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Thermodynamics of two-dimensional helium films on textured substrates

J. J. Rehr and Manu Tejwani
*Department of Physics, University of Washington,
Seattle, Washington 98195*
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Effects of substrate potential and geometry on the thermodynamics of physisorbed, low-density, submonolayer helium films are investigated using a tight-binding formalism, a quantum virial expansion, and a lattice version of potential scattering theory. Calculations for a two-parameter triangular-lattice model are presented which exhibit systematic trends in the specific heat that are in qualitative agreement with presently available experimental data.

The thermodynamics of submonolayer helium films has been a subject of much experimental and theoretical interest[1] since the early work of Bretz and Dash.[2] Recent experimental work in this field has dealt with the role of the substrate,[3,4] which, though essentially passive, can strikingly modify the behavior of the overlayer. Low-density (about $\frac{1}{4}$ monolayer) specific-heat measurements of ^{4}He on Ar-plated Grafoil,[3] for example, have revealed peaks at twice the "condensation" temperature of ^{4}He on bare Grafoil, that are larger by an order of magnitude. In effect, different substrates lead to "new" quantum systems with dramatically different phase-transition properties and possibly new types of critical behavior.[5] Compared to Grafoil,[6] the substrates of current interest[3,4] are often highly *textured.* For example, the lateral potential variation over Ar-plated Grafoil[7] is ~50 K (Grafoil, ~20 K). Physically, this results in localization of the He wave functions at the absorption sites, and hence alters the competition between single-particle properties and interactions to an extent which depends on the geometry and potential of the substrate.

Such textured substrates are naturally treated with a general tight-binding formalism, which is the approach adopted here. We present results for a two-parameter model which, for the first time, accounts for the variation in behavior observed for ^{4}He on several rare-gas substrates.[3,4] Our calculations are based on a quantum virial expansion,[8] carried to first order in the coverage. We derive and evaluate a new generalization of the formula for the second virial coefficient in terms of bound states and "lattice phase shifts." The theory is simpler in some respects than that for ideally flat substrates[9]; for example, only a finite number of lattice phase shifts are involved (e.g., two for ^{4}He on a triangular lattice). Analytical expressions for these phase shifts are obtained by a novel application of the recursion method of Haydock *et al.*[10]

The present article describes the first fully quantum-mechanical treatment of the low-density thermodynamics of He on textured substrates, albeit for a simple model. Nevertheless, many refinements are possible, and we believe that the general approach followed here will be of value in more detailed calculations; in understanding similar substrate effects in more complex systems; and, perhaps in designing new quantum systems with specific desired characteristics.

To begin, let us consider a system of interacting bosons (or fermions) confined, for simplicity, to a regular, two-dimensional Bravais net with periodic substrate potential $V(\vec{r})$. We assume that the system can be described adequately by the tight-binding Hamiltonian[11]

$$H = \sum_{\vec{i},\vec{j}} \left(T_{\vec{j}}\, a_{\vec{i}+\vec{j}}^{\dagger}\, a_{\vec{i}} + \tfrac{1}{2} U_{\vec{j}}\, n_{\vec{i}+\vec{j}}\, n_{\vec{i}} \right) , \tag{1}$$

where $a_{\vec{i}}^{\dagger}$ ($a_{\vec{i}}$) is a Wannier-state creation (annihilation) operator at site $\vec{i}$, and $n_{\vec{i}}$ is the number operator. The substrate potential appears implicitly in this model in the hopping matrix elements,

$$T_{\vec{i}} \equiv \langle a_{\vec{i}} | \frac{-\hbar^2 \nabla^2}{2M} + V(\vec{r}) | a_{\vec{0}} \rangle \quad ;$$

these may be determined by fitting the known single-particle energy bands,[7,12] and lead to substrate-dependent effective masses. Since we are interested in low-temperature properties, we concentrate on the lowest band and suppress band indices. Substrate geometry and potential both influence the interaction parameters $U_{\vec{i}} \equiv \langle a_{\vec{0}} a_{\vec{i}} | U | a_{\vec{0}} a_{\vec{i}} \rangle$, where U is the two-body potential. In writing Eq. (1) we have neglected motion perpendicular to the substrate and any indirect interaction via the substrate that can not be lumped into $U_{\vec{i}}$.

To describe the low coverage[13] thermodynamics, it suffices to use a virial expansion[1] in powers of the areal density $n = N/A$. We need only the second virial coefficient,

$$B_2(T) = -\frac{A}{Z_1^2}(Z_2 - \tfrac{1}{2}Z_1^2) = B_2^0 - \frac{A}{Z_1^2}(Z_2 - Z_2^0) \ . \tag{2}$$

Here, $Z_N = \int dE\, g_N(E) e^{-\beta E}$ is the N-particle partition function, $g_N(E)$ is the density of levels, and quantities with a superscript zero are calculated in the absence of interactions. It is easy to show with symmetrized plane waves that $g_2^0(E) = \pm\frac{1}{4}g_1(\frac{1}{2}E)$, where the upper and lower signs refer to Bose and Fermi statistics, respectively.

Due to the invariance of the Hamiltonian (1) under crystal translations, the calculation of Z_2 can be reduced to a one-particle problem. For example, the eigenstates $\Psi(\vec{i},\vec{j})$ may be factored into center of mass and relative wave functions,

$$\Psi(\vec{i},\vec{j}) = \exp[i\vec{K}\cdot(\vec{i}+\vec{j})/2]\phi(\vec{i}-\vec{j}) \ ,$$

where $\phi(\vec{i})$ satisfies

$$\sum_{\vec{j}} 2T_{\vec{j}}\cos(\tfrac{1}{2}\vec{K}\cdot\vec{j})\phi(\vec{i}+\vec{j}) + U_{\vec{i}}\phi(\vec{i}) = E\phi(\vec{i}) \ . \tag{3}$$

Equation (3) represents a potential scattering problem on a lattice and is soluble in terms of the lattice Green's functions,[14]

$$G^0_{\vec{i}\,\vec{j}}(\vec{K};E) = \frac{1}{N}\sum_{\vec{k}}^{BZ} \frac{e^{i\vec{k}\cdot(\vec{i}-\vec{j})}}{E - (\epsilon^0_{\vec{k}+\frac{1}{2}\vec{K}} + \epsilon^0_{\vec{k}-\frac{1}{2}\vec{K}}) + i0^+} \ , \tag{4}$$

where $\epsilon^0_{\vec{k}}$ is the single-particle energy. The formalism we use is based on a lattice version of Fredholm theory.[15] With the separability of $\Psi(\vec{i},\vec{j})$, the difference between the two-particle density of states is then given by

$$g_2(E) - g_2^0(E)$$

$$= -\frac{\mathrm{Im}}{\pi}\sum_{\vec{K}}\frac{\partial}{\partial E}\ln\det\,[\delta_{\vec{i}\,\vec{j}} - G^0_{\vec{i}\,\vec{j}}(\vec{K};E)\,U_{\vec{j}}] \ . \tag{5}$$

The zeros of det $(\delta_{\vec{i}\,\vec{j}} - G^0_{\vec{i}\,\vec{j}}U_{\vec{j}})$ correspond to bound states $E_\mu(\vec{K})$, while its argument defines a phase shift $\delta(\vec{K};E)$. Consequently Eq. (2) for $B_2(T)$ becomes

$$B_2(T) = B_2^0 + \frac{A}{Z_1^2}\left(\sum_{\vec{K},\mu} e^{-\beta E_\mu(\vec{K})} + \sum_{\vec{K}}\int\frac{dE}{\pi}\,\frac{\partial\delta(\vec{K};E)}{\partial E}e^{-\beta E}\right) \ . \tag{6}$$

While Eq. (6) is exact, it is not easy to evaluate numerically.

To simplify the calculations we make two approximations. First we assume that the two-particle energy eigenvalues can also be separated into center of mass and relative contributions, as in the uniform substrate model. The error in this approximation is negligible for small $\vec{k}$ or $\vec{K}$, which is the range that dominates the low-temperature behavior. Second, since the substrates of interest[3,4] are highly textured and the He-He interaction short ranged, we retain in Eq. (1) only the nearest-neighbor terms, designated by $-t$ (hopping) and $-u$ (interaction); hard-core repulsion is introduced by setting $U_0 = +\infty$. The competition between single-particle motion and interactions is then governed by the dimensionless ratio u/t. Also we treat only the case of a triangular lattice. This choice is mandated by several physical and technical considerations, though the actual lattice of He adsorption sites on rare-gas substrates is usually a honeycomb: (i) He-He hard-core repulsion precludes nearest-neighbor occupation on the honeycomb; (ii) the lowest band on the honeycomb can be simulated by "bonding" Wannier functions on a triangular lattice; and (iii) the non-Bravais character of the honeycomb considerably complicates the analysis. Thus, the triangular lattice simulates both the single-particle states and the geometry of the short-range interactions on the substrates of interest.

With these simplifications the Green's function (4) has sixfold rotational symmetry and depends on $\vec{K}$ only via an energy shift $\epsilon \equiv E - 2\epsilon^0_{\vec{K}/2}$. Consequently, $Z_2 = Z_C Z_R$. The relative motion problem is isomorphic to potential scattering on a triangular lattice [Eq. (3) with hopping matrix element $-2t$]; the center of mass motion is that of an independent particle of a triangular net of lattice constant $\frac{1}{2}a$, whence

$$Z_C = 2\int dE\, g_1(E/2)e^{-\beta E} \ .$$

By symmetry, the 7 × 7 matrix $\delta_{\vec{i}\,\vec{j}} - G^0_{\vec{i}\,\vec{j}}U_{\vec{j}}$ can be diagonalized[14] using irreducible representations of the C_{6v} point group, e.g., with the states $|\vec{0}\rangle$ and

$$|m\rangle = (1/6^{1/2})\sum_{j=1}^{6}|\vec{j}\rangle e^{i2\pi jm/6} \ ,$$

$$m = 0, \ldots, 5, \mathrm{mod}_6 \ .$$

Here j lables in counterclockwise (ccw) order the six nearest-neighbor sites to the origin, and m is an "angular momentum" index. We may therefore write

$$\det(\delta_{ij} - G^0_{ij}U_j) = \prod_{m=0}^{5} |D_m(\epsilon)| e^{-i\delta_m(\epsilon)} \ , \tag{7}$$

where

$$D_0 = -G^0_{\bar{0}\,\bar{0}}\left(1 + \frac{\epsilon u}{24t^2}\right) + \frac{u}{24t^2} ,$$
$$D_m = 1 + G^0_{mm} u \ , \quad m = 1, \ldots, 5 \ , \tag{8}$$

and we have set $D_m \equiv |D_m| e^{-i\delta_m}$. The "lattice phase shifts" δ_m appearing in Eq. (7) are directly analogous to those in continuum scattering theory.[15,16] The zeros of the "Jost functions," $D_m(\epsilon)$ correspond to energies $\epsilon_{m,\mu}$ of bound states of a particular symmetry ($m = 0 \equiv$ "s wave," $m = \pm 1 \equiv$ "p wave," etc.). On incorporating these results into Eq. (6), we obtain a model independent formula for $B_2(T)$, which is structurally similar to that for ideally flat substrates.[9]

$$B_2(T) = -\frac{AZ_c}{Z_1^2}\left\{ \pm\frac{1}{8} + \sum_{m,\mu} e^{-\beta\epsilon_{m,\mu}} + \sum_m \int \frac{d\epsilon}{\pi}\frac{\partial\delta_m(\epsilon)}{\partial\epsilon} e^{-\beta\epsilon} \right\} \ . \tag{9}$$

The prefactor in Eq. (9), $AZ_c/Z_1^2 \equiv 2\lambda^2(T)\gamma(T)$, where λ is the thermal wavelength, and $\gamma(T)$ is a dimensionless factor independent of U, which is unity when $g_1(\epsilon)$ has its flat substrate value.

For spin zero bosons (fermions),[17] wave-function parity implies that the m sums in Eq. (9) are further restricted to even (odd) integers. Also, by time-reversal symmetry $\delta_1 \equiv \delta_{-1}$ and $\delta_2 \equiv \delta_{-2}$. Thus the problem for ^{4}He on a triangular net reduces to a calculation of *only s* and *d* phase shifts!

We remark that analytical expressions for the lattice Green's functions needed to evaluate $D_m(\epsilon)$ may be obtained from rapidly convergent continued-fraction expansions,

$$G^0_{mm}(\epsilon) = \cfrac{1}{\epsilon - a_0^m - \cfrac{b_0^m}{\epsilon - a_1^m - \cfrac{b_1^m}{\epsilon - a_2^m - \cdots}}} \ . \tag{10}$$

The coefficients a_j^m and b_j^m can be determined efficiently by the recursion method of Haydock *et al.*[10] In our calculations 19 pairs of coefficients (a_j^m, b_j^m) were used for each $G^0_{mm}, m = 1, \ldots, 5$, and 23 pairs for $G^0_{\bar{0}\,\bar{0}}$. The local densities of states, $\rho_m \equiv -(1/\pi)\,\mathrm{Im}\, G^0_{mm}$, are thereby accurate to 38 moments (46 for $G^0_{\bar{0}\,\bar{0}}$). The details of these calculations will be presented elsewhere.

Let us briefly discuss the results of our calculations. At temperatures (above condensation) where the virial expansion is valid, one expects that the low-density[13] specific-heat data, plotted in the form

$$\frac{C - C^0}{Nk_B n} \equiv C_2(T) = -\beta^2 \frac{\partial^2}{\partial\beta^2} B_2(T) \ , \tag{11}$$

will be a *universal curve* independent of coverage. Here $C^0 = \beta^2\partial^2 \ln Z_1/\partial\beta^2$ is the specific heat of noninteracting particles moving in the substrate field $v(\vec{r})$. Our results for $C_2(T)$ for spin zero bosons (e.g., ^{4}He) are plotted in Fig. 1, for several values of u/t. The solid curve is the result of the one-band theory. As a rough estimate of the effects of higher bands (dashed curve) we used a tight-binding model for the second band and we assumed all higher bands to be parabolic.

For comparison, rough estimates of u/t for Ar, Kr, and Xe substrates are 5.8, 4.3, and 2.3, respectively.

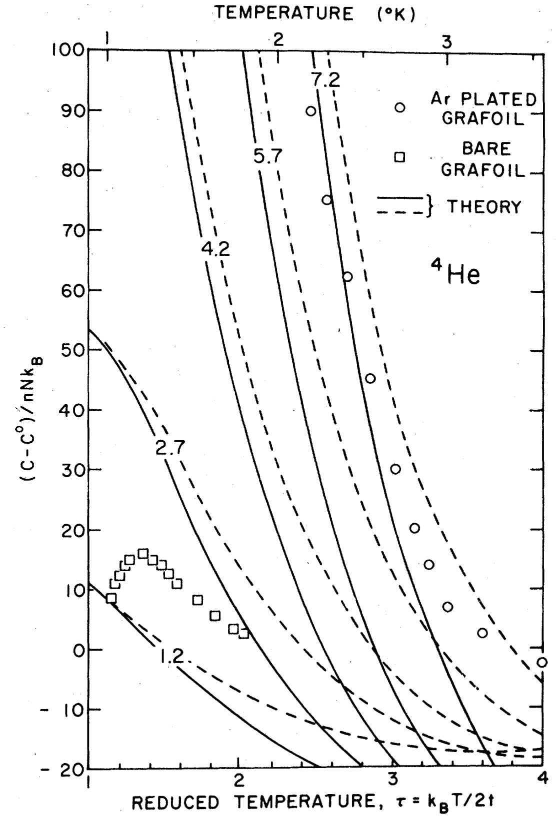

FIG. 1. Behavior of $C_2(T)$ [Eq. (11)] vs temperature ($t = 0.45$ K) for various substrate parameters u/t: solid lines, one band theory; short dashes, theory plus estimated higher-band corrections (see text); squares and circles, data for unplated[2] and Ar-plated Grafoil,[3] respectively, vs real temperature.

We used $t = B/9$, where $B(\cong 4\,^\circ\mathrm{K}$ for Ar,[7] Kr, and[12] Xe) is the lowest single-particle bandwidth. We approximated $-u$ as the Lennard-Jones interaction ($\epsilon = 10.2\,^\circ\mathrm{K}$, $\sigma = 2.556$ Å)[1] at the observed first (allowed) nearest-neighbor distances[3,4]: $u(a) = 2.5\,^\circ\mathrm{K}$ (3.8 Å), 1.9 °K (4.0 Å), and 1.0 °K (4.5 Å) for Ar, Kr, and Xe, respectively. Since the Wannier functions have a finite spread, these values are probably underestimates. While the contribution from higher bands is not negligible even at 2 °K, and while a better choice of parameters may be possible, this will not change the trends in Fig. 1. These results are consistent with the available ^{4}He experimental data,[3,4] in which the Kr data lies intermediate between that for Ar and Xe, and data for Xe is roughly comparable to that on bare Grafoil. Similar calculations for ^{3}He are in progress.

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[17] For $s \neq 0$ bosons (fermions), $B_2 = [s(B_2^E + B_2^O) + B_2^{E(O)}]/(2s+1)$, where E and O refer to the parity of $\Psi(\vec{i}, \vec{j})$.