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Mean-field theory of multilayer physisorption. II. Thermodynamic functions for ^{3}He and ^{4}He adsorbed on graphite

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Isotherms, isosteric heat of adsorption, and excess specific heat due to excitation into higher bound states of the surface potential are calculated in mean-field theory for ^{3}He and ^{4}He adsorbed on graphite up to and beyond the monolayer coverage for fluid adsorbates.

I. INTRODUCTION

The thermodynamics of ^{3}He and ^{4}He adsorbed on the basal plane of graphite has been studied extensively,[1,2] in particular, after it was found that grafoil provided a sample with (a) a large surface-to-volume ratio and (b) exceptionally uniform basal plane surfaces. Isotherms, entropies, specific heats, and heats of adsorption have been measured, among others, as functions of temperature, ambient gas pressure, and coverage.

In the theoretical attempts to understand the He-C system two main thrusts have developed. Following earlier work by Steele,[3] Jackson,[4] and others, Cole and co-workers[5,6] have looked in detail at the interaction of a single He atom with the basal plane of graphite constructing surface potentials

$$V_s(\vec{r})=\sum_i V(\vec{r}-\vec{r}_i) \tag{1}$$

that result from the two-body interaction $V(\vec{r}-\vec{r}_i)$ of a He atom at position $\vec{r}$ and a C atom at position $\vec{r}_i$ in the solid. It turns out that apart from small band-structure effects $V_s(\vec{r})$ is essentially dependent on the distance z of the He atom above the surface plane, i.e., $V_s(\vec{r})\equiv V_s(z)$. The latter develops five bound states for the ^{4}He-C system and three for the ^{3}He-C system into which He atoms can get trapped to form the adsorbate. Because the lowest two bound states are separated by energies $(\epsilon_1-\epsilon_0)/k_B=66$ K for ^{4}He-C and 72 K for ^{3}He-C, and because the spread of the ground-state wave function is of the order of only 1 Å, one argues that for $T\lesssim 10$ K one can safely reduce the problem to a two-dimensional one by ignoring (a) excitations into higher bound states and (b) the motion of adsorbed He atoms perpendicular to the surface. For systems at low coverage (less than half a monolayer) Schick and co-workers[1] have developed a two-dimensional virial expansion from which spreading pressures, specific heats, etc., can be calculated that are in fair agreement with experiment at low temperatures, $T\lesssim 5$ K. There are, however, features of the He-C system that cannot be understood in two-dimensional theories. Foremost is the whole range of adsorption and desorption kinetics for which the dynamic coupling of the adsorbate to the solid and the gas phase must be included. It also turns out that the two-dimensional theories are not capable of reproducing experimental isotherms.[7] In addition, an Eucken-type specific-heat anomaly in ^{4}He-C for coverages Θ between 0.35 and 0.61 measured so far for 6 K$\lesssim T\lesssim$12 K due to excitation of He atoms into the first excited state of $V_s(z)$ cannot be explained satisfactorily.[7]

Therefore, we have recently developed a mean-field theory of physisorption at finite coverages.[8] Although our main interest is in developing a kinetic theory of adsorption and desorption we present in this paper a calculation of isotherms, excess specific heats due to excitations perpendicular to the surface, and heats of adsorption.

Starting from a quantum mechanical many-body Hamiltonian a variational calculation leads, for fermionic gas particles, to the spin-averaged, temperature-dependent Brueckner-Hartree-Fock equations (details can be found in Ref. 8)

$$\left[-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_1}+V_s(\vec{r}_1)-E_{\vec{i}}\right]\psi_{\vec{i}}(\vec{r}_1)$$
$$+\sum_{\vec{j}} n_{\vec{j}}\int d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \psi^*_{\vec{j}}(\vec{r}_2)\langle\vec{r}_1,\vec{r}_2\,|K|\,\vec{r}_3,\vec{r}_4\rangle[(2s+1)\psi_{\vec{i}}(\vec{r}_3)\psi_{\vec{j}}(\vec{r}_4)-\psi_{\vec{j}}(\vec{r}_3)\psi_{\vec{i}}(\vec{r}_4)]=0\ , \qquad (2)$$

where $E_{\vec{i}}$ and $\psi_{\vec{i}}$ are the single-particle energies and wave functions, respectively, s is the spin, and K is Brueckner's K matrix. The thermal occupation functions are given by

$$n_{\vec{j}}=[\exp\beta(E_{\vec{j}}-\mu)+1]^{-1}\ , \qquad (3)$$

where μ is the chemical potential per particle and $\beta=1/k_BT$. Because we assume that the gas phase is very large (infinite), it controls μ in equilibrium. Thus if, away from the surface, the gas can be described satisfactorily by the ideal gas law then

$$\mu=k_BT\ln\frac{h^3P}{(2\pi m)^{3/2}(k_BT)^{5/2}}$$
$$=k_BT\ln(\lambda^3_{\text{th}}P/k_BT)\ , \qquad (4)$$

where P is the pressure in the gas phase and λ_{th} is the thermal wavelength. Virial corrections can be included in (4) if necessary.

To decouple the mean-field self-consistency in (2) from the Brueckner self-consistency in calculated K, one invokes a local density approximation. Also one observes that as long as the adsorbate remains fluid, one can assume that

$$\psi_{\vec{i}}(\vec{r})=L^{-1}\Phi_i(z,\vec{q})e^{i\vec{q}\cdot\vec{\rho}}\ , \qquad (5)$$

where L^2 is the surface area, $\vec{q}=(q_x,q_y)$ is a two-dimensional wave vector, $\vec{r}=(\vec{\rho},z)$, and $\vec{i}=(q_x,q_y,i)$ with i enumerating the bound states and the continuum. Inserting (5) into (2) and integrating out the lateral degrees of freedom one obtains a set of one-dimensional integro-differential equations for $\phi_i(z,\vec{q})$ which is still too formidable to allow us a numerical solution. Two avenues for further approximations are open: We can integrate out the perpendicular degrees of freedom and ignore all states except those with $i=0$. We then have an essentially two-dimensional mean-field theory that allows us to calculate self-consistently the energy dispersion

$$E_{\vec{i}}=\epsilon_i(\vec{q})+\frac{\hbar^2q^2}{2m} \qquad (6)$$

for $i=0$, assuming that all gas particles in the adsorbate are in that state. This seems a very promising alternative to the two-dimensional virial theory and we will briefly return to it below. Following Ref. 8 we develop a different line of approximations that essentially replaces the nonlocal K matrix by a local effective density-dependent softcore two-body interaction between He atoms within the adsorbate. This results for a highly mobile adsorbate for which $V_s(\vec{r})\equiv V_s(z)$ in our mean-field equations

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}+V_s(z)-\epsilon_i(\vec{q})\right]\Phi_i(z,\vec{q})$$
$$+\sum_j\frac{1}{(2\pi)^2}\int d\vec{q}\,'\left\{\exp\left[\beta\left[\epsilon_j(\vec{q}\,')+\frac{\hbar^2q'^2}{2m}-\mu\right]\right]\mp 1\right\}^{-1}$$
$$\times\int dz'\Phi^*_j(z',q')\int d\vec{\rho}\,V_{\text{eff}}(z-z',\vec{\rho})[(2s+1)\Phi_i(z,\vec{q})\Phi_j(z',\vec{q}\,')\pm e^{-i(\vec{q}\,'-\vec{q})\cdot\vec{\rho}}\Phi_i(z',\vec{q})\Phi_j(z,\vec{q}\,')]=0\ , \qquad (7)$$

where the upper (lower) sign must be used if the gas particles obey Bose-Einstein (Fermi-Dirac) statistics. Indeed, to a good approximation the factor

$$\exp[-i(\vec{q}\,'-\vec{q})\cdot\vec{\rho}]$$

in the exchange term can be replaced by one for a highly mobile adsorbate so that

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}+V_s(z)-\epsilon_i\right]\Phi_i(z)+\sum_j\tilde{n}_j\int dz'\tilde{V}(z-z')\Phi^*_j(z')[(2s+1)\Phi_i(z)\Phi_j(z')\pm\Phi_i(z')\Phi_j(z)]=0\ , \qquad (8)$$

with

$$\tilde{n}_j = \frac{\sigma_g^2}{L^2} \sum_{\vec{q}} n_{\vec{q}j} = (2\pi)^{-1}\sigma_g^2 \int_0^\infty q\,dq \left\{ \exp\left[\beta\left(\epsilon_j + \frac{\hbar^2 q^2}{2m} - \mu\right)\right] \mp 1 \right\}^{-1}$$

$$= \mp(2\pi)^{-1} m k_B T \sigma_g^2 \hbar^{-2} \ln(1 \mp e^{-\beta(\epsilon_j - \mu)}) \tag{9}$$

and

$$\tilde{V}(z) = \sigma_g^{-2} \int d\vec{\rho}\, V_{\text{eff}}(z, \vec{\rho}) , \tag{10}$$

where σ_g is the range of the two-body interaction $V_{\text{eff}}(\vec{r})$.

Starting from a bare Lennard-Jones interaction

$$V_2(r) = 4\epsilon_g[(\sigma_g/r)^{12} - (\sigma_g/r)^6] \tag{11}$$

between isolated He atoms we have shown in Ref. 8 that (10) can be adequately parametrized by

$$\tilde{V}(z) = 2\pi\epsilon_g z^{10}\{z^{10} + A\sigma_g^{10}\exp[-(z/z_1)^\alpha]\}^{-1}[\tfrac{2}{5}(\sigma_g/z)^{10} - (\sigma_g/z)^4] , \tag{12}$$

where α is of order 10 to 15, $z_1/\sigma_g \sim 0.8$, and A is a density-dependent parameter that can be calculated for fermionic gas particles from Brueckner theory. Note that $\tilde{V}(0) = 4\pi\epsilon_g/5A$ is finite. A similar effective two-body interaction has been used in a mean-field theory of ^{4}He by Bernardes and Primakoff[9] and is discussed by Brueckner and Frohberg.[10]

In Ref. 8 we have solved (8) numerically for a number of model systems to study the dependence of the single-particle energies ϵ_i, the wave functions Φ_i, the coverage, and the adlayer positions on the potential parameters in $V_s(z)$ and $\tilde{V}(z)$ and on the particle statistics. We will now use the self-consistent solutions of (8) to calculate the isotherms, excess specific heats, and heats of adsorption for ^{3}He and ^{4}He adsorbing on graphite, returning only briefly to (7) and (2) to look for correction terms.

II. ISOTHERMS

A. ^{4}He on graphite

We begin with the isotherms for ^{4}He adsorbed on graphite. The relevant experiments on grafoil have been reported by Elgin and Goodstein.[7] For a mean-field calculation we must specify the bare surface potential V_s seen by a single ^{4}He atom in front of a bare graphite surface. Although it is known by now that there is a small lateral variation in V_s along the graphite surface leading to band-structure effects,[6] we begin with the simpler laterally averaged zeta potential[5] [for which the underlying He-C interaction is of the Lennard-Jones type (11) with parameters ϵ_s and σ_s]

$$V_s(z) = 2\pi\epsilon_s\sigma_s^6 c_s a_s^{-1} d_s^{-4} \times [\tfrac{2}{5}(\sigma_s/d_s)^6 \zeta(10, z/d_s) - \zeta(4, z/d_s)] , \tag{13}$$

where

$$\zeta(n,x) = \sum_{j=0}^{\infty} (j+x)^{-n} \tag{14}$$

is a Riemann zeta function. d_s is the distance between crystal planes and $n_s = c_s/a_s$ is the average lateral density of the basal plane whose two-dimensional unit cell of area a_s contains c_s atoms. For ^{4}He-C these parameters are[5] $\epsilon_s/k_B = 16.23$ K, $\sigma_s = 2.74$ Å, $d_s = 3.37$ Å, $c_s = 2$, and $a_s = 5.24$ Å^2. This potential reproduces the experimentally determined single-particle energies fairly well.

The parameters ϵ_g and σ_g in the effective two-body interaction $\tilde{V}(z)$ in (12) are known from the underlying Lennard-Jones interaction between two isolated ^{4}He atoms to be $\epsilon_g/k_B = 10.22$ K and $\sigma_g = 2.556$ Å. The parameters A, z_1, and α determining the soft-core repulsion are less certain. We have shown in Ref. 8 how they can be determined for a system of interacting fermions by Brueckner-type calculation. For two ^{3}He atoms interacting in a ^{3}He fluid of liquid density we found that $z_1 \approx 0.8\sigma_g$, $\alpha \approx 15$, and $A \approx 1.7$ which gives $\tilde{V}(0) \approx -1.5\tilde{V}(z = z_{\min})$, i.e., a repulsion at $z = 0$

that is as high as the attraction is deep at $z = z_{\min}$. We also saw that $\tilde{V}(z=0)$ varies roughly linearly with density up to liquid density. In solving (8), self-consistently, we therefore fix A at each coverage such that $\tilde{V}(0) \approx -0.2\tilde{V}(z=z_{\min})$ at $\Theta = 0$ rising linearly to $\tilde{V}(0) \approx -1.2\tilde{V}(z=z_{\min})$ for $\Theta \geq 1$. As argued in Ref. 8 a similar effective interaction can be assumed in a mean-field theory of interacting ^{4}He atoms.

In the upper panel of Fig. 1 we plot the single-particle energies $\epsilon_i = \epsilon_i(T)$ for adsorbed ^{4}He atoms as calculated from the Hartree-Fock equations (8). As the adsorbate builds up at fixed P by lowering T, the single-particle energies move up to avoid crossing the chemical potential μ and thus to keep the single-particle occupation functions (9) for Bose-Einstein statistics finite. The center panel of Fig. 1 gives the adsorption isobar $\Theta = \Theta(T)$ where the coverage Θ is calculated from the occupation functions $\tilde{n}_i$ in (9) by

$$\Theta = \sum_{\vec{i}} \frac{n_{\vec{i}}}{n_{\vec{i}}(\max)}$$

$$= (2\pi)^{-1} \sum_i [\tilde{n}_i(\max)]^{-1} \int_0^\infty q\,dq \left\{ \exp\left[\beta\left[\epsilon_i + \frac{\hbar^2 q^2}{2m} - \mu\right]\right] - 1 \right\}^{-1} , \qquad (15)$$

where $\tilde{n}_i(\max)$ is the maximum occupation in the ith layer. The lower panel in Fig. 1 gives the mean position of a ^{4}He atom trapped into the ith bound state

$$\bar{z}_i = \int \Phi_i^2(z) z \, dz \; .$$

A good overall picture is given by the effective coverage-dependent surface potential, as introduced and discussed extensively in Ref. 8,

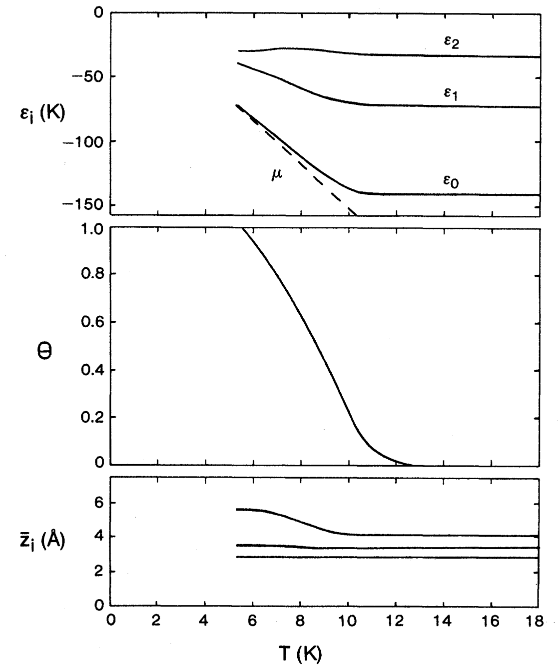

FIG. 1. Lowest three single-particle energies ϵ_i from (8), coverage Θ from (15), and mean positions $\bar{z}_i$ for ^{4}He-C at $P = 1.33$ Pa. Chemical potential μ from (4).

$$V_s(z,\Theta) = V_s(z) + V_{\mathrm{mf}}(z,\Theta) \; , \qquad (16)$$

where $V_s(z)$ is the bare surface potential seen by a single ^{4}He atom and $V_{\mathrm{mf}}(z,\Theta)$ is the mean-field potential generated by all other ^{4}He atoms already adsorbed. A perspective view of $V_s(z,\Theta)$ over the (z,Θ) plane is given in Fig. 2.

In Fig. 3 we present the isotherms Θ vs $(T \log_{10} P)$ as calculated in our mean-field theory for the above potential parameters. The experimental curves are taken from the work of Elgin and Goodstein.[7] Starting at high temperatures we find remarkable agreement of the $T = 12$ K and $T = 15$ K isotherms. We want to stress that with the above identification (12) of the effective interaction between ^{4}He atoms, our mean-field theory is parameter free. We should, therefore, examine

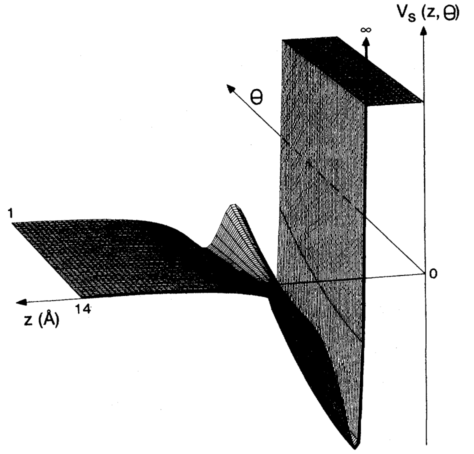

FIG. 2. The average coverage-dependent surface potential (16) for ^{4}He-C.

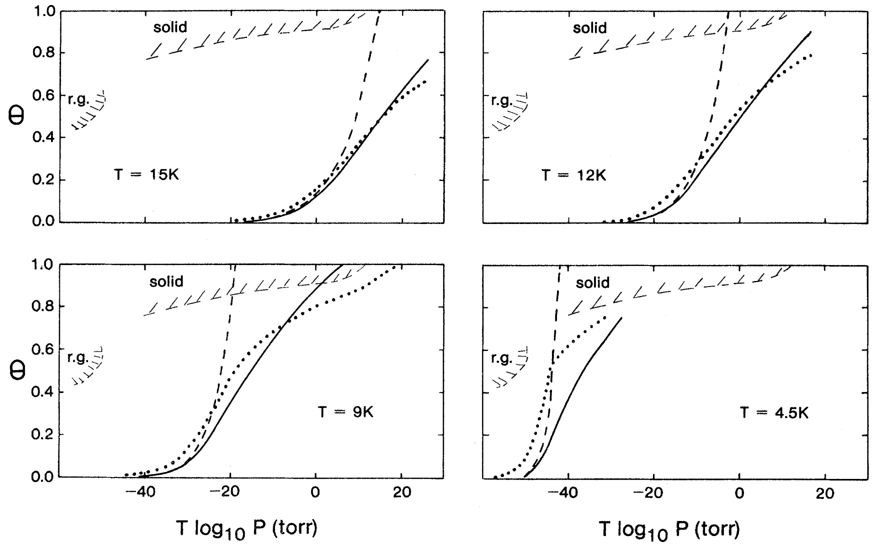

FIG. 3. Isotherms for ^{4}He-C. Dotted line: experimental data by Elgin and Goodstein (Ref. 7). Dashed line: virial theory from (17) and (18). Solid line: mean-field theory (15). Hatched areas indicate regions where ^{4}He exists in a solid phase or a registered lattice gas on graphite.

critically how great a success this agreement really is.

Langmuir and BET-type isotherms appropriate in gas-solid systems with localized adsorption are, of course, inadequate for the He-graphite system in which adsorbed He atoms are highly mobile. However, the two-dimensional virial theories[1] allow the calculation of an isotherm for low coverage. One inverts the virial expansion for the chemical potential μ_2, the subscript "2" indicating the two-dimensionality of the theory,

$$\mu_2 = \ln(\lambda_{th}^2 \Theta n_{\max}) + \sum_{l=1}^{\infty} l^{-1}(l+1) B_{l+1}(\beta)(\Theta n_{\max}) , \quad (17)$$

where $n_{\max} = 0.115$ Å^{-2} is the monolayer density for the ^{4}He-C system, λ_{th} is the thermal wavelength in (4), and B_{l+1} are virial coefficients. To introduce the pressure of the ambient gas above the graphite surface one identifies

$$\mu_2 = \mu - \epsilon_0 , \quad (18)$$

where μ is given by (4) and $\epsilon_0 / k_B = -140$ K is the (experimentally determined) energy of the lowest bound state in the surface potential $V_s(z)$. The resulting isotherms are indicated in Fig. 3. They are obviously too steep demonstrating the importance of the substantial rise in the bound-state energies ϵ_i as the coverage builds up. Indeed the virial correction is negligible for all examples shown.

The agreement between the mean-field theory and experiments becomes increasingly poorer as we go to lower T. To understand this trend we have examined the $T = 4.5$ K isotherm carefully. At such low T only the $i = 0$ term (ground state) contributes in (15) which thus reads

$$\Theta = -\frac{2\pi m k_B T}{h^2 n_{\max}} \ln(1 - e^{-\beta(\epsilon_0 - \mu)}) . \quad (19)$$

Recall that the chemical potential, given in (4), is controlled by the gas phase. The input into (19) from our mean-field theory is thus the binding energy

$$\epsilon_0 = \epsilon_0(T, P) . \quad (20)$$

To find out how accurately ϵ_0 must be known to reproduce the $T = 4.5$ K isotherm with an expression (19) we have used the latter to extract ϵ_0 (expt) from the experimental data. As we see from Table I ϵ_0 (expt) is within 2% of μ for coverages $\Theta > 0.1$. This is also the case for the eigenvalues ϵ_0 (theory) as calculated by mean-field theory. However, ϵ_0 (theory) and ϵ_0 (expt) differ by about 1%. This difference of course is magnified significantly in $(\epsilon_0 - \mu)$ leading to the discrepancies in the isotherms. To remove it the theory should be able to determine ϵ_0 to better than 1%, as a direct calculation of $(\epsilon_0 - \mu)$ seems not possible. Note from Table I that at higher temperatures $(\epsilon_0 - \mu)$ is

TABLE I. Data on two isotherms for ^{4}He-C. Experimental data by Elgin and Goodstein (Ref. 7) are analyzed with (19).

T (K)	P (Pa)	$T\log_{10}P$ (Torr)	Θ_{expt}	Θ_{theor}	μ/k_B (K)	ϵ_0/k_B (K) Expt.	Theor.
4.5	0.133×10^{-9}	-54	0.3×10^{-1}	0.24×10^{-2}	-164.08	-150.76	-139.86
	0.133×10^{-8}	-49.5	0.12	0.23×10^{-1}	-153.718	-146.65	-139.63
	0.133×10^{-7}	-45	0.42	0.15	-143.35	-140.797	-137.19
	0.266×10^{-7}	-43.66	0.53	0.21	-140.234	-138.23	-135.35
	0.133×10^{-6}	-40.5	0.599	0.35	-132.99	-131.26	-129.8
	0.399×10^{-6}	-38.36	0.67	0.433	-128.04	-126.59	-125.49
	0.133×10^{-5}	-36	0.69	0.51	-122.62	-121.189	-120.54
	0.133×10^{-4}	-31.51	0.74	0.65	-112.26	-111.01	-110.74
12	0.366	-30.738	0.14×10^{-1}	0.55×10^{-2}	-206.128	-150.76	-139.82
	0.998	-25.508	0.28×10^{-1}	0.15×10^{-1}	-194.085	-147.03	-139.71
	2.66	-20.396	0.696×10^{-1}	0.394×10^{-1}	-182.316	-146.09	-139.42
	11	-12.995	0.15	0.143	-165.274	-137.94	-137.4
	26.6	-8.391	0.33	0.26	-154.673	-136.16	-133.61
	80	-2.65	0.48	0.43	-141.45	-126.7	-125.63
	133	0.0	0.55	0.51	-135.35	-121.93	-121.14
	266	3.614	0.6	0.6	-127.03	-114.5	-114.5
	399	5.728	0.64	0.66	-122.16	-110.22	-110.42
	1330	12	0.737	0.806	-107.708	-97.08	-97.76

much larger so that the accuracy of about 1–2 % with which mean-field theory seems to determine the eigenvalues ϵ_0 is sufficient to reproduce the experimental isotherms for $\Theta \lesssim 0.7$. The bending over of the isotherms at higher coverages in Fig. 3 is not followed too well by our theory though the typical S shape is reproduced. But note that, e.g., for the $T=9$ K isotherm at $T\log_{10}P=0$ to pull the theoretical coverage $\Theta=0.87$ down to the experimental value $\Theta=0.8$ requires a raising of ϵ_0 (theory) by only 5%.

Using (19) to extract energy eigenvalues $\epsilon_0=\epsilon_0(T,P)$ from the experimental isotherms leads in the low-temperature–low-coverage regime to a confirmation of the fact that a small fraction of ^{4}He gets adsorbed into well localized adsorption sites at corners and steps in the grafoil surface.

Table I shows that, e.g., on the $T=4.5$ K isotherm for $\Theta \lesssim 0.1$ ϵ_0 drops down to about $\epsilon_0/k_B=-150$ K, in good agreement with the binding energy of localized states determined from data on the entropy, the specific heat, and the chemical potential.[7] Recall that the binding energy for mobile states as determined by scattering from zero coverage surfaces is only $\epsilon_0/k_B=-140$ K.

The problem is left to correct the low temperature isotherms. Just adding the virial corrections is not enough. We have indications that the answer will come from the dispersion in $\epsilon_i(\vec{q})$ in (6) which we neglect completely in (8). In a preliminary calculation we have kept the term $\exp[-i(\vec{q}\,'-\vec{q})\cdot\rho]$ in (7). Retaining at low temperature the terms with $i=j=0$ only, we multiply (7) by $\Phi_0(z,\vec{q})$ and integrate over z to get

$$\epsilon_0(q)=\epsilon_0+\int q'dq'\left[\exp\left\{\beta\left[\epsilon_0(q')+\frac{\hbar^2q'^2}{2m}-\mu\right]\right\}\mp1\right]^{-1}$$
$$\times\int dz\,dz'\Phi_0^2(z,q)\Phi_0^2(z',q')\int\rho\,d\rho V_{\text{eff}}(z-z',\rho)[(2s+1)\pm j_0(q\rho)j_0'(q'\rho)]\;, \tag{21}$$

where $j_0(y)$ is a spherical Bessel function.

Fitting a Gaussian to the density $\Phi_0^2(z,q)$, as calculated from (8), one finds that the integrations over z to z' do little more than replace $V_{\text{eff}}(z-z',\rho)$ by $V_{\text{eff}}(0,\rho)$. With this approximation we solved (21) self-consistently and found that $\epsilon_0(q)$ drops by a few percent with increasing q. The resulting coverage calculated from (15) turns out to be too large now for all temperatures. This is not surprising because in going from (2) to (7) (for fermionic gas particles) we have dropped higher partial wave contributions in the K matrix which are known[11] to be repulsive. Also, in addition to the explicit q dependence in the exchange term in (21), there are similar factors present in the direct term in (2). We hope to investigate a dispersion relation like (21) derived directly from (2) in the near future.

As our theory is so far developed for highly mobile adsorbates only, one expects some difficulties close to the gas-solid and gas-(registered gas) transitions. We are currently working to extend our theory into these regions using the approach outlined in the Appendix of Ref. 8. This also seems to become important in view of the band-structure effects found by Carlos and Cole.[6,2] These authors calculated the single-particle density of states for ^{3}He and ^{4}He adsorbed on graphite in the zero coverage limit, i.e., neglecting the He-He interaction completely. They found that the density of states develops a gap of 11.1 K$\leq E/k_B \leq 17.5$ K for ^{4}He-C and at 17.2 K$\leq E/k_B \leq 21.4$ K for ^{3}He-C. We have incorporated an approximate parametrization of their density of states into our mean-field equations (8). The low-temperature isotherms are not effected at all; the $T=12$ K and $T=15$ K isotherms are slightly depressed. However, some cautionary comments are called for at this stage, because the above band structure is calculated at zero coverage. One would expect considerable modification as the coverage builds up which could be incorporated in a mean-field approximation. Such a calculation has not been done to date.

B. ^{3}He on graphite

Before we discuss the isotherms for the ^{3}He-C system we point out that for Fermic-Dirac statistics monolayer saturation can be easily incorporated into the occupation functions (9) by introducing a momentum cutoff $q_j^{(c)}$ such that

$$\tilde{n}_j = 2(2\pi)^{-1}\sigma_g^2 \int_0^{q_j^{(c)}} q\,dq \left\{ \exp\left[\beta\left[\epsilon_j + \frac{\hbar^2 q^2}{2m} - \mu\right]\right] + 1 \right\}^{-1}$$
$$= (\sigma_g/\lambda_{\mathrm{th}})^2 \ln\left[(1+e^{-\beta(\epsilon_j-\mu)}) \Big/ \left\{ 1+\exp\left[-\beta\left[\epsilon_j - \mu + \frac{\hbar^2 q_j^{(c)2}}{2m}\right]\right] \right\} \right], \qquad (22)$$

which would lead at zero temperature to a two-dimensional number density $q_j^{(c)2}/2\pi$ in the jth adlayer which should be equal to $n_{\max}=0.107$ Å^{-2}. We have calculated the thermodynamic functions of the ^{3}He-C system from (8) without a cutoff and with a cutoff in the occupation functions.

In Fig. 4 we give the single-particle energies ϵ_i, the coverage Θ, and the adlayer positions $\bar{z}_i$ as a function of T for a fixed pressure P. Contrary to the ^{4}He-C system the single-particle energies ϵ_i can now cross the chemical potential μ without introducing a singularity in $\tilde{n}_i$. Without a momentum cutoff the occupation of the lowest bound state ϵ_0 rises continuously and, indeed, above the experimentally known saturation density $n_{\max}=0.107$ Å^{-2} of the first monolayer. Introducing the momentum cutoff via (22) avoids this situation and, indeed, flattens $\Theta=\Theta(T)$ for $T\leq 7$ K down to $T\sim 3$ K below which a second layer starts to fill up. Although this is a nice qualitative feature it is not too meaningful to ^{3}He-C because the adsorbate undergoes a gas-solid phase transition[1] in this temperature regime which cannot be handled by (8).

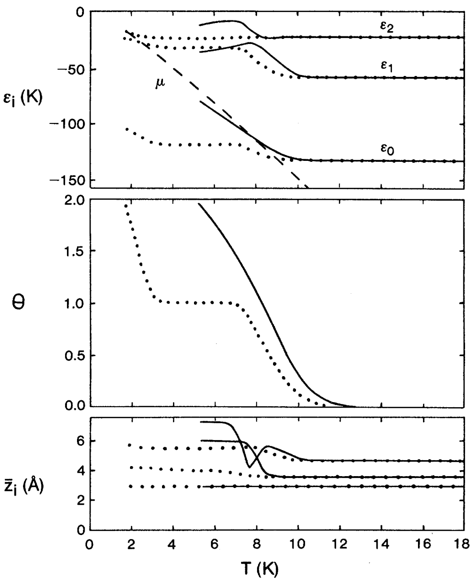

FIG. 4. Lowest three single-particle energies ϵ_i from (8), coverage Θ from (15), and mean positions $\bar{z}_i$ for ^{3}He-C at $P=1.33$ Pa. Chemical potential μ from (4). Solid line: without a cutoff in $\tilde{n}_i$. Dotted line: with a cutoff in $\tilde{n}_i$ according to (22).

In Fig. 5 we present some isotherms Θ vs $T\log_{10}P$, again calculated with and without a momentum cutoff, to be interpreted as lower and upper bounds. Also given are the isotherms as calculated from the virial expansion[1] of the chemical potentials (17) and (18) keeping $\epsilon_0/k_B=-135$ K fixed. Unfortunately we have not found any measured isotherms for ^{3}He-C in the literature with which we could compare our theory.

III. SPECIFIC HEAT

A. ^{4}He on graphite

Within the mean-field theory the entropy of a system of particles obeying Bose-Einstein statistics is given by

$$S/k_B=\sum_{\vec{i}}(1+n_{\vec{i}})\ln(1+n_{\vec{i}})-\sum_{\vec{i}}n_{\vec{i}}\ln n_{\vec{i}}\ , \tag{23}$$

where the single-particle energies are

$$E_{\vec{i}}=\epsilon_i(\vec{q})+\frac{\hbar^2q^2}{2m}\ .$$

In arriving at the one-dimensional Hartree-Fock equations (8) we have neglected the $\vec{q}$ dependence of $\epsilon_i(\vec{q})$ in order to perform an average over the lateral degrees of freedom of the adsorbate particles along the surface. Within this approximation we can evaluate (23) and get

$$S=\frac{L^2}{N}\frac{2\pi mk_BT}{h^2}\times\sum_i\int_{e^{\beta(\epsilon_i-\mu)}-1}^{\infty}dy\left[\frac{\ln(y+1)}{y}-\frac{\ln y}{y+1}\right]\ . \tag{24}$$

To calculate the specific heat at constant area or adsorbate density

$$\frac{C_A}{k_B}=-\beta\frac{d}{d\beta}\left[\frac{S}{Nk_B}\right]\Bigg|_A \tag{25}$$

we must fix the chemical potential μ for N adsorbed particles via

$$N=\sum_{i,\vec{q}}\left\{\exp\left[\beta\left[\epsilon_i-\mu+\frac{\hbar^2q^2}{2m}\right]\right]-1\right\}^{-1} \tag{26}$$

or

$$\frac{N}{L^2}=-\frac{2\pi mk_BT}{h^2}\sum_i\ln(1-e^{-\beta(\epsilon_i-\mu)})\ . \tag{27}$$

The specific heat (25) as calculated from (24) and (27) does not include the two-dimensional virial corrections calculated by Schick and co-workers[1] but accounts properly for the possible excitation of gas particles into the higher bound states ϵ_i in the effective, coverage-dependent surface potential (15), i.e., for the perpendicular degree of freedom of the adsorbate. The latter can, of course, not be included in a two-dimensional theory. Elgin and Goodstein[7] have identified this contribution by subtract-

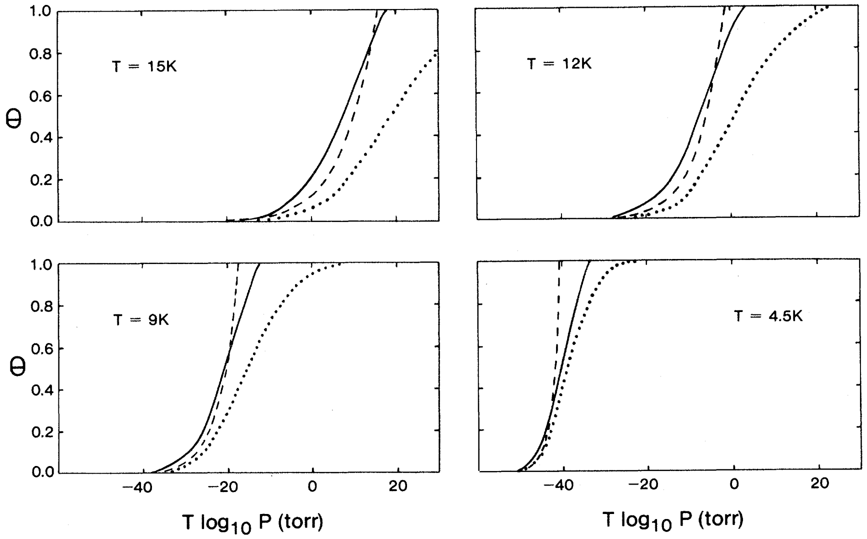

FIG. 5. Isotherms for ^{4}He-C. Dashed line: virial theory according to (17) and (18). Dotted line: mean-field theory with cutoff. Solid line: mean-field theory without a cutoff.

ing from their measured specific heat the contribution, including quantum and virial corrections, calculated for a two-dimensional gas restricted to the ground-state ϵ_0 only, i.e.,

$$\Delta C = C(\text{expt}) - C(2\text{D}) \ . \tag{28}$$

They have then argued that ΔC is mainly determined by the first excited state ϵ_1 so that, in the classical limit, it is given by the Eucken formula

$$\Delta C = \left[\frac{(\epsilon_1 - \epsilon_0)/2k_B T}{\cosh[(\epsilon_1 - \epsilon_0)/2k_B T]} \right]^2 . \tag{29}$$

Trying to fit their experimental data for $0.35 < \Theta < 0.61$ they are led to identify[7]

$$(\epsilon_1 - \epsilon_0)/k_B = 54 \text{ K} \quad \text{for } 0.35 < \Theta < 0.61 \ . \tag{30}$$

Scattering experiments on zero coverage surfaces have in the meantime measured[2,12]

$$(\epsilon_1 - \epsilon_0)/k_B = 66 \text{ K} \quad \text{for } \Theta = 0 \ . \tag{31}$$

The explanation for this difference, as it arises from our mean-field theory, is contained, e.g., in Figs. 1 and 2 which say that as the coverage builds up the lowest energy eigenvalue ϵ_0 moves up to avoid crossing the chemical potential μ, decreasing the difference $(\epsilon_1 - \epsilon_0)$. The experimentally determined excess specific heat due to the perpendicular excitations of the adsorbate in the surface potential with the curves as calculated from mean-field theory is given in Fig. 6. However, we should mention that (29) applied to the present system is only correct to within 10 to 20% because (a) quantum correction for a two-level system reduces (29) for $T \lesssim 15$ K by that amount, and (b) excitations into the higher bound-state levels add about twice that; see dashed curves in Fig. 6. Contrary to (29) the excess specific heat as calculated from mean-field theory is coverage dependent. Its values at $\Theta = 0.35$ and $\Theta = 0.61$ bracket the experimental data perfectly for $T > 7$ K. The fact that $\Delta C < 0$ for $T < 7$ K is attributed by Elgin and Goodstein[7] to inhomogeneities on the grafoil surfaces. A likely explanation is also provided by Carlos and Cole[6] who have shown that the gap in the single-particle density of states due to band-structure effects leads to a depression in the specific heat at about half the gap energy. Because their band-structure calculations are done at zero coverage a qualitative comparison with experimental data on C is not too meaningful. Carlos and Cole calculated C at finite coverage neglecting the He-He interaction completely. They find that for a given temperature $T < 20$ K C decreases for larger Θ, contrary to the mean-field result contained in Fig. 6. It would be very interesting to see whether a band-structure calculation including the He-He interaction in mean-field approximation would reduce this coverage dependence of C. Before such a calculation is done a reexamination of experimental data without reference to a coverage-independent model would be very desirable.

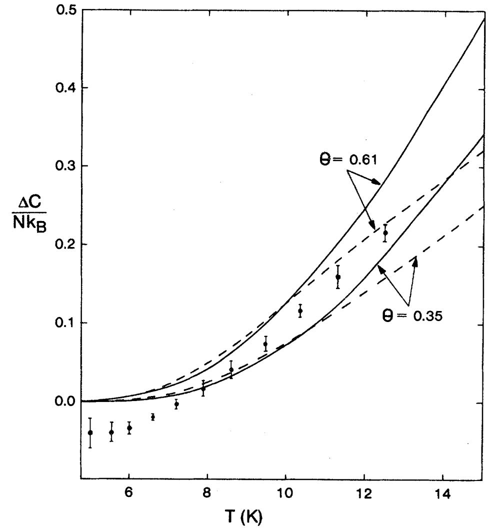

FIG. 6. Excess specific heat for ^{4}He-C due to perpendicular degrees of freedom. Data points from Elgin and Goodstein (Ref. 7). Solid line: mean-field theory. Dashed line: Eucken formula (29) with ϵ_0 and ϵ_1 from mean-field theory.

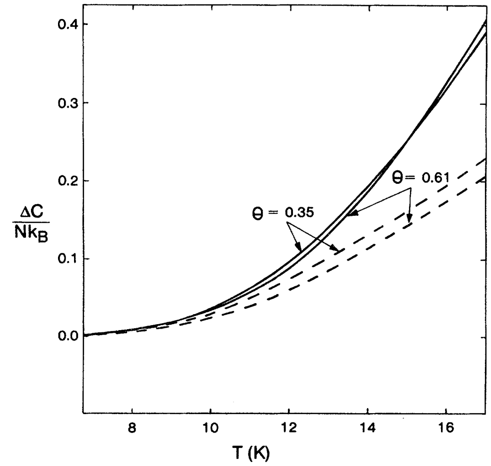

FIG. 7. Excess specific heat for ^{3}He-C due to perpendicular degrees of freedom. Solid line: mean-field theory. Dashed line: Eucken formula (29) with ϵ_0 and ϵ_1 from mean-field theory without cutoff.

B. ^{3}He on graphite

The ^{3}He-C system should also show an excess specific heat due to excitations into the higher bound states of the surface potential. Our predictions (without cutoff) are given in Fig. 7. Because $(\epsilon_0-\epsilon_1)$ changes little as a function of coverage $\Delta C/Nk_B$ stays the same for Θ varying from 0.35 to 0.61, though the Eucken formula (29) (dashed curves in Fig. 7) underestimates $\Delta C/Nk_B$ because of contributions from excitations into higher bound states. Overall the excess specific heat in the ^{3}He-C system is less at a given temperature than in the ^{4}He-C system because $(\epsilon_0-\epsilon_1)$ is larger in the former.

IV. ISOSTERIC HEAT OF ADSORPTION

The isosteric heat of adsorption per particle is defined as

$$Q=k_BT^2\,\frac{\partial(\ln P)}{\partial T}\Bigg|_{\Theta}\;. \qquad (32)$$

With Θ given in (15) this can be written as

$$Q=\left\{\sum_{\vec{j}} n_{\vec{j}}(1-n_{\vec{j}})\left[\tfrac{5}{2}k_BT-E_{\vec{j}}+T\left[\frac{\partial E_{\vec{j}}}{\partial T}\right]_P\right]\right\}\Bigg/\left\{\sum_{\vec{i}} n_{\vec{i}}(1-n_{\vec{i}})\left[1-\frac{P}{k_BT}\left[\frac{\partial E_{\vec{j}}}{\partial P}\right]_T\right]\right\}. \qquad (33)$$

Because the higher bound states $i>0$ have negligible occupation for $\Theta<1$ and $T\lesssim 20$ K (33) can be approximated quite well by

$$Q\approx\left[-\epsilon_0+\tfrac{5}{2}k_BT+T\left[\frac{\partial\epsilon_0}{\partial T}\right]_P\right]\Bigg/\left[1-\frac{P}{k_BT}\left[\frac{\partial\epsilon_0}{\partial P}\right]_T\right]\approx-\epsilon_0+\tfrac{3}{2}k_BT\;. \qquad (34)$$

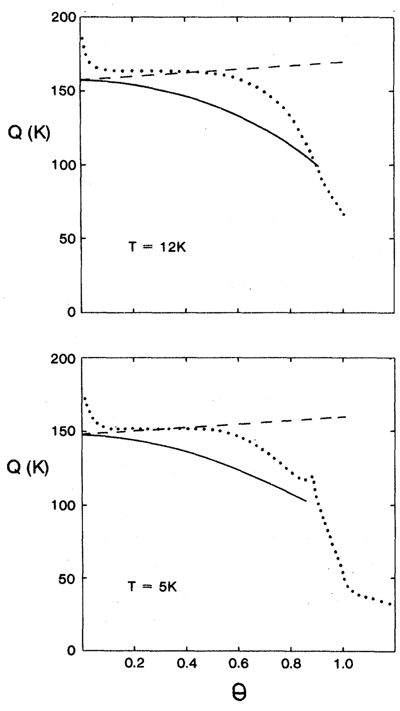

FIG. 8. Isosteric heat of adsorption Q (32) for ^{4}He-C. Dotted line: experimental data from Elgin and Goodstein (Ref. 13). Dashed line: virial theory (35). Solid line: mean-field theory.

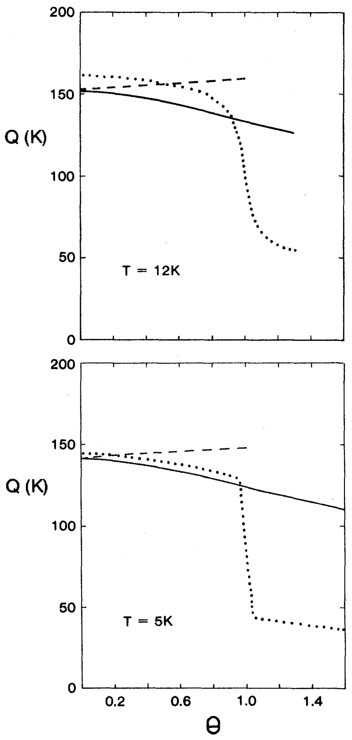

FIG. 9. Isosteric heat of adsorption Q (32) for ^{3}He-C. Dashed line: virial theory (35). Solid line: mean-field theory without a cutoff. Dotted line: mean-field theory with a cutoff.

A. ^{4}He on graphite

Data on the isosteric heat of adsorption for ^{4}He adsorbed on grafoil have been reported by Elgin and Goodstein.[13] They are plotted in Fig. 8 together with our mean-field results for $T=5$ and 12 K as calculated from (32). The rise in the experimental data for small Θ has been attributed to localized adsorption sites at edges of grafoil platelets, an effect that is not induced in our mean-field theory. The plateau in Q for $0.2<\Theta<0.6$ is not reproduced too well by our theory, indicating again that the dispersion $\epsilon_i(\vec{q})$ in (6) should be included at the next stage of the theory. This is also suggested by a calculation of Q from the virial expansion, i.e., from (17) and (18). One gets

$$Q_{\text{virial}}=-\epsilon_0+\tfrac{3}{2}k_BT-k\sum_{l=1}^{\infty}\frac{l+1}{l}\Theta n_{\max}\left.\frac{dB_{l+1}}{d(1/T)}\right|_{\Theta}. \tag{35}$$

Q_{virial} rises as a function of Θ.

B. ^{3}He on graphite

In Fig. 9 we have plotted the isosteric heat of adsorption Q calculated without and with a cutoff in the occupation functions (22), solid and dotted lines, respectively. Saturation in the latter case leads to the characteristic drop in Q around monolayer completion.

V. CONCLUDING REMARKS

Though mean-field theory as developed in Ref. 8 and used in this paper seems to be capable of reproducing most of the qualitative and some of the quantitative features of isotherms, heats of adsorption, and excess specific heat, a great deal remains to be done: (a) The reduction of (2) to (8) should be avoided to be able to account properly for the dispersion (6) which in turn should lead to monolayer saturation. (b) Band-structure effects so far calculated by Carlos and Cole[7] at zero coverage, should be included self-consistently in the mean-field approach. The energy gap in the single-particle density of states shoud be partially responsible for saturation. (c) Taking the lattice periodicity of the basal plane of graphite into account, at least the transition to the registered gas phase should come out of the mean-field theory.

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[*] On leave of absence from Maria-Curie-Sklodowska University, Lublin, Poland.

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