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Interacting Submonolayer Quantum Films

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A one-dimensional system of particles in an external periodic potential interacting via two-body hard-core repulsions is considered as a qualitatively valid model of a submonolayer film adsorbed on a solid substrate. At particular values of the hard-core diameter, the free energy is found exactly for all coverages in both the classical and the quantum regimes. We conclude that the thermal implications of adsorbed particle localization (i.e., "mobility") proposed by Hill and developed by Dash and co-workers are *qualitatively unchanged* by including hard-core interactions for both classical films and quantum films obeying Fermi statistics. The effects of dimensionality on Bose systems appear to be too drastic to reach any firm conclusions on the basis of a one-dimensional model.

I. INTRODUCTION

Classical investigations of submonolayer films adsorbed on solid substrates are largely concerned with the thermal implications of particle localization.[1] Consider a dilute submonolayer where an independent particle picture is valid. At high temperatures, the adsorbed particle may move quite freely over the substrate surface ("mobile" adsorption). In the low-temperature limit, the adsorbed particle may be localized at a "site" ("immobile" adsorption). Of course the particle can diffuse from one site to another because of random thermal activation or because of quantum tunneling. This latter process has been extensively investigated by Dash and co-workers,[2] and is of prime importance in the study of helium submonolayers. The purpose of this paper is examine the extent to which the above picture remains valid when the submonolayer is not dilute and the adsorbed particles strongly interact with one another.[3]

Ideally the thermal properties of films should be computed from a strictly three-dimensional viewpoint.[4] Here we consider a one-dimensional model:

$$H=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i=1}^{N}\varphi(x_i)+\sum_{i<j}v(x_i-x_j)\ , \qquad (1)$$

where

$$\varphi(x+a)=\varphi(x) \qquad (2)$$

is the periodic substrate potential and

$$v(x)=0 \ \text{ if } |x|>b, \quad v(x)=\infty \ \text{ if } |x|<b\ , \qquad (3)$$

is a two-body hard-core interaction. The hope is that the disadvantages of unphysical dimensionality are surmounted by the advantages of an exact analytic expression for the free energy in this strongly interacting model. However, recent investigations of long-range order in Bose systems[5] indicate extreme sensitivity to dimensionality. Therefore, we restrict our attention to classical films and quantum films obeying Fermi statistics.

II. STATISTICAL THERMODYNAMICS

The free energy of our model is calculated from the canonical partition function

$$Q_N(L,T)=\mathrm{tr}_{(N,L)}e^{-H/kT} \tag{4}$$

via the usual thermodynamic limit

$$f(\theta,T)=-(kT\theta/b)\lim N^{-1}\ln Q_N\ (L=Nb/\theta,T) \quad \text{as } N\to\infty, \tag{5}$$

where b is the hard-core diameter and θ is the submonolayer coverage (normalized to $\theta=1$ for a complete submonolayer). The thermal properties follow from

$$df=-s\,dT+\mu\,d(\theta/b). \tag{6}$$

In particular, the heat capacity per adsorbed particle is given by

$$c_\theta=\frac{bT}{\theta}\left(\frac{\partial s}{\partial T}\right)_\theta, \tag{7}$$

and the adsorption isotherms are found by equating $b(\partial f/\partial\theta)_T$ to the chemical potential of an ideal gas at the appropriate vapor pressure.

Alternatively, the spreading pressure ensemble may be used:

$$Z_N(\sigma,T)=\lambda^{-1}\int_0^\infty e^{-\sigma L}Q_{N-1}(L,T)\,dL, \tag{8}$$

where

$$\lambda=(2\pi\hbar^2/mkT)^{1/2} \tag{9}$$

is the thermal wavelength. If Φ denotes the spreading pressure of the film, then as $N\to\infty$,

$$\mu(\Phi,T)=-kT\lim N^{-1}\ln Z_N(\sigma=\Phi/kT,T), \tag{10}$$

$$d\Phi=s\,dT+(\theta/b)d\mu. \tag{11}$$

Equations (6) and (11) are thermodynamically equivalent:

$$f=-\Phi+\mu\theta/b. \tag{12}$$

III. CLASSICAL STATISTICS

The canonical partition function in the classical regime is given by

$$Q_N(L,T)=\frac{1}{\lambda^N}\frac{1}{N!}\int_0^L dx_1\cdots\int_0^L dx_N e^{-u/kT}, \tag{13}$$

where

$$u(x_1\cdots x_N)=\sum_{i=1}^{N}\varphi(x_i)+\sum_{i<j}v(x_i-x_j). \tag{14}$$

The evaluation of one-dimensional classical partition functions can usually be reduced to an eigenvalue problem.[6]

Since $u(x_1\cdots x_N)$ is a symmetric function, the relevant region of integration is

$$R: 0<x_1<x_2<\cdots x_N<L. \tag{15}$$

The effect of the hard core is to limit this region of integration from R to

$$\Omega:\ 0<y_1<y_2<\cdots<y_N<L-b(N-1), \tag{16}$$

where

$$x_j=y_j+(j-1)b.$$

Therefore, we have

$$Q_N(L,T)=\lambda^{-N}\int_\Omega dy_1\cdots dy_N\prod_{j=1}^{N}f[y_j+(j-1)b], \tag{17}$$

where

$$f(x)=\exp[-\varphi(x)/kT]. \tag{18}$$

We define the sequence of functions

$$Z_0(x,\sigma)=e^{-\sigma(x-b)}, \tag{19}$$

$$Z_{N+1}(x,\sigma)=\lambda^{-1}\int_x^\infty f(y)Z_N(y+b,\sigma)\,dx. \tag{20}$$

These functions have the properties

$$Z_N(x+a,\sigma)=e^{-\sigma a}Z_N(x,\sigma), \tag{21}$$

$$\frac{-d/dx}{Z_{N+1}(x,\sigma)}=\lambda^{-1}f(x)Z_N(x+b,\sigma), \tag{22}$$

$$Z_N(\sigma,T)=Z_N(x=0,\sigma). \tag{23}$$

Let

$$\Psi(x)=\lim[Z_N(x,\sigma)/Z_N(x=0,\sigma)] \quad \text{as } N\to\infty. \tag{24}$$

Then $\Psi(x)$ is a solution of the eigenvalue problem

$$\frac{d\Psi(x)}{dx}=-\zeta f(x)\Psi(x+b), \tag{25a}$$

$$\Psi(x+a)=e^{-\sigma a}\Psi(x), \tag{25b}$$

which yields ζ as a function of σ. The thermal properties follow from

$$\mu=kT\ln(\lambda\zeta),\quad \Phi=kT\sigma. \tag{26}$$

The eigenvalue problem is easily solved for the following special cases:

Case (i). There is no external potential. Then we obtain

$$f(x)=1,\quad \Psi(x)=e^{-\sigma x},\quad \zeta=\sigma e^{\sigma b}, \tag{27}$$

$$\mu(\Phi,T)=kT\ln(\lambda\Phi/kT)+\Phi b. \tag{28}$$

This is the well-known Takahashi[7] result.

Case (ii). The hard-core diameter is zero. Then we find

$$\ln\Psi(x) = -\,\zeta \int_0^x f(y)dy, \quad \sigma a = \zeta \int_0^a f(x)dx, \tag{29}$$

$$\mu(\Phi,\, T) = kT\ln[\lambda\Phi a/kT \int_0^a f(x)dx]\;. \tag{30}$$

This corresponds to the classical independent-particle model.

Case (iii). The hard-core diameter is one of the "critical" values

$$b = na, \quad n = 0,\, 1,\, 2,\, 3,\, \ldots \quad . \tag{31}$$

For these values of b, we find

$$\ln\Psi(x) = -\,\zeta e^{-\sigma b} \int_0^x f(y)dy, \quad \sigma a = \zeta e^{-\sigma b} \int_0^a f(x)dx\;, \tag{32}$$

$$\mu(\Phi,\, T) = b\Phi + kT\ln(\lambda a\Phi/kT \int_0^a e^{-\varphi(x)/kT}dx)\;. \tag{33}$$

IV. CLASSICAL FILMS

The adsorption isotherm implied by Eq. (33) can be computed from the thermodynamic relation $\theta = b(\partial\Phi/\partial\mu)_T$:

$$\mu(\theta,\, T) = kT\ln[\theta/(1-\theta)] + kT\theta/(1-\theta) + \mu^\dagger(T). \tag{34}$$

The first term is the Langmuir adsorption logarithm; the second term is a hard-core volume exclusion effect; and $\mu^\dagger$ depends on temperature alone. The question of adsorbed particle "mobility" is connected to the behavior of the specific heat c_θ.

Assume that the external potential $\varphi(x) = \varphi(x+a)$ is a smoothly varying function of x with one oscillatorlike minimum per cell (i.e., per period of variation). At sufficiently high temperatures the external potential $\varphi(x)$ is unimportant and the kinetic energy is the sole contributor to the specific heat:

$$\lim c_\theta = \tfrac{1}{2}k \quad \text{as} \quad T \to \infty\;. \tag{35}$$

For sufficiently low temperatures the particles are localized at the oscillatorlike minima, so that equipartition of energy implies[8]

$$\lim c_\theta = k \quad \text{as} \quad T \to 0. \tag{36}$$

This argument is independent of hard-core interactions and coverage. Equations (35) and (36) follow from Eq. (33) via straightforward (but somewhat lengthy) thermodynamic differentiation. However, Eq. (33) is only rigorously exact for the "special" values of the hard-core diameter given in Eq. (31). We wish to argue that these values are not "critical" in a physical sense, but merely "convenient" for obtaining an analytical formula. In the high-temperature limit, Eq. (35) holds for any b since case (i) is a good approximation. In the low-temperature limit $f(x) \propto \sum_n \delta(x - x_n)$, where x_n denotes the positions of particle localization. Equation (32) is then approximately valid for all b. We therefore conclude that Eq. (33) is rigorously exact for all coverages when $b = 0,\, a,\, 2a,\, 3a,\, \ldots,$ and qualitatively correct for all values of b. For mathematical convenience we restrict the values of b to integer multiples of a in the considerations which follow. There are no restrictions on the coverage θ.

V. QUANTUM STATISTICS

Associated with the external potential is a spectrum of single-particle eigenvalues[9]

$$-\,(\hbar^2/2m)\psi_k''(x) + \varphi(x)\psi_k(x) = E_k\psi_k(x) \tag{37}$$

and a density of states

$$g(E) = (2\pi)^{-1} \int_{-\infty}^{+\infty} \delta(E - E_k)\,dk. \tag{38}$$

We assume that this single-particle problem has been solved and that $g(E)$ is a known function. What is the effect of including hard-core interactions?

The hard-core quantum system in the absence of a periodic potential in one dimension has been discussed in detail by Lieb and Mattis.[10] The major effect is a renormalization of the single-particle spectrum. Introduction of a periodic potential [restricted by Eq. (31)] leaves their arguments virtually unchanged. The density of states is simply renormalized to

$$g(\theta, E) = (1-\theta)^{1/2}g(E)\;, \tag{39}$$

and the free energy for all coverages is found by eliminating the parameter Z from the equations

$$f(\theta,\, T) = (kT\theta/b)\ln Z - kT \int_0^\infty g(\theta, E)\ln(1 + Ze^{-E/kT})\,dE\;, \tag{40}$$

$$\theta = b \int_0^\infty g(\theta, E)(Z^{-1}e^{E/kT} + 1)\,dE\,. \tag{41}$$

The change in the thermal properties of the film due to the hard-core interactions is rigorously determined by the simple renormalization $g(E) \to g(\theta, E)$ for all temperatures and coverages.

VI. CONCLUSIONS

In a one-dimensional problem with hard cores, the unique and permanent ordering of particles permits an analytic solution. The result is simply interpreted in terms of a volume exclusion effect. Higher-dimensional systems are quantitatively more difficult to analyze since the particles "move around each others hard cores." Nevertheless, the simple volume exclusion effect remains qualitatively valid although extrapolations to higher dimensions are quantitatively crude.

What is to be expected for a He^3 submonolayer film? In the dilute submonolayer region the film acts like an ideal "two-dimensional" Fermi gas with a density of states $g(E)$. There should be clear evidence of a linear term in the specific heat in the low-temperature limit. As the coverage is increased, the coefficient of the linear term should become smaller owing to "volume" exclusion from hard cores. Finally, the linear term should vanish at monolayer coverage. These qualitative expectations are in agreement with experiment,[11] especially the most recent data of Stewart and Dash.[12]

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Low-Temperature Ion Mobility in Fermi Liquids*

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The mobility of a large hard-sphere impurity in a Fermi liquid has been calculated by solving the transport equation for the quasiparticles exactly to order T^2. Using the Landau parameters known for He^3, the correction to the zero-temperature mobility, which was previously found to be proportional to T^2, turns out to be somewhat too small. The temperature dependence is in agreement with experiment.

I. INTRODUCTION

Over the past years, considerable attention has been given to the transport properties of Fermi liquids. On the experimental side, there are the accurate measurements by Wheatley and co-workers[1] on He^3 and He^3-He^4 mixtures, while on the theoretical side, Abrikosov and Khalatnikov[2] were the first to obtain approximate solutions of the quasiparticle transport equation. A brief summary of recent theoretical developments can be found in the paper by Dy and Pethick.[3]

While the mobility of an impurity in the zero-temperature limit does not depend on the transport properties of the Fermi liquid, this is not true at finite temperatures where quasiparticle collisions become important. For $T \to 0$ the quasiparticle mean free path λ diverges like T^{-2} and eventually becomes much larger than the size a of the impurity – a situation often called the Knudsen limit. In this case the distribution of quasiparticles is essentially undistorted in the vicinity of the impurity. The mobility of an impurity in the Knudsen limit has been calculated for a Fermi liquid by various methods.[4–11]

In a previous paper[11] we have suggested that the increase of the mobility with temperature observed by Anderson *et al.*[12] and Kuchnir *et al.*[13] with negatively charged impurities in He^3 arises as a consequence of quasiparticle collisions. The quasiparticles scattered off the moving impurity will alter the distribution around the impurity by such collisions. In I we solved the problem for a Boltzmann gas and showed that generally the effect is of order a/λ and increases the mobility. Thus in a Fermi liquid the first correction to the Knudsen limit leads to a contribution proportional to T^2.

In this paper, the quasiparticle transport equation is solved exactly to order T^2 and the mobility of a large hard-sphere impurity is found in terms of Landau's Fermi-liquid parameters.[14,15] In Sec. II we will derive a general expression for the mobility and in Sec. III the expression is evaluated to order T^2. The comparison with experiments[12,13] in Sec. IV shows fair agreement. Also in Sec. IV some deficiencies of our treatment are pointed out and a different explanation of the temperature rise of the mobility[10] is discussed.

II. GENERAL MOBILITY FORMULA

We will adopt the notation of Ref. 15. The transport equation for the quasiparticle distribution func-