent term in the low-temperature region varies at T^6 and is negative.

B. High-Temperature Limit

For large values of the temperature, the argument of Δ in Eq. (29) becomes big and the large f expansion of the surface Green's function is needed. By making the identification,

$$\omega_L^2 f^2 \to a_n^2 T^2 \tag{60}$$

and by using Eqs. (14b) and (47) we obtain for the leading term

$$G(000, m_1 m_2 0; -a_n^2 T^2) = -\frac{(m_1+m_2)!}{\gamma m_1!\, m_2!} \times \left(\frac{\hbar^2\omega_L^2}{48\pi^2 k_B^2 T^2 n^2}\right)^{m_1+m_2+1}. \tag{61}$$

Using this Green's function, the logarithm of $\Delta(-a_n^2 T^2)$ can be easily found by using Eq. (33) and the identification (60). We obtain

$$\ln\Delta(-a_n^2 T^2) = -\left(\frac{\gamma'}{\gamma}\right)^2 \left(\frac{(m_1+m_2)!}{m_1!\, m_2!}\right)^2 \times \left(\frac{\hbar^2\omega_L^2}{48\pi^2 k_B^2 T^2 n^2}\right)^p, \tag{62}$$

where we have set

$$p = 2(m_1 + m_2 + 1). \tag{63}$$

Substituting Eq. (62) into Eq. (29) gives

$$\Delta F(T) = -3k_B T\left(\frac{\gamma'(m_1+m_2)!}{\gamma m_1!\, m_2!}\right)^2 \left(\frac{\hbar^2\omega_L^2}{4k_B^2 T^2}\right)^p \times \frac{1}{3^p(2\pi)^{2p}} \sum_{n=1}^{\infty}\left(\frac{1}{n}\right)^{2p}. \tag{64}$$

To evaluate this sum, we use the definition of the Bernoulli number

$$B_p = \frac{2(2p)!}{(2\pi)^{2p}} \sum_{n=1}^{\infty}\left(\frac{1}{n}\right)^{2p}. \tag{65}$$

Thus, we finally obtain for the interaction free energy in the high-temperature limit

$$\Delta F(T) = -\frac{3B_p}{2(2p)!\,3^p}\left(\frac{\gamma'(m_1+m_2)!}{\gamma m_1!\, m_2!}\right)^2 \times \left(\frac{\hbar\omega_L}{2k_B T}\right)^{2p} k_B T. \tag{66}$$

This result shows that the interaction free energy decays to zero very rapidly for values of the temperature $T > \hbar\omega_L/2k_B$. The speed of the decay is a function of the separation distance of the adatoms.

Upon combining this result with the low-temperature result in Eq. (55), we obtain a qualitative picture of the dependence of the interaction free energy upon temperature over the entire temperature range. The interaction free energy at $T = 0$ °K begins at a negative value equal to the zero-point energy and at first becomes more negative as T^6 for small temperatures and then increases to zero as T^{-2p+1} at higher temperatures. Thus, in the intermediate temperature range where $\hbar\omega_0 < k_B T < \frac{1}{2}\hbar\omega_L$, there is a minimum in the interaction free energy.

V. CONCLUSIONS

We have examined the contribution to the free energy from two adatoms on the (100) surface of a simple cubic monatomic crystal due to their indirect interaction through the perturbed crystal phonon field. We have found the following.

(1) The zero-point interaction energy ΔE_0 is

negative and decays to zero as the inverse seventh power of the separation distance for distances greater than about $8a_0$. At these large distances, ΔE_0 varies with the square of the adatom mass M', and is independent of the spring constant γ' binding the adatom to the surface.

(2) At smaller separation distances, the dependence of ΔE_0 on M' and γ' changes until for nearest-neighbor separation distance, ΔE_0 varies nearly linearly in both variables.

(3) The interaction free energy ΔF is anisotropic when the two adatoms are not too far apart. For large separations, however, ΔF depends only on the magnitude of the separation distance.

(4) At low temperatures, ΔF becomes more negative as the sixth power of the temperature. At higher temperatures, ΔF decays to zero at least as fast as the inverse seventh power of temperature. The exponent of T at higher temperatures depends upon the separation distances.

(5) The gradient of the zero-point energy with respect to separation distance is always positive, showing that the adatoms are always attracted toward each other due to this interaction.

(6) The interaction energy we have calculated is small. For example, $-\Delta E_0$ is less than $10^{-4}\hbar\omega_L$. However, the contribution to ΔF from perturbed electronic levels can sometimes vanish,[2] leaving the effect we have reported the largest indirect interaction contributing to the free energy.

(7) Schick and Campbell[11] calculate the phonon contribution to the free energy of helium atoms adsorbed on argon-plated copper. We can apply the results of our paper to this system (using He^4) if we make the following two assumptions: (i) the resonant frequency of the helium adatom, ω_0, is related to the Debye temperature of the adsorbed helium atoms, Θ_D^{He}, by

$$\hbar\omega_0 = k_B \Theta_D^{\text{He}},$$

where k_B is Boltzmann's constant, and (ii) the maximum frequency ω_L of the argon substrate is related to the Debye temperature of bulk argon by

$$\hbar\omega_L = k_B \Theta_D^{\text{Ar}}.$$

Using these assumptions, the ratio of the force constants is

$$\frac{\gamma'}{\gamma} = 12\,\frac{M'}{M}\left(\frac{\Theta_D^{\text{He}}}{\Theta_D^{\text{Ar}}}\right)^2.$$

The Debye temperature of adsorbed He^4 is found to vary from 15 to 30 °K depending upon temperature and concentration.[12] For low concentration and for low temperature, the Debye temperature approaches the value $\Theta_D^{\text{He}} = 15$ °K. The Debye temperature of solid argon also varies with temperature, but it approaches the value $\Theta_D^{\text{Ar}} = 93$ °K at low temperatures.[13] Using the fact that the mass ratio $M'/M = 0.10$, we find that the force-constant ratio $\gamma'/\gamma = 0.03$.

From Figs. 3 and 4 by double extrapolation we find that the phonon contribution to the interaction free energy when the adatoms are nearest neighbors (100) is about $-10^{-6}\hbar\omega_L$. The actual value obtained by performing the numerical calculation of Sec. III B is $\Delta E_0 = -3.9\times10^{-7}\hbar\omega_L \approx -2.6\times10^{-5} k_B$ °K.

Schick and Campbell have calculated the phonon contribution to the zero-point energy of interaction by a method much different from that presented in this paper. They describe the adsorbed atoms with Bloch functions having quasimomentum K parallel to the surface. They calculate the scattering matrix element which takes the adatom from state K to K' accompanied by the emission of a phonon. The effect of the interaction between the adatoms is, in second-order perturbation theory, to introduce a phonon-mediated retarded interaction. The complexity of the calculation they perform requires that a large number of assumptions be made.

The two conclusions that Schick and Campbell make are in sharp disagreement with the results of this paper. First, they conclude that the zero-point interaction energy decays to zero for large separation distances between the adsorbed atoms as const$\times\rho^{-3/2}\cos(\sigma/\rho - \frac{1}{4}\pi)$, where σ is the characteristic length in the Lennard-Jones potential, and ρ is the distance between the adatoms. This is in contrast with our result that the interaction energy decays monotonically as the separation distance to the inverse seventh power. Schick and Campbell's result is undoubtedly due to their truncation of the Fourier transform of the interaction potential. It is well known from the theory of Fourier transforms[14] that the asymptotic behavior of a Fourier integral is determined by the singularities, including discontinuities, of the Fourier coefficient. In the present case, the truncation of the Fourier coefficients yields the oscillatory behavior of the interaction energy at large separation distances noted above, and can give rise to a slower dependence on adatom separation than would be obtained from using the complete Fourier coefficient.

Second, Schick and Campbell conclude that the zero-point energy of interaction is of the order of $\Delta E_0 = -1 k_B$ °K. This disagrees with our result by more than four orders of magnitude. Although their result is based on a large number of assumptions, they state that the order of magnitude of their result should be independent of the assumptions. At present, it is unclear to us as to what causes the large discrepancy between their result and ours. We find their result surprisingly large, however, in light of the comments made by Grimley.[3]

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