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Substrate-Mediated Interaction between Adsorbed Atoms*

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An effective interaction between atoms adsorbed on a substrate is calculated. The interaction arises from the exchange of phonons in the substrate and makes a density-dependent contribution to the ground-state energy per particle of the adsorbed system. Our results are applied to the submonolayer helium film adsorbed on argon-plated copper studied by Stewart and Dash. It is shown that, for this system the interaction is attractive and contributes to the ground-state energy per particle an amount of the order of $-1\,^\circ\mathrm{K}$, which is a significant fraction of the observed binding energy. The role of the effective interaction in bringing about the enhancement of the binding energy and the formation of dense clusters observed by Stewart and Dash is discussed.

INTRODUCTION

We shall be concerned in this paper with two interesting observations made by Stewart and Dash[1] concerning the properties of submonolayer helium films adsorbed on argon-plated copper. The first observation is that the helium is condensed into two-dimensional clusters of high density. This behavior is contrary to one's expectations that the submonolayer helium remain a quantum liquid even at the absolute zero of temperature for the same reason that the bulk system remains in the liquid state; i.e., the large zero-point energy of the helium.[2] Further, as discussed in the paper of Stewart and Dash, there is no experimental evidence that the observed solidification can be attributed to localization of the adsorbed atoms at preferential sites caused by the underlying substrate potential.[3]

The second observation of Steward and Dash that concerns us is that the lateral binding energy per particle of the monolayer[4] solid, denoted q by them, is at least $15.3k\,^\circ\mathrm{K}$, where k is Boltzmann's constant. This figure seems rather high in light of the binding energies of the bulk solid and liquid, 5.9 and $7.1k\,^\circ\mathrm{K}$, respectively.

It is the purpose of this paper to point out a mechanism which is relevant to the above observations: the effective interaction between helium atoms due to the exchange of phonons in the substrate. It will be shown that the interaction is attractive and contributes approximately 1 °K to the ground-state energy per particle and thus accounts for part of the enhanced binding noted above. In addition, the contribution of this interaction is density dependent and lowers the energy of the solid more than that of the liquid and therefore provides a possible mechanism to bring about the observed solidification.

It should be emphasized that there exist no calculations of the ground-state energy of the monolayer system of helium adsorbed on argon-plated copper, so that a quantitative discussion of the role of the effective interaction is not yet possible. It will be sufficient in this paper to estimate the contribution of the effective interaction to the ground state of the adsorbed monolayer and show it to be of sufficient magnitude that its effects must be taken into account in a complete description of the adsorbed monolayer helium system.

CALCULATIONS

The problem is essentially one of calculating the vertex for the scattering of an adsorbed atom accompanied by the emission of a phonon in the substrate and closely resembles the analogous problem of calculating the electron-phonon vertex.[5] We consider an atom adsorbed on a semi-infinite substrate with a surface in the x-y plane and extending in the negative z direction. Cylindrical coordinates are employed, and the position of an adsorbed atom is specified by the vector $\vec{\rho}$ in the x-y plane and the vertical coordinate z. Similarly, the position of the ith substrate atom is specified by $\vec{\rho}\,'$ and z'. Let the potential between the adsorbed and substrate atoms be denoted by $V((\vec{\rho}-\vec{\rho}\,')^2+(z-z')^2)$ and the total potential between the adsorbed atom and substrate by $\mathcal{V}(\rho, z)$, so that

$$\mathcal{V}(\vec{\rho}, z)=\textstyle\sum_i\left[V(\vec{\rho}-\vec{\rho}_i')^2+(z-z_i')^2\right] . \tag{1}$$

The presence of a phonon in the substrate perturbs the potential $\mathcal{V}(\vec{\rho}, z)$ by an amount $\delta\mathcal{V}(\vec{\rho}, z)$ which can be taken to be

$$\delta\mathcal{V}(\vec{\rho}, z)=\textstyle\sum_i \vec{\eta}_i \cdot \partial\mathcal{V}(\rho, z)/\partial\vec{\eta}_i ,$$

where $\vec{\eta}_i$ is the operator which gives the displacement of the ith substrate atom. As usual, this operator can be expanded in terms of the operators which create and annihilate the normal modes of the substrate including both bulk and surface phonons. We shall restrict our attention to those modes which propagate parallel to the surface of the substrate and which, therefore, may be characterized by a wave vector $\vec{q}$ in the x-y plane and a polarization index μ. In addition, the z dependence of the bulk phonons is characterized by a wave vector l. The spatial dependences of the normal modes of the substrate are then of the form

$$\exp(i\vec{q}\cdot\vec{\rho}_i')u_{q,l,\mu}(z_i') \ .$$

The Bloch functions of the adsorbed atoms with quasimomentum $\vec{K}$ in the x-y plane will be denoted $\Psi_{\vec{K}}(\vec{\rho},z)$. Then, the matrix element $g_{K,K',q,l,\mu}$ for the scattering of an adsorbed atom from the state $\vec{K}$ to $\vec{K}'$ accompanied by the emission of a phonon characterized by the quantum numbers q, l, μ is given by

$$g_{K,K',q,l,\mu}=\sum_i\int\Psi_K^*\vec{\epsilon}_\mu\cdot\frac{\partial\mathcal{V}}{\partial\vec{\eta}_i}e^{i\vec{q}\cdot\vec{\rho}_i'}u_{q,l,\mu}\times(z_i')\Psi_{K'}\,d^2\rho\,dz, \tag{2}$$

where $\vec{\epsilon}_\mu$ is a set of three polarization vectors. It has been assumed that the substrate is initially in its ground state so that no phonons are present before the scattering event. The sum over the coordinates ρ_i' may be carried out and yields the expected result that the vector $\vec{q}$ must be equal to the difference of the quasimomenta $\vec{K}$-$\vec{K}'$ to within a reciprocal-lattice vector of the substrate.

We now employ a series of approximations in order to reduce the general form given above. It will be seen at the conclusion of the calculation that the factors governing the order of magnitude of the effective interaction we seek are completely determined by the nature of the process and that the effects of the approximations can only be to change the results by numerical factors.

The structure of the substrate will subsequently be ignored and will be approximated by a continuum of particle density ρ_s. The total potential between the adsorbed atom and substrate, $\mathcal{V}(\rho,z)$ of Eq. (1), is then only a function of the coordinate z and will be denoted $\mathcal{V}(z)$. Because of the assumed homogeneity of the substrate, the wave function Ψ_K may be written

$$\Psi_K(\rho,z)=A^{-1/2}e^{i\vec{K}\cdot\vec{\rho}}\,\Phi(z)\ , \tag{3}$$

where A is the area of the substrate and $\Phi(z)$ will be taken to be the normalized ground-state solution of the one-dimensional Schrödinger equation containing the potential $\mathcal{V}(z)$. Of the normal modes of the substrate only the bulk phonons will be retained. The surface modes are ignored because it can be shown that they make no contribution to the ground-state energy per particle of the adsorbed system. The treatment of the bulk phonons is considerably complicated by the boundary condition that there be vanishing stress at the surface of the substrate which couples the longitudinal and transverse components. Because this boundary condition has little effect on the magnitude of the matrix element of interest, the bulk phonons will be approximated by independent longitudinal and transverse waves. The spatial part of each wave is taken to be of the form

$$(2/AL)^{1/2}e^{i\vec{q}\cdot\vec{\rho}}\cos lz'\ , \tag{4}$$

where $l=n\pi/L$, n is a positive integer, and L is the thickness of the substrate, a parameter which will be taken to be large and which disappears from all final results. The z-dependent part of the above has been chosen to be of the form appropriate to a one-dimensional system with free surfaces at z equal to zero and L merely for convenience. Periodic boundary conditions are assumed in the x-y plane. The time dependence of the wave is harmonic with frequency

$$\omega(q,l)=c(q^2+l^2)^{1/2}\ ,$$

where c is the appropriate speed of sound.

With the above approximations, the matrix element of Eq. (2) can be written

$$g_{K,K',q,l,\mu}=-i\rho_s B_{q,l,\mu}\int d^2\rho'\,dz'\cos lz'\,e^{i\vec{q}\cdot\vec{\rho}'}\times\int\Psi_K^*\vec{\epsilon}_\mu\cdot\frac{\partial V}{\partial\vec{\eta}}\Psi_K\,d^2\rho\,dz\ , \tag{5}$$

where

$$B_{q,l,\mu}=[\hbar/m\rho_s AL\omega_\mu(q,l)]^{1/2}\ , \tag{6}$$

and m is the mass of a substrate atom. The integrand of the second integral above is simplified by making use of the rigid-ion approximation[5] in which

$$\frac{\partial V}{\partial\vec{\eta}}=-\vec{\nabla}V[(\vec{\rho}-\vec{\rho}')^2+(z-z')^2]\ ,$$

the gradient acting on the unprimed variables. Introducing the change of variables from $\vec{\rho}$, $\vec{\rho}'$ to $\vec{\rho}$, $\vec{y}=\vec{\rho}-\vec{\rho}'$ simplifies the operation of the gradient. Lastly the expression of Eq. (3) for the wave function Ψ_K is substituted into Eq. (5) and the integration over $\vec{\rho}$ is carried out yielding for the matrix element the expression

$$g_{K,K'q,l,\mu}=g_{q,l,\mu}\,\delta_{\vec{K}-\vec{K}',\vec{q}}\ ,$$

where

$$g_{q,l,u}=-B_{q,l,u}\int dz\,|\Phi(z)|^2[\vec{\epsilon}_\mu\cdot\vec{q}\,U(z,q,l)+i\vec{\epsilon}_\mu\cdot\hat{z}\,\frac{\partial}{\partial z}\,U(z,q,l)]\ , \tag{7}$$

$\hat{z}$ is a unit vector in the z direction, and

$$U(z,q,l,)\equiv\rho_s\int e^{-i\vec{q}\cdot\vec{y}}\;V[y^2+(z-z')^2]\cos lz'\,d^2y\,dz'\quad,$$

which is essentially the Fourier transform of the interaction V.

The effect of the interaction between the adsorbed atom and phonon is, in second order of perturbation theory, to introduce a phonon-mediated retarded interaction $W(\rho,t)$ between the two adsorbed atoms on the surface separated by a distance ρ. The Fourier transform of this interaction $\mathcal{W}(q,\omega)$ in two spatial dimensions and time is given by

$$\mathcal{W}(q,\omega)=A\sum\nolimits_{l,\mu}\mathfrak{D}_\mu(q,l,\omega)\left|g_{q,l,\mu}\right|^2\,, \tag{8}$$

where $\mathfrak{D}_\mu(q,l,\omega)$ is the phonon propagator

$$\mathfrak{D}_\mu(q,l,\omega)=2\hbar\omega_\mu(q,l)/\{(\hbar\omega)^2-[\hbar\omega_\mu(q,l)]^2\}\ . \tag{9}$$

We shall only be concerned with those situations in which the frequencies ω of the adsorbed atoms are negligible compared to the frequencies of the phonon modes $\omega_\mu(q,l)$. Therefore, it is sufficient to investigate the zero-frequency (static) component of the interaction $\mathcal{W}(q,0)\equiv\mathcal{W}(q)$. Substituting Eq. (9) into Eq. (8) and making use of Eqs. (6) and (7) yields a manifestly attractive interaction,

$$\mathcal{W}(q)=-2(\rho_s mL)^{-1}\sum\nolimits_l(q^2+l^2)^{-1}\{[qC_L^{-1}I_L(q,l)]^2+[C_T^{-1}I_T(q,l)]^2\}\quad, \tag{10}$$

where

$$I_L(q,l)\equiv\int_0^\infty dz\,|\Phi(z)|^2\,U(z,q,l)$$

and

$$I_T(q,l)\equiv\int_0^\infty dz\,|\Phi(z)|^2\,\frac{\partial U(z,q,l)}{\partial z}\quad.$$

The value of this expression in the limit of vanishing q is of interest because the contribution of the phonon-induced interaction to the ground-state energy per adsorbed atom is simply $\frac{1}{2}s\mathcal{W}(0)$ in the Hartree approximation, where s is the areal density of the adsorbed system. In the limit of a semi-infinite substrate, the sum over the index l in Eq. (10) can be replaced by an integral. By carrying out the integral it is easy to show that the first term in Eq. (10) vanishes linearly with q as q goes to zero. The contribution of the second term remains finite in this limit. It is shown in the first Appendix that $\mathcal{W}(0)$ can be written in the particularly simple form

$$\mathcal{W}(0)=-(m\rho_s c_T^2)^{-1}\int_{-\infty}^0 dz'\left[\int_0^\infty dz\,|\Phi(z)|^2\,U(z-z')\right]^2, \tag{11}$$

where

$$U(z-z')\,dz'=dz'\,\rho_s\int V[y^2+(z-z')^2]\,d^2y\ , \tag{12}$$

and is recognized as the potential between an adsorbed atom and a plane of the substrate of thickness dz' located a distance $-z'$ from the surface. The total potential $\mathcal{V}(z)$ is simply related to the above quantity by

$$\mathcal{V}(z)=\int_{-\infty}^0 dz'\,U(z-z')\ . \tag{13}$$

It should be noted that the result of Eq. (11), although derived quantum mechanically, reflects this derivation only in the presence of the wave function $\Phi(z)$. The classical limit of this expression is obtained by localizing the adsorbed atom at z_0, the minimum of the potential $\mathcal{V}(z)$. Upon using Eq. (13), the expression determining z_0 can be written $\mathcal{J}(z_0)=0$, and the classical limit of Eq. (11) is

$$\mathcal{W}^c(0)=-(m\rho_s c_T^2)\int_{-\infty}^0 dz'\,U^2(z_0-z')\ .$$

APPLICATION TO ADSORBED HELIUM FILMS ON ARGON-PLATED COPPER

We now wish to apply the above analysis to the system studied by Stewart and Dash[1]; that of helium adsorbed on an argon-plated copper substrate. That the approximation of a static interaction is justified for this system follows from the fact that the Debye temperature of the adsorbed helium is found[1] to vary from 15 to 30 °K, while the Debye temperatures of solid argon[6] and copper[7] are 94 and 345 °K, respectively.

For the interaction V, we take the helium-argon interaction which means, in effect, that the helium is considered to be adsorbed on a semi-infinite plane of argon. The copper is ignored. This seemingly drastic assumption will be justified *a posteriori* by showing that the largest contribution to $\mathcal{W}(0)$ comes from the first surface layer of atoms because of the short range of the van der Waals interaction. The specific form taken for the helium-argon interaction is a Lennard-Jones 6–12 potential

$$V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]\ ,$$

where

$$r=[y^2+(z-z')^2]^{1/2}\ . \tag{14}$$

The ground-state wave function $\Phi(z)$ of the helium atoms obtained from the Schrödinger equation containing the total potential $\mathcal{V}(z)$ extends over a distance of the order of σ. It is appropriate, therefore, to define a dimensionless wave function $\Phi(z)$ by the relation

$$\Phi(z)=\sigma^{-1/2}\,\phi(z)\ . \tag{15}$$

With the use of Eqs. (11), (12), (14), and (15), the effective interaction at zero wave number $\mathcal{W}(0)$ becomes

$$\mathcal{W}(0) = -(4\pi\epsilon)^2(\rho_s\sigma^3)(mc_T^2)^{-1}\sigma^2 b \,, \tag{16}$$

where b is the dimensionless quantity

$$b = \int_{-\infty}^{0} \sigma^{-1} dz' \left\{ \int_0^\infty \sigma^{-1} dz \,|\phi(z)|^2 [0.2(\sigma/z - z')^{10} - 0.5(\sigma/z - z')^4] \right\}^2 . \tag{17}$$

From Eq. (16) it is now easy to show that the relative contribution of the induced phonon interaction to the ground-state energy per particle is small. This follows from the fact that the zeroth-order effect of the adsorbed atom-substrate interaction is to bind the former to the latter with a binding energy of order ϵ. The effective interaction lowers the ground-state energy per particle by an amount of order $\epsilon(\epsilon/mc^2)$. The quantity in parentheses is usually small. It will be found to be about 0.02 for the helium on argon system. Higher powers of this quantity will occur in calculating the effect of multiple phonon exchange. Therefore, in first approximation, these processes can be ignored.

NUMERICAL EVALUATION

Some of the parameters which appear in Eq. (16) deserve comment. It should be recalled that the interaction between the helium and argon atoms was taken to be the Lennard-Jones potential given in Eq. (14). Upon treating the substrate as a continuum, one obtains for the total interaction between the helium atom and the substrate the result

$$\begin{aligned} \mathcal{V}(z) &= \rho_s \int V[y^2 + (z - z')^2]\, d^2y\, dz' \\ &= 4\pi\epsilon\rho_s\sigma^3[\tfrac{1}{45}(\sigma z^{-1})^9 - \tfrac{1}{6}(\sigma z^{-1})^3] \,. \end{aligned} \tag{18}$$

The mean density of solid argon at very low temperatures is[8] 1.77 g/cm^3 which yields a number density

$$\rho_s = 2.67 \times 10^{-2}\ \text{Å}^{-3} \,.$$

The Lennard-Jones parameters ϵ, σ appropriate to the helium-argon system are[9] $35k$ °K and 2.98 Å, respectively. With these parameters, the potential $\mathcal{V}(z)$ has a minimum equal to $-54k$ °K. This is a somewhat shallow minimum. Lai, Woo, and Wu[10] have calculated the potential between a helium atom and argon substrate with its (100) planes parallel to the surface. Averaging this potential over a unit cell in the x-y plane yields a potential $\mathcal{V}_0(z)$ with a minimum of $-70k$ °K.

In order to compensate for the error introduced by the continuum approximation, the potential $\mathcal{V}_0(z)$ is fitted with the functional form of Eq. (18) with ξ and σ taken to be adjustable parameters. The values of these parameters which give the best fit are found to be

$$\epsilon = 28.5k\ \text{°K}, \quad \sigma = 3.54\ \text{Å} \,.$$

The one-dimensional Schrödinger equation containing the potential $\mathcal{V}(z)$ with the parameters ρ_s, ϵ, and σ set off above was solved numerically and the ground-state wave function $\phi(z)$ was obtained. The value of the parameter b given by Eq. (17) was then calculated. As expected most of the contribution to b comes from atoms within a distance σ from the surface. Essentially, this includes only the surface layer of atoms, thereby justifying the approximation that the substrate is pure argon. The value of b obtained is

$$b = 0.02,$$

which is not very different from the classical value of this parameter obtained by localizing the particle at the minimum of the potential well. This value is 0.03 and is independent of the choice of ϵ and σ.

The value of mc_T^2 appropriate to argon is $3.14 \times 10^3 k$ °K, where the value of the transverse speed of sound in bulk argon,[11] 8.1×10^4 cm/sec, has been used. As we are concerned with the propagation of a disturbance in the vicinity of the surface where the lattice is less rigid than in the bulk, the above value is somewhat of an overestimate. On the basis of a simple force-constant model, one estimates that the effect of removing the substrate atoms above the surface is[12] to decrease the speed of sound by a factor of $\sqrt{2}$. An independent estimate of this effect can be obtained by noting that the mean-square displacement of an atom is, for low temperatures, inversely proportional to the speed of sound. Allen and de Wette[13] calculate the ratio of the mean-square displacement of an atom perpendicular to the surface in the bulk to one at the surface to be $(1.6)^{-1}$. This is quite close to the value $\sqrt{2}$ given by the simple force-constant argument. Taking the value of the transverse speed of sound to be reduced by a factor of $\sqrt{2}$ relative to the bulk value yields

$$mc_T^2 = 1.57 \times 10^3 k\ \text{°K} \,.$$

The dimensionless ratio ϵ/mc_T^2 is 0.018 which is indeed small, as stated previously.

Collecting the various values of the parameters and substituting into Eq. (16) yields for the effective interaction at zero wave number

$$\mathcal{W}(0) = -24.3k\ \text{°K}\,\text{Å}^2 \,.$$

An estimate of the contribution of this interaction to the ground-state energy per particle may be obtained by assuming a uniform areal density s of adsorbed helium of

$$s = 0.08\ \text{Å}^{-2} \,,$$

the value estimated by Stewart and Dash. This value yields a contribution of

$$\tfrac{1}{2} s\mathcal{W}(0) = -0.97k\ {}^\circ\mathrm{K}$$

to the ground-state energy per particle of the adsorbed helium. This estimate will be altered somewhat on taking into account the fact that the density is not uniform as the helium is solidified, as well as the effects of the other approximations employed in this calculation. However, the order of magnitude of the effect is expected to remain unaltered as it is governed by the factor $\epsilon^2/mc_T^2 \sim 0.5k\ {}^\circ\mathrm{K}$, which necessarily follows from the nature of the assumed interaction.

RANGE OF INTERACTION

With the interaction between helium and argon atoms V assumed to be given by Eq. (14), we may return to Eq. (10) and calculate the effective interaction $\mathcal{W}(q)$ as a function of wave number q. Although it does not appear possible to obtain $\mathcal{W}(q)$ in closed form, it is demonstrated in the second Appendix that $\mathcal{W}(q)$ falls off very rapidly with q for $q\sigma$ much greater than unity. We therefore approximate $\mathcal{W}(q)$ by

$$\mathcal{W}(q) = \mathcal{W}(0) \quad \text{for } q\sigma < 1,$$

$$\mathcal{W}(q) = 0 \quad \text{otherwise.}$$

Such an approximation yields for the two-dimensional Fourier transform of the interaction $W(\rho)$ the result

$$W(\rho) = \int \mathcal{W}(q)\, e^{-i\vec{q}\cdot\vec{\rho}}\, d^2q = 2\pi\sigma^{-2}\, \mathcal{W}(0)(\sigma/\rho) J_1(\sigma/\rho)\ ,$$

where J_1 is the cylindrical Bessel function of order unity. The above expression for $W(\rho)$ has the asymptotic form for large distances

$$W(\rho) = (8\pi)^{1/2}\sigma^{-2}\, \mathcal{W}(0)(\sigma/\rho)^{3/2} \cos(\sigma/\rho - \tfrac{3}{4}\pi)\ , \quad \rho/\sigma \gg 1$$

which decreases essentially as $\rho^{-3/2}$.

SUMMARY AND DISCUSSION

The phonon-induced interaction $\mathcal{W}(q)$ between atoms adsorbed on a substrate has been calculated and the zero wave-number limit of this interaction has been evaluated for the helium, argon-plated copper system studied by Stewart and Dash. The contribution of this interaction to the ground-state energy per particle in the dense clusters was estimated to be about $-1k$ °K. As the lateral binding of the adsorbed helium atoms will be increased by this amount, part of the observed enhancement of the binding energy can be attributed to the effective interaction. Only the order of magnitude of the observed enhancement can be estimated, however, as calculations of the ground-state energy of a monolayer solid system have not been carried out.

It is to be further noted that the contribution of the effective interaction to the ground-state energy per particle is a significant fraction of the observed energy ($\sim -15k$ °K). This indicates that the phonon-induced interaction should be included in any first principles calculation of the properties of the many-body monolayer system. Such a calculation would illuminate the role of this interaction in bringing about several interesting effects. For example, the effective interaction lowers the energy of the solid phase with respect to the less-dense liquid phase and could be responsible for the observation of the solid phase. If this hypothesis is correct then the strength of the effective interaction must be reduced in order to prepare a quantum-liquid monolayer. According to Eq. (16), the choice of a substrate which interacts weakly with the adsorbed atoms and which is highly incompressible is indicated. A final effect of interest in the liquid state of an adsorbed He^3 monolayer is, of course, the transition[14] to the superfluid state[15] which would be enhanced by the residual attractive effective interaction.

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APPENDIX A

In this Appendix it will be shown that, in the limit of vanishing q, the second term of Eq. (10)

$$T \equiv -2(\rho_s mc_T^2)^{-1} L^{-1} \textstyle\sum_l \left[l^{-1} I_T(0,l)\right]^2\ , \tag{A1}$$

with

$$I_T(0,l) = \int_0^\infty dz\, |\Phi(z)|^2\, \frac{\partial U(z,0,l)}{\partial z}\ , \tag{A2}$$

can be written in the form given in Eq. (11) of the text. Recall that $U(z,0,l)$ is related to the interaction between adsorbed and substrate atoms V by

$$U(z,0,l) = \rho_s \int V[y^2 + (z-z')^2] \cos lz'\, d^2y\, dz' \equiv \int_{-\infty}^{0} U(z-z') \cos lz' dz', \tag{A3}$$

and that $U(z,0,0)$ is identical to $\mathcal{V}(z)$, the total interaction between an adsorbed atom and the substrate. We shall make use of the fact that, as $\Phi(z)$ is the time-independent solution of the one-dimensional Schrödinger equation containing the potential $\mathcal{V}(z)$, the integral

$$\int dz\, |\Phi(z)|^2\, \frac{\partial \mathcal{V}(z)}{\partial z} = I_T(0,0) = 0\ . \tag{A4}$$

This follows from the Ehrenfest relation

$$\frac{\langle -\partial \mathcal{V}(z)\rangle}{\partial z}=\frac{d\langle P_z\rangle}{dt}$$
$$=0\ ,$$

the second equality following from the fact that $\Phi(z)$ is time independent. The brackets denote quantum-mechanical expectation values. As $I_T(0,l)$ is, from Eq. (A2) and Eq. (A3), an even function of l, it vanishes as l^2 with vanishing l.

The sum over l in Eq. (A1) is replaced by an integral from zero to infinity and we integrate over l by parts. The integrated part is proportional to $l^{-1} I_T^2(0,l)$ which, we have just seen, vanishes at l equal to zero. In addition, inspection of Eqs. (A2) and (A3) indicates that the integrated part also vanishes when evaluated at infinitely large l.

The remaining integral over l is of the form[16]

$$\int_0^\infty dl\, l^{-1}\sin lz'\cos lx'=\tfrac{1}{2}\pi \quad \text{for } x'<z'\ ,$$

$$\int_0^\infty dl\, l^{-1}\sin lz'\cos lx'=\tfrac{1}{4}\pi \quad \text{for } x'=z'\ ,$$

$$\int_0^\infty dl\, l^{-1}\sin lz'\cos lx'=0 \quad \text{for } x'>z'\ ,$$

so that T can be written

$$T=-2(\rho_s mc_T^2)^{-1}\int_0^\infty dz\,|\Phi(z)|^2\frac{\partial}{\partial z}\int_{-\infty}^0 z'U(z-z')$$
$$\times\int_0^\infty dx\,|\Phi(x)|^2\frac{\partial}{\partial x}\int_{-\infty}^{z'}U(x-x')dx'\,dz'\ .$$

Assuming that $U(z-z')$ vanishes for infinitely large argument so that

$$\frac{\partial}{\partial x}\int_{-\infty}^{z'}U(x-x')dx'=-\int_{-\infty}^{z'}\frac{\partial}{\partial x'}U(x-x')dx'=U(x-z'),$$

the above expression for T is brought to the form

$$T=2(\rho_s mc_T^2)^{-1}\int_0^\infty dz\,|\phi(z)|^2$$
$$\times\int_0^\infty dx\,|\phi(x)|^2\frac{\partial}{\partial z}\int_{-\infty}^0 z'\,U(z-z')U(x-z')dz'.$$

This expression is further simplified by taking the partial with respect to z inside the integral, allowing it to act on $U(z-z')$ and changing the partial to one with respect to z' with a change of sign. A partial integration with respect to z' is carried out with the integrated part vanishing. Upon noting that z and z' are dummy variables, one finds that the integral over x, z, and z' above is equal to

$$-\tfrac{1}{2}\int dx\,dz\,|\Phi(x)|^2|\Phi(z)|^2\int_{-\infty}^0 U(z-z')\,U(x-z')dz',$$

so that T takes the form

$$T=-(\rho_s mc_T^2)\int_{-\infty}^0 dz'\left[\int_0^\infty dz\,|\Phi(z)|^2\,U(z-z')\right]^2\ ,$$

as given by Eq. (11) of the text.

APPENDIX B

The expression for $\mathcal{W}(q)$ given in Eq. (10) contains two terms. Replacing the sum over l by an integral from zero to infinity the second of these terms is proportional to

$$S(q)=\int_0^\infty\frac{dl}{(q^2+l^2)}\left[\int_0^\infty dz\,|\phi(z)|^2\frac{\partial}{\partial z}U(z,q,l)\right]^2, \tag{B1}$$

where $U(z,q,l)$ is given in the text immediately following Eq. (7) and can be written

$$U(z,q,l)$$
$$=2\pi\rho_s\int J_0(qy)V[y^2+(z+z')^2]\cos lz'\,d^2y\,dz'\ . \tag{B2}$$

The function J_0 is the cylindrical Bessel function of zero order and a change of variables from z' to $-z'$ has been made for reasons of symmetry. The integral over l in Eq. (B1) is[17]

$$\int_0^\infty dl\,(q^2+l^2)^{-1}\cos lz'\cos lx'$$
$$=(\pi/2q)\cosh z'q\,e^{-x'q},\quad z'<x'$$

$$\int_0^\infty dl(q^2+l^2)^{-1}\cos lz'\cos lx'$$
$$=(\pi/2q)\cosh x'q\,e^{-z'q},\quad x'<z'\ .$$

The function $S(q)$ is then reduced to

$$S(q)=\pi q^{-1}\int dz\,dx\,|\Phi(x)|^2|\Phi(z)|^2$$
$$\times\int_{-\infty}^0 dz'\,P(q,z+z')e^{-z'q}$$
$$\times\int_0^{z'}P(q,x+x')\cosh x'q\,dx'\,dz'\ , \tag{B3}$$

where

$$P(q,z+z')$$
$$=2\pi\rho_s\int_0^\infty dy\,y\,J_0(qy)\frac{\partial}{\partial z}V[y^2+(z+z')^2]\ . \tag{B4}$$

Although it is not at all apparent from Eq. (B3) that $S(q)$ is well behaved in the limit of vanishing q, it can be shown that it is upon making use of Eq. (A4). The Lennard-Jones potential

$$V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]\ ,$$
$$r=[y^2+(z+z')^2]^{1/2}$$

is substituted into Eq. (B4) and the integrals over y carried out with the aid of the relation[18]

$$\int_0^\infty(y^2+c^2)^{-\mu-1}J_0(qy)dy=q^\mu K_\mu(qc)/(2c)^\mu\,\mu!$$
for integer μ,

where K_μ is the modified Bessel function of order μ. Upon introducing the variables $\gamma\equiv q(z+z')$ and

$\delta \equiv q(x+x')$, one finds

$$S(q) \propto q^{-1} \int dz\, dx\, |\phi(z)|^2 |\phi(x)|^2 \int_{qz}^{\infty} R(q,\gamma) \times \exp - [(\gamma - qz)] \int_{qx}^{\infty} R(q,\delta) \cosh(\delta - xq)\, d\delta\, d\gamma, \tag{B5}$$

where

$$a \equiv \gamma + q(x-z)$$

and

$$R(q,\gamma) \equiv [(12/2^5 6!)(\sigma q)^{10} \gamma^{-5} K_6(\gamma) - (\tfrac{1}{4})(\sigma q)^4 \gamma^{-2} K_3(\gamma)] .$$

This function has the asymptotic behavior

$$R(q,\gamma) \rightarrow e^{-\gamma} \gamma^{-2} \quad \text{for } \gamma \gg 1,$$
$$R(q,\delta) \rightarrow \gamma^{-11} \quad \text{for } \gamma \ll 1.$$

Therefore, the integrands of the last two integrals of Eq. (B5) are only large for γ, δ less than, or of, the order unity. From the limits on the integrals it can be seen that this implies that $S(q)$ will only be large if $\sigma q \ll \sigma z^{-1}$ and $\sigma q \ll \sigma x^{-1}$.

Let us now assume that $\sigma q \gg 1$. The integrals can then only be large if $x\sigma^{-1}$ and $z\sigma^{-1}$ are much less than unity. However, the behavior of $\phi(z)$, the ground-state solution of the Schrödinger equation containing the potential $\mathcal{V}(z)$, has the asymptotic form

$$\phi(z) \rightarrow z^{9/4} \exp[-d(\sigma/z)^{7/2}] \quad \text{for } z\sigma^{-1} \ll 1,$$

where d is a constant. Thus if $z\sigma^{-1}$ or $x\sigma^{-1}$ is much less than unity, the wave functions are vanishingly small, so that $S(q)$ is vanishingly small for $\sigma q \gg 1$ as was to be proved.

The first term in the expression for $\mathcal{W}(q)$ given in Eq. (10) can be treated in a manner similar to the above with the same results.

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[3] See, for example, F. Ricca, C. Pisani, and E. Garrone, J. Chem. Phys. 51, 4079 (1969).

[4] The term "monolayer" as employed here conveys only that the coverage of the substrate nowhere exceeds a thickness of one atom.

[5] An excellent treatment of the electron-phonon coupling may be found in J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960).

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