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Isotherms of Mobile and Localized Ideal Quantum Gases Adsorbed on Crystalline Substrates*

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A translational band model is applied to the calculation of adsorption isotherms of noninteracting fermions and bosons adsorbed on a crystalline surface. The theory yields analytic expressions for the vapor pressure as a function of temperature and monolayer coverage, in terms of the band parameters of the adsorption system. In the case of fermions, the actual band widths and band gaps can be mapped by a low-temperature isotherm, which will display multiband steps analogous to the multilayer steps of interacting adatoms. The significance of "mobility" and "localization" is discussed, and it is argued that the words have physical meanings only in terms of comparisons between the dwell time of an atom on a specific site and a characteristic time of the experiment in question. In the case of adsorption isotherms, the experimental time is related to the vapor pressure, and the band theory offers a criterion for mobility in terms of the energy spectrum of the adsorbed atoms. Numerical estimates indicate that helium monolayers satisfy the criterion for mobility at 4 °K and below, but that Ar and N_2 monolayers may be localized at 77 °K. The isotherms of all physically adsorbed systems satisfy the criterion for mobility at sufficiently low temperatures. In contrast to the heat capacity, isotherms in the localized and mobile regimes are not qualitatively different. The effects of interactions among the adatoms and of surface inhomogeneities are briefly discussed.

I. INTRODUCTION

Current experimental studies[1,2] of helium films indicate that the first adsorbed helium monolayer can retain a considerable degree of surface mobility at temperatures down to 0.1 °K. The low-temperature mobility is interpreted as evidence of rapid tunneling among the individual adsorption sites of the substrate.[3] A band theory of the surface states has been used to calculate the heat capacity of noninteracting fermions and bosons[4] and of hard-sphere adatoms at moderate- to high-surface densities.[5]

Attention has been drawn to other properties of the helium-surface system. Widom[6] has shown that the details of atomic scattering may be analyzed to yield the density of states of an adsorbed film. In the present paper, we study the vapor pressure of adsorbed fermions and bosons from the standpoint of the band theory, and show how the structure of the energy bands influences, and in the case of fermions can be deduced from, the adsorption isotherms.

The previous application of the band model to a calculation of monolayer heat capacities made use of numerical techniques.[4] The present study of adsorption isotherms is analytic in nature.

II. BAND STRUCTURE

Assume a crystalline solid possessing N_S equivalent adsorption sites on its surface. If the potential barriers between adjacent sites are arbitrarily high, an adsorbed atom is completely localized at a specific site, where it can occupy one of several bound-state energy levels of sharply defined energy. Each energy level is N_S-fold degenerate, since the sites are equivalent. In all physical systems, the barriers between sites have finite heights and widths, and therefore the lifetime of an adatom in any given site is finite due to tunneling. The finite lifetime lifts the degeneracy of each localized level, broadening it into an energy band of N_S translational states. When the bandwidths are less than the interband gaps, the energy spectrum of the adatoms will have the structure shown in Fig. 1.

For thermodynamic calculations, we require a knowledge of the interband gaps and densities of states in each of the bands. Subsequent calculations will be made according to this implicit knowledge, but we will also assume an explicit simple spectrum for illustrative examples. The simple model is based on the assumption of a square array of sites, for which the single-particle energy-momentum dispersion relation is

$$\epsilon_i(k) = \epsilon_i^{(0)} - \alpha_i - 2\gamma_i \cos ak_x - 2\gamma_i \cos ak_y , \quad (1)$$

where $\epsilon_i(k)$ is the single-particle energy in the ith band, $\epsilon_i^{(0)}$ is the energy of the original unperturbed level, $\hbar k_x$ and $\hbar k_y$ are the components of momenta, and a is the edge length of the surface net. The constants α_i and γ_i are the usual matrix elements of the delocalizing perturbing potential for each band. For momenta near the bottom

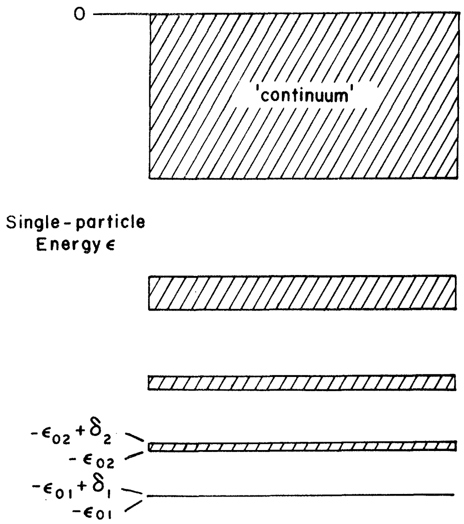

FIG. 1. Band structure of an ideal monolayer.

of each band, we expand the energy to obtain

$$\epsilon_i(k) = -\epsilon_{0i} + \gamma_i k^2 a^2 \quad , \tag{2}$$

where ϵ_{0i} is now the binding energy of the lowest translational state in the ith band, and $k^2 = k_x^2 + k_y^2$. The effective mass near the bottom of the band is

$$m^*_{i\,k=0} = \hbar^2 \left(\frac{\partial^2 \epsilon_i}{\partial k^2}\right)^{-1} = \frac{\hbar^2}{2\gamma_i a^2} \quad . \tag{3}$$

The effective mass varies over the width of the band, but we will make the "standard" effective mass approximation that it remains constant at its average value m_i^* throughout each band, for this will enable us to display the general features of the model in explicit calculations. We can express m_i^* and the density of states $g_i(\epsilon)$ in terms of the bandwidth δ_i, the total number of sites N_S, and the surface area A. For particles with nuclear spin degeneracy g_n,

$$\int_{-\epsilon_{0i}}^{-\epsilon_{0i}+\delta} g_i(\epsilon)\, d\epsilon = g_n N_s \quad . \tag{4}$$

For quasiparticles of effective mass m_i^*,

$$g_i(\epsilon) = 2\pi A g_n m_i^* / h^2 ; \quad -\epsilon_{0i} \leqslant \epsilon \leqslant -\epsilon_{0i} + \delta_i \, . \tag{5}$$

Hence if m_i^* is constant, $g_i(\epsilon)$ is uniform throughout each band and, using Eqs. (4) and (5), is given by

$$g_i(\epsilon) = g_n N_s / \delta_i \quad . \tag{6}$$

Our procedure will be first to calculate the thermodynamic properties – principally the vapor pressure – of noninteracting fermions and bosons having the band structure just described, to develop a mobility criterion applicable to the gas-film system, and then to explore some consequences of introducing interactions among the adatoms.

III. VAPOR PRESSURES

The total number $N_\pm$ of adsorbed fermions (+) or bosons (−) is the sum of the equilibrium populations in each band i:

$$N_\pm = \textstyle\sum_i N_{i\pm} \quad , \tag{7}$$

$$\text{where} \quad N_{i\pm} = \int_{-\epsilon_{0i}}^{-\epsilon_{0i}+\delta_i} \frac{g_i(\epsilon)\, d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} \quad , \tag{8}$$

where μ is the chemical potential. Using the density of states Eq. (6), the band occupations are

$$N_{i\pm} = \pm \frac{g_n N_s}{\beta \delta_i} \ln \left(\frac{e^{-\beta\mu} \pm e^{\beta\epsilon_{0i}}}{e^{-\beta\mu} \pm e^{\beta(\epsilon_{0i}-\delta_i)}} \right) . \tag{9}$$

The absolute activity $\lambda = e^{\beta\mu}$ of each band is

$$\lambda_\pm = \pm\, e^{-\beta\epsilon_{0i}} (\alpha_{i\pm} - 1)/(1 - \alpha_{i\pm} e^{-\beta\delta_i}) , \tag{10}$$

$$\text{where} \quad \alpha_{i\pm} = \exp(\pm \beta\delta_i N_{i\pm} / g_n N_s) \; .$$

The particles in each band and in the vapor have the same chemical potential. If the vapor is sufficiently dilute as to be treated as an ideal classical gas, we obtain the vapor pressure p in the gas:

$$p = \pm \left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{e^{-\beta\epsilon_{0i}}(\alpha_{i\pm} - 1)}{\beta^{5/2}(1 - \alpha_{i\pm} e^{-\beta\delta_i})} \quad . \tag{11}$$

The character of the adsorption isotherm is distinctly different in the Fermi and Bose systems, and will be discussed separately in Secs. III A and III B, respectively.

A. Fermions

It is convenient to describe the band occupations in terms of the fractional occupations θ_i:

$$\theta_i \equiv N_i / g_n N_s \quad , \tag{12}$$

where for fermions, $0 \leqslant \theta_i \leqslant 1$. Then the adsorption isotherm for each band is, according to Eq. (11),

$$p(\theta_i) = A_i (e^{\beta\delta_i\theta_i} - 1)/(1 - e^{-\beta\delta_i(1-\theta_i)}) \; , \tag{13}$$

where $A_i = (2\pi m/h^2)^{3/2} e^{-\beta\epsilon_{0i}}/\beta^{5/2}$.

The isotherm for a well-isolated band is qualitatively similar to the Langmuir isotherm[7,8] owing to the limited capacity of the band for fermions. Expanding Eq. (13) about $\theta_i = 0$, we see that the initial portion of the isotherm for each band is linear:

$$p(\theta_i \ll 1) \cong A_i \beta\delta_i \theta_i /(1 - e^{-\beta\delta_i}) \ . \tag{14}$$

As the coverage increases, the pressure rises more rapidly and becomes exponential as $\theta_i \to 1$. Figure 2 displays the fermion isotherm, Eq. (13).

In the case of a band whose width is much less than kT, the single-band isotherm is formally identical to the Langmuir isotherm: Eq. (13) yields, on expansion,

$$p \cong A_i \theta_i/(1 - \theta_i)\ ; \quad \beta\delta_i \ll 1 \ . \tag{15}$$

In the opposite limit of a relatively wide band, the isotherm approaches a pure exponential:

$$p \cong A_i e^{\beta\delta_i\theta_i}\ ; \quad \beta\delta_i \gg 1. \tag{16}$$

The dominant parameter controlling the pressure at which a particular band begins to fill is the energy of the bottom of the band. If bands are relatively narrow and well separated, then the adsorption isotherm can show steps resembling those that correspond to multilayer formation,[9] and the form of the multiband isotherm is similar to the isotherms of classical adatoms with interactions.[10,11] In the present theory, however, the steps result from the purely statistical interactions of ideal fermions; there are no layers in the usual sense. Using the low-coverage expression Eq. (14), we can determine the condition for the appearance of distinct multiband steps. For uniform band densities,

$$e^{\beta(\epsilon_{01} - \epsilon_{02})}(\delta_2/\delta_1)(1 - e^{-\beta\delta_1})/(1 - e^{-\beta\delta_2}) \gg 1, \tag{17}$$

where the indices 1, 2 refer to any two adjacent bands, with $\epsilon_{01} > \epsilon_{02}$. According to Eq. (17), multiband steps appear whenever the temperature is low in comparison to the interband gaps. The bandwidths δ_1 and δ_2 appear in Eq. (17) owing to their influence on the densities of states in the bands. For relatively high temperatures, $\beta\delta_{1,2} \ll 1$, the bandwidth factors cancel and only the first factor remains.

The preceding isotherms correspond to uniform densities of states in the individual bands. If $g(\epsilon)$ is an unknown arbitrary function it is, in principle, possible to determine the actual density of states by a low-temperature isotherm. In the limit of very low temperatures, the fermions occupy all low-lying states up to a Fermi level of energy $\epsilon_F = \mu_0$. The Fermi level at $T = 0$ is given by an integral over all states up to ϵ_F. At finite temperatures $T \ll \mu/k$, we can expand the equation for particle number N in a familiar manner[12]:

$$N = \int_{-\infty}^{0} \frac{g(\epsilon)d\epsilon}{e^{\beta(\epsilon - \mu)} + 1} = \int_{-\infty}^{\mu} g(\epsilon)d\epsilon + \tfrac{1}{6}\pi^2(kT)^2 \left(\frac{\partial g(\epsilon)}{\partial\epsilon}\right)_{\mu} + \cdots \ . \tag{18}$$

In contrast to the conventional treatment for the heat capacity of a degenerate Fermi gas, we now differentiate with respect to particle number instead of T: The first term in the expansion is dominant, and we obtain simply

$$g(\mu) = \frac{p}{kT}\left(\frac{\partial p}{\partial N}\right)_T^{-1} \ . \tag{19}$$

Hence, the effective density of states of noninteracting particles can be mapped by a low-temperature fermion isotherm.

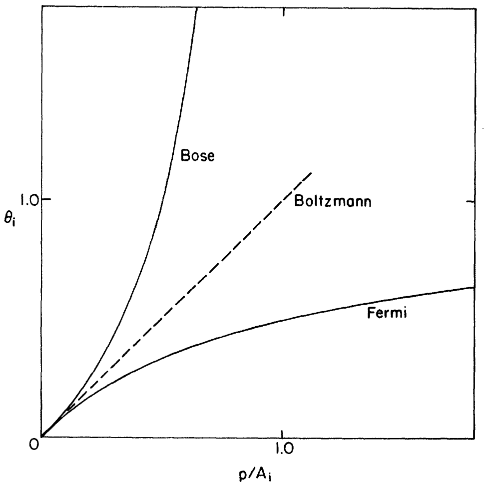

FIG. 2. Single-band isotherms of ideal monolayers.

B. Bosons

Although the band states can accept unlimited numbers of bosons, it is still convenient to use the occupation factors $\theta_i = N_i/g_n N_S$ as in Sec. III A.

The boson isotherm according to Eq. (11) is

$$p = \frac{A_i(1 - e^{-\beta\delta_i\theta_i})}{1 - e^{-\beta\delta_i(\theta_i + 1)}} \ , \tag{20}$$

where A_i is the same as defined in Eq. (13). It is readily seen that the isotherm begins with a linear dependence on θ_i, as for fermions. However, in this case the pressure rises less steeply as the occupation increases and tends to the finite value A_i as $p \rightarrow \infty$. The finite asymptotic pressure is a result of the statistical attraction between bosons: Although momentum ordering does not occur at finite temperatures in systems having uniform densities of states, the statistical interaction dominates the isotherm behavior at high densities. Equation (20) is displayed in Fig. 2.

Owing to the infinite capacity of every band, we cannot obtain a stepwise multiband isotherm for noninteracting bosons. Thus, a boson isotherm will not map out the density of states, although it can be used to determine the density of states near the bottom of the lowest band.

In the narrow band limit $\beta\delta_i \ll 1$, the isotherm takes the simple form

$$p = A_i[\theta_i/(1+\theta_i)] \quad . \tag{21}$$

IV. MOBILE AND LOCALIZED ADSORPTION

In the band theory of monolayer heat capacity,[4] it was shown that the "transitions" between mobile and localized adsorption are clearly evidenced in the temperature dependence of the specific heat. If mobility is judged purely from the nature of the specific heat, then the criteria are, for single particles,

$$\begin{aligned} &\text{“thermal mobility”} : \Delta/kT \gtrsim 1 \ , \\ &\text{“quantum mobility”} : \delta/kT \lesssim 1, \end{aligned} \tag{22}$$

where Δ is the energy gap between the lowest band and the next higher "thermal" band. An important additional condition, not explicitly discussed in the theory of the heat capacity, is the assumption that the characteristic time τ_{expt} of the experiment is much longer than the equilibrium time of the system. This condition, which must always be satisfied in measurements of the heat capacity, has a special significance in studies of quantum mobility. Since the lifetime τ_t of an adatom in a specific site due to tunneling in the lowest band is directly related to the bandwidth δ and the temperature $\sim T_\delta$ of the heat-capacity peak due to quantum mobility, the experiment must satisfy

$$\tau_{\text{expt}} \gtrsim \hbar/kT_\delta \tag{23}$$

in order for quantum mobility to be observed. If, on the other hand, a specific-heat experiment were to be performed so rapidly that $\tau_{\text{expt}} \ll \tau_t$, then a monolayer would appear to be "localized" even at $T \ll T_\delta$. Thus, it can be seen that localization does not have any absolute significance except as the limiting condition of physically unreal, i.e., classical, models: To the same degree, it is profitless to identify mobility with the dynamical properties of a monolayer adsorbed on a mathematically plane surface. "Mobility" and "localization" can have relevant meanings only in terms of comparisons between the migration time of an atom and the characteristic time of observation of a particular experiment.

In the case of specific-heat studies, quantum mobility can be observed at sufficiently low temperatures if the experiment is performed slowly enough. In vapor-pressure measurements, however, the experimental time is not normally under the control of the experimenter, but is determined by the system itself. The measured vapor pressure $p(T)$ is determined by the conditions of vapor-film exchange at the monolayer surface, and to the extent that the vapor pressure is influenced by the degree of translational mobility of the monolayer, the vapor pressure will correspond to mobility or localization: If the characteristic time for vapor-film equilibrium is rapid in comparison to the site lifetime, then the monolayer will present to the gas phase an array of essentially fixed atoms: In the opposite extreme, the monolayer is effectively mobile. Vapor-film equilibrium can be characterized by the mean time τ_c between impacts of vapor molecules on a single adsorption site, which in equilibrium is comparable to the mean dwell time of an atom on the surface. (Here we ignore difficulties associated with the internal equilibrium time of the vapor, the sticking coefficient, the fraction of impacts perfectly reflected from the surface, and the speed with which inelastic energy exchanges can be equilibrated through the substrate.) The impact time can be easily obtained for a classical ideal gas on a site of area $a_s = A/N_s$:

$$\tau_c = (2\pi mkT)^{1/2}/a_s p \quad . \tag{24}$$

The site lifetime τ_t has already been given for a monolayer at temperatures so low that only the lowest band is occupied. Since we will be concerned with the distinction between localized and mobile isotherms at all temperatures, we must also determine the temperature dependence of the site lifetime. In the low-temperature regime, particles can migrate by tunneling only through the lowest band, but as the temperature rises, thermally excited particles can diffuse via faster, i.e., wider bands. The net site lifetime is the inverse of the unit-time probability W due to escape via all bands, and W is the weighted thermal average of the escape probabilities $W_i \simeq \delta_i/\hbar$. Hence, at finite temperature,

$$\langle \tau_t \rangle = \hbar \sum_i e^{-\beta\epsilon_i} / \sum_i \delta_i e^{-\beta\epsilon_i} \ , \tag{25}$$

where, for simplicity, we have assumed relatively narrow bands and Boltzmann statistics. Thus, Eqs. (24) and (25) can be used to estimate the characteristic time of vapor-film equilibrium and site lifetime to test the mobility criterion, which is

$$\tau_c = \langle \tau_t \rangle \ . \tag{26}$$

When we now turn to the isotherms of Sec. III to apply the mobility criterion, we find that these isotherms have been based upon the implicit assumption of mobility at all temperatures. This is because the calculations were done completely in terms of translational band states with time-independent coefficients, and no allowance was made for the evolution time from localized to translational quantum states. Thus, the monolayers were treated in terms of complete internal equilibrium states, independent of the magnitudes of the bandwidths and energy gaps of the excitation spectrum, as if Eq. (26) were satisfied at all temperatures.

V. ISOTHERMS IN THE LOCALIZED REGIME

It is now natural to investigate what changes occur in the isotherms upon passage to the localized regime. Although localized adsorption isotherms are presented in several standard works[7,13] on statistical mechanics, it will be useful to reexamine them here, in the context of the energy spectrum of Fig. 1.

We will consider four distinct cases of localized adsorption: ideal Bose and Fermi adatoms without interactions, and adatoms with hard-core interactions that limit occupancy to 0 or 1 atom per site. In all cases, we will assume that the energy-level structure within each site consists of a set of discrete levels having energies $-\epsilon_i$ relative to the potential energy of atoms in the gas phase. The discrete levels may have finite lifetimes due to evaporation or tunneling, in which case they have finite energy widths. For present purposes, the broadening will be left implicit in the single-particle partition function z_i corresponding to the ith level in a site.

The N_i atoms in each quantum state are, in principle, distinguishable from those in other states, and hence the Helmholtz free energy of the adsorbed phase is

$$F = -kT \ln \left(\Pi_i Q(N_s, N_i) z_i^{N_i} \right) , \tag{27}$$

where $Q(N_S, N_i)$ is the degeneracy factor for the number of distinct configurations of N_i particles among N_S sites. Therefore, the free energy is the sum of contributions from each quantum species:

$$F = \sum_i F_i ; \quad F_i = -kT \ln \left(Q(N_s N_i) z_i^{N_i} \right) . \tag{28}$$

A. Ideal Localized Bosons

In this case, the configuration factor for unrestricted occupancy of sites and localized levels is, for each quantum species,

$$Q(N_s, N_i) = (N_s + N_i - 1)!/N_i!(N_s - 1)! \ . \tag{29}$$

The free energy is then a sum of terms of the form

$$F_i/kT = -(N_s + N_i)\ln(N_s + N_i) + N_i \ln N_i + N_s \ln N_s - N_i \ln z_i \ . \tag{30}$$

The chemical potential of the ith species is

$$\mu_i = \left(\frac{\partial F_i}{\partial N_i} \right)_{T, N_j \neq N_i} = kT \ln \left[\left(\frac{N_i}{N_s + N_i} \right) z_i^{-1} \right] . \tag{31}$$

Equation (30) is strictly correct only for low occupancy of any single quantum state, being based on the Boltzmann approximation. With this approximation, we can equate the chemical potential for each quantum species to that in the gas phase, in which all particles are assumed indistinguishable. Thus, at equilibrium, the (ideal-gas) pressure in the vapor is

$$p = (2\pi m/h^2)^{3/2} (\beta^{5/2} z_i)^{-1} \theta_i / (1 + \theta_i) \ , \tag{32}$$

where $\theta_i = N_i/N_S$.

Comparing Eq. (32) with the narrow-band approximation Eq. (21) for bosons, we see little to distinguish between mobile and localized regimes. There are indeed differences between the narrow- and wide-band isotherms, but the changes are gradual with temperature, and do not show any conspicuous features such as are seen in the monolayer heat capacity.

B. Ideal Localized Fermions

The Pauli exclusion principle prevents the multiple occupation of individual localized energy levels, but a single site may contain particles in different levels. If we take account of a nuclear spin degeneracy g_n, then the maximum capacity of the surface is $g_n N_S$ for each species: The configuration factor is

$$Q(N_s, N_i) = (g_n N_s)!/N_i!(g_n N_s - N_i)! \quad . \tag{33}$$

Now we obtain the vapor pressure

$$p = (2\pi m/h^2)^{3/2}(\beta^{5/2} z_i)^{-1}\theta_i/(1 - \theta_i) \quad . \tag{34}$$

Thus, as for the boson isotherm, we find little difference between the localized fermion isotherm and that for mobile fermions in the narrow band limit, Eq. (15).

C. Site Exclusion

In all cases of physical interest, each site can localize no more than a single particle in the first adsorbed monolayer. This site exclusion can be attributed to a repulsive δ-function interaction between particles on specific sites denoted by s_m, s_n: $u(s_m, s_n) = \delta(s_m - s_n)$. The number of distinguishable configurations is then

$$\Pi_i\, Q(N_s, N_i) = N_s!/(N_s - N)!\, \Pi_i\, N_i! \, . \tag{35}$$

Proceeding as before, the vapor pressure is

$$p = (2\pi m/h^2)^{3/2}(\beta^{5/2} z_i)^{-1}\theta_i/(1 - \theta). \tag{36}$$

The partition function z_i is now correctly given by the Boltzmann limit, since it is impossible to have more than one particle in any one of the localized quantum states of a site. Hence, there is no distinction between fermions and bosons in the case of site exclusion. Summing over all species, $\theta = \sum_i \theta_i$, Eq. (36) yields

$$p = (2\pi m/h^2)^{3/2}(\beta^{5/2} \textstyle\sum_i z_i)^{-1}\theta/(1 - \theta) \, . \tag{37}$$

Equation (37) is a variant of the Langmuir isotherm: In the usual treatments, there are no distinctions among the quantum species.

VI. DISCUSSION

Older theories of adsorption neglect tunneling. As a consequence, surface diffusion appears to arise only from the thermal activation of adatoms to energies greater than the lateral binding to specific sites. Accordingly, monolayers have been considered relatively mobile at temperatures well above the characteristic temperature for activated diffusion, and localized when substantially colder. The present theory, however, yields a more complicated criterion to distinguish between mobility and localization; a comparison between the characteristic time of gas-film relaxation and of the lifetime in a specific surface site.

We will now apply the mobility criterion to two physical systems of interest: helium adsorbed on argon-plated copper at $T \lesssim 4$ °K, and argon adsorbed on graphite at 77 °K. The width of the lowest band of helium adsorbed on argon-plated copper is estimated to be at least several °K,[1] corresponding to $\tau_t < 10^{-11}$ sec. For a nearly completed He^4 monolayer at 4 °K the vapor pressure is approximately 10^{-3} Torr[1]: The corresponding time between impacts of vapor molecule on a site of area 10^{-15} cm^2 is $\tau_c \sim 10^{-4}$ sec. Hence, $\tau_c \ll \tau_t$: The films are mobile. Since the vapor pressure falls exponentially at lower temperatures, the condition for mobility is also satisfied at all lower T, and, of course, also at lower coverages.

Most systems for physical adsorption involve more massive adsorbates and higher temperatures: Typical are Ar or N_2 on carbon black or rutile adsorbents at 77 °K.[14] For such systems, the isosteric heat of adsorption ranges from about 2000–6000 cal/mole in the first monolayer. Hill's semiclassical criterion[15] predicts that such systems are mobile, and indeed that mobility persists to considerably lower temperatures, where the monolayers become localized and remain localized down to 0 °K. Hill's criterion specifies mobility under the conditions

$$T \gtrsim \Delta V/10k \quad , \tag{38}$$

where ΔV is the height of surface potential barriers between sites. Estimating the surface barriers to be on the order of 10% of the isosteric heat of adsorption, Eq. (38) predicts mobility for N_2 and Ar down to temperatures of 10–30 °K. The present theory requires a comparison between gas impact and adatom mobility times. If we take as a typical vapor pressure at nearly complete monolayer coverage $p \sim 0.1$ atm, then the gas impact time is $\tau_c \sim 10^{-9}$ sec. The surface diffusion time is difficult to estimate. It is certain that for relatively massive adatoms the widths of all bands lying below the potential barrier tops are extremely narrow, and, therefore, that diffusion takes place almost exclusively through the highest band. Equation (24) therefore reduces to the classical activation energy expression. Consequently, we require an estimate of the width of the highest band. The necessary estimate is made possible by Eq. (6) and the assumption of a semiclassical density of states for two dimensions, Eq. (5). With this assumption, Eq. (24) reduces to

$$\langle \tau_t \rangle = (m^* a_s/h)e^{\beta\epsilon} \quad . \tag{39}$$

If we now take for ϵ the same estimate as we used in applying Hill's criterion, and $m^* = m(N_2)$ and $a_s = 10^{-15}$ cm^2, the site lifetime for N_2 or Ar at

77 °K ranges from about 10^{-11} to 5×10^{-10} sec. These values approach τ_c and therefore indicate that the films are in a transition region between mobility and localization. Appreciably lower vapor pressures – as occur at reduced coverage – would make the film more mobile. Since the vapor pressure (and hence τ_c) is an exponential function of the total binding energy to the surface, whereas the lateral mobility depends on a fraction of that energy, the film becomes more localized at *higher* temperature. At considerably lower temperatures, the film may return to the localized regime: This will depend on the actual widths and separations of the lower bands. However, it can be predicted that the film will always tend to mobility at the lowest T. Since every band must have a finite tunneling width, however small, this will be true for the lowest band. Therefore, there is a maximum but finite value τ_t corresponding to the ground state of the system at $T=0$. τ_c, on the other hand, must increase exponentially as T falls, and therefore will definitely surpass τ_t at sufficiently low T.

Although the band model affords a physical gauge of mobility specifically relevant to adsorption isotherms, the theory also demonstrates that there are no essential differences between the isotherms of mobile and localized noninteracting particles. This result contradicts a conclusion of Hill[16]; that a mobile monolayer has a lower vapor pressure than a localized monolayer at the same coverage. The error arises from a comparison between an ideal two-dimensional gas model (equivalent to a single wide translational band having a quasiclassical density of states) with the Langmuir model. But as we have emphasized, the classical Langmuir model includes particle interactions, whereas the ideal-gas model does not. If we treat the localized adatoms as ideal, then there is no essential distinction between localized and mobile regimes.

The introduction of more realistic interactions between adatoms can cause the capacities of localized monolayers, i.e., in which the energy levels are relatively narrow, to exceed those having wide bands. Such a reversal of the commonly expected situation has been described earlier[4] for He monolayers, and is due to the preferential suppression of positive potential and kinetic terms in the monolayer interaction energy.

The general influence of adatom interactions may be expected to lead to virial terms in the monolayer equation of state, which have been treated to date in the context of a two-dimensional gas.[15] On a crystalline substrate the adatom interactions can, in principle, be treated as interactions between the quasiparticles of the band model.

A further distinction between the present model and real systems should be noted here. We have idealized the substrate to an array of equivalent adsorption sites, but in physical systems one expects some variation of properties, e.g., of adsorption energies and localized energy levels over the surface. Such a distribution of discrete levels can produce an energy-level spectrum resembling Fig. 1 even if the quantum states of each site are arbitrarily sharp. Therefore, due to the similarities between the isotherms in the localized and mobile regimes, it would be impossible to determine from the vapor pressures whether the finite widths of the monolayer "bands" were due to inhomogeneities or to finite lifetimes. A corollary to this observation is that surface inhomogeneities can appear to be present as a result of finite lifetimes in individual sites. Such confusion does not exist, however, in the behavior of the heat capacity, for the effect of inhomogeneities would be to broaden the transition peaks, while mobility will always be accompanied by heat capacities of appreciable magnitude.

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Variational Calculation of the Multiplet Spacings in the $(3d)^2$ Electron Configurations

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The effect of spatial correlation of the two valence electrons on the multiplet spacings has been investigated for atoms with the $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2$ ground configuration. The atom is taken as a two-electron system with each electron moving in a Hartree-Fock effective potential. The zeroth-order wave function is taken to be a Clebsch-Gordan combination of products of one-electron Hartree-Fock orbitals. A variational function of the form $1+cr_{12}+c'(r_1-r_2)^2$ is inserted into this wave function for each of the multiplet members, and c and c' are determined by the variational method. When unrestricted Hartree-Fock functions are used as the zeroth-order basis set, good results which are insensitive to c' are obtained for the multiplet spacings. The ${}^1G$-${}^3F$ spacing is overcorrected by about -12% compared to $+23\%$ without correlation, while the ${}^1D$-${}^3F$ spacing is overcorrected by -3% compared to $+34\%$ without correlation.

I. INTRODUCTION

It is well known that the Hartree-Fock theory gives good average energies and ionization energies for many-electron atoms but gives poor results for the multiplet spacings for open-shell atoms. This is because the multiplet spacings, in the case of $(3d)^2$, depend on two Slater-Condon integrals and the Hartree-Fock theory overestimates these integrals by 20–30%. Apparently these poor results are due to the inadequate inclusion of the electron correlations. In an early paper[1] on the subject, an old technique due to Hylleraas[2] was applied to the separate multiplet levels of the $(3d)^2$ electron configuration in an effort to correct the multiplet spacings without disturbing the Hartree-Fock (HF) average energies. In this case, a variational function of the form $1+cr_{12}$ was inserted into the wave function for each multiplet level, and the value of c was determined by the variation method. The zeroth-order wave function for this two-electron system was taken as a Clebsch-Gordan combination of products of one-electron orbitals. These orbitals were chosen as analytic HF average-of-configuration (HFAC) functions. The multiplet spacings were found to be overcorrected by 13–25% in the case of Ti III. It was conjectured that the simple one-parameter variation function and the way in which the core model was employed were responsible for the major part of the discrepancy from the experimental-term values.

This conjecture was investigated further[3] in a study of the multiplet structure of the $(2p)^2$ configuration. This carbonlike configuration was chosen as a test of the core model because of the penetrating nature of the $2p$ orbital. It was thought that the inadequacy of the core model would manifest itself in poor results for the multiplet spacings. However, it was found that the use of a one-parameter variation function and unrestricted Hartree-Fock (UHF) orbitals gave results in satisfactory agreement with experiment. Thus, the core model using UHF functions seemed to be a reasonable approach, and it remained only to study the variational function. This was done by inserting a two-parameter function of the form $1+cr_{12}+c'(r_1-r_2)^2$ into the UHF function for each multiplet level and again using the variation method to determine c and c'. Again, good agreement with experiment was obtained for the carbon isoelectronic sequence.[4] The conclusion from these studies was that, in spite of the expected large $2s$-$2p$ correlations,[5] the core model as represented by the UHF functions was adequate and that a two-parameter variation function could slightly improve the results.

In this paper, the results of a similar calcula-