[1] J. E. Drummond, *Plasma Physics* (McGraw-Hill, New York, 1961), pp. 1–32; D. Gabor, E. A. Ash, and D. Dracott, Nature (Lond.) **176**, 916 (1955); I. Langmuir, Phys. Rev. **26**, 585 (1925); H. Boersch, J. Geiger, and M. Topschowsky, in *Abstracts of the Sixth International Conference on the Physics of Electronic and Atomic Collisions* (MIT, Cambridge, Mass., 1969), p. 263; I Klavan, D. M. Cox, H. H. Brown, and B. Bederson, Phys. Rev. Lett. **28**, 1254 (1972); P. D. Goldan and W. M. Leavens, Phys. Fluids **13**, 433 (1970); R. S. Harp, A. B. Cannara, F. W. Crawford, and G. S. Kino, Rev. Sci. Instrum. **36**, 960 (1965).

[2] P. Morrison, S. Olbert, and B. Rossi, Phys. Rev. **94**, 440 (1954); R. J. Gould and G. R. Burbridge, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1967), Vol. 46-2, p. 265.

[3] H. A. Bethe, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1933), Vol. 24, p. 273.

[4] H. A. Bethe and J. Ashkin, in *Experimental Nuclear Physics*, edited by E. Segré (Wiley, New York, 1953), Vol. 1, p. 166.

[5] U. Fano, Annu. Rev. Nucl. Sci. **13**, 1 (1963).

[6] H. Raether, Springer Tracts Mod. Phys. **38**, 84 (1965); C. J. Powell, in *Methods of Experimental Physics*, edited by L. Marton, B. Bederson, and W. L. Fite (Academic, New York, 1968), Vol. 7B, p. 275.

[7] L. Pages, E. Bertel, H. Joffre and L. Sklavenitis, At. Data **4**, 1 (1972).

[8] S. Hayakawa and K. Kitao, Prog. Theor. Phys. **16**, 131 (1956); Prog. Theor. Phys. **16**, 139 (1956).

[9] J. Neufeld and R. H. Ritchie, Phys. Rev. **98**, 1632 (1955).

[10] A. I. Larkin, Zh. Eksp. Teor. Fiz. **37**, 264 (1959) [Sov. Phys.-JETP **10**, 186 (1960)].

[11] V. N. Tsytovich, Zh. Eksp. Teor. Fiz. **42**, 803 (1962) [Sov. Phys.-JETP **15**, 561 (1962)].

[12] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), pp. 429–463.

[13] R. J. Gould, Physica (Utr.) **58**, 379 (1972); Physica (Utr.) **60**, 145 (1972).

[14] D. Pines and D. Bohm, Phys. Rev. **85**, 338 (1952).

[15] D. Pines, Phys. Rev. **92**, 626 (1953).

[16] D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1963).

[17] U. Fano, Phys. Rev. **103**, 1202 (1956).

[18] M. Lampe, Phys. Fluids **13**, 2578 (1970).

[19] R. H. Williams and H. E. de Witt, Phys. Fluids **12**, 2326 (1969).

[20] R. Landshoff, Phys. Rev. **76**, 904 (1949); M. R. C. McDowell, Phys. Fluids **4**, 1332 (1961).

[21] D. C. Montgomery and D. A. Tidman, *Plasma Kinetic Theory* (McGraw-Hill, New York, 1964), pp. 84, 93.

[22] I. P. Shkarofsky, T. W. Johnston, and M. P. Bachynski, *The Particle Kinetics of Plasmas* (Addison-Wesley, Reading, Mass., 1966), pp. 242–312, and references herein.

[23] F. Perkins, Phys. Fluids **8**, 1361 (1965).

[24] Y. Itikawa and O. Aono, Phys. Fluids **9**, 1259 (1966).

[25] L. Vriens, in *Case Studies in Atomic Collision Physics 1*, edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1969), p. 335.

[26] H. A. Kramers, Physica (Utr.) **13**, 401 (1947).

[27] M. Inokuti, Rev. Mod. Phys. **43**, 297 (1971).

[28] E. J. Williams, Rev. Mod. Phys. **17**, 217 (1945).

[29] N. G. van Kampen, Physica (Utr.) **21**, 949 (1955).

PHYSICAL REVIEW A VOLUME 8, NUMBER 1 JULY 1973

Ordering Transitions in a Quantum Lattice-Gas Model of Adsorbed Systems*

M. Schick and R. L. Siddon
Department of Physics, University of Washington, Seattle, Washington 98195

(Received 9 February 1973)

A quantum lattice-gas model of adsorbed systems is studied to determine the importance of quantum-mechanical processes upon order-disorder transition temperatures. The phase diagram of systems interacting with nearest-neighbor attractive and repulsive potentials is obtained within the Bethe-Peierls approximation. It is found that the transition temperature depends, in order of increasing importance, upon particle statistics, quantum tunneling, and the nearest-neighbor interaction strength. The results are applied to systems of helium adsorbed on graphite.

INTRODUCTION

Recent heat-capacity studies of submonolayer He^4 and He^3 films adsorbed on graphite indicate that near temperatures of 3 K and within a range of densities, an order-disorder transition takes place in the film.[1] The ordered phase is thought to be characterized by a superlattice of adsorbed atoms which is in registry with the triangular array of adsorption sites provided by the graphite. Within this superlattice, there is one helium atom for every three adsorption sites.

The usual approach to the problem of calculating the order-disorder transition temperature of an adsorbed system is to assume that the adsorbate may be treated classically. Within this approximation, the phase diagram depends upon the interparticle interaction and the particular array of adsorption sites. With the further approximation that the adsorbed atoms are well localized at the adsorption sites, the system can be described by a classical lattice gas for which numerous methods for obtaining approximate, and sometimes exact, solutions are known.[2] The phase diagram for the order-disorder transition of helium on graphite has recently been calculated within this scheme.[3]

The above approximations are probably adequate over a wide range of densities, provided that the adsorbate is one of the heavier noble gases. However, for the case of adsorbed helium in which quantum-mechanical effects are more likely to be manifest, it is unclear *a priori* for what range of densities, if any, these approximations are adequate. *A posteriori*, the assumption that the atoms are well localized in adsorption sites is most likely valid in the density range for which the heat-capacity signals associated with order-disorder phenomena are observed.[4] However, even within this range, it is to be expected that a classical description will not be entirely adequate and that quantum-mechanical tunneling from site to site and effects of particle statistics will be reflected in differences between the He^3 and He^4 phase diagrams.

It is the purpose of this paper to examine analogous differences within a model of the simpler system of atoms adsorbed onto a square array of sites. In particular, we examine the relative importance of the interparticle interactions, the isotopic mass, and the particle statistics on the order-disorder transition temperature of such a system. This is accomplished using a quantum lattice-gas model which is formulated in Sec. I. It is shown in Sec. II that mean-field theory is inadequate to explicate the effects we seek. We therefore employ the Bethe-Peierls approximation. The case of a nearest-neighbor attractive interaction is treated in this section and that of a repulsive interaction in Sec. III. Our results are summarized in Sec. IV and applied to the systems of helium adsorbed on graphite. There results a qualitative explanation of the initially surprising experimental result that the lighter isotope orders at a higher temperature.

I. MODEL

We consider N atoms adsorbed on an area which is divided into cells representing adsorption sites. For convenience and clarity of the exposition, we take a square array rather than the more complicated triangular array appropriate for graphite. The area of each cell is denoted d^2. The Hamiltonian of the system is taken to be the first finite difference approximation to the usual many-body Hamiltonian, so that

$$H-\mu N=\xi\sum_{\langle ij\rangle}(\psi_i^\dagger-\psi_j^\dagger)(\psi_i-\psi_j)+\tfrac{1}{2}\sum_{i,j}v_{ij}\psi_i^\dagger\psi_j^\dagger\psi_j\psi_i-\mu\sum_i\psi_i^\dagger\psi_i,$$

where $\xi\equiv\hbar^2/2md^2$, μ is the chemical potential, $\langle ij\rangle$ denotes a sum over all nearest-neighbor pair of sites in the substrate, and ψ_i is the operator which annihilates a particle at the site i. The cross terms in the kinetic-energy operator permit the particles to tunnel from site to site. In the potential-energy operator, an interaction with an infinite hard core is assumed. The effects of this hard-core interaction are incorporated into the model by demanding that the operators ψ_i, and $\psi_i^\dagger$ obey fermion anticommutation relations on the same site. This is of course equivalent to restricting the eigenvalues of the number operator $n_i\equiv\psi_i^\dagger\psi_i$ to zero or 1 and permits us to ignore the terms involving v_{ii} in the two-body term of the above Hamiltonian. In addition, we accommodate particle statistics by requiring that all field operators commute on different sites for bosons and anticommute for fermions. This, together with the hard-core exclusion, alters the usual boson relation to read

$$\begin{aligned}&[\psi_i,\psi_j^\dagger]=(1-2n_i)\delta_{ij},\\&[\psi_i,\psi_j]=-2\psi_j\psi_i\delta_{ij}.\end{aligned}\tag{1.1}$$

As it is easily shown that the above operators continue to satisfy the usual commutation relation with the total number operator,

$$\Big[\psi_i,\sum_j\psi_j^\dagger\psi_j\Big]=\psi_i,$$

the interpretation of ψ_i and $\psi_i^\dagger$ as destruction and creation operators remains valid.

For a system of fermions with spin, the effect of the hard core alters the usual anticommutation relations between particles with different spin projection.[5] In view of the fact that the spin plays no fundamental role in bringing about an order-disorder transition in our model, we shall avoid this complication by considering a system of spinless fermions. In this case, the usual anticommutation relations

$$\begin{aligned}&\{\psi_i,\psi_j^\dagger\}=\delta_{ij},\\&\{\psi_i,\psi_j\}=0\end{aligned}\tag{1.2}$$

prevent multiple occupation of any site and need not be modified.

For convenience we include only those two-body interactions between atoms on adjacent sites and assign a magnitude v to the strength of the nearest-neighbor interaction. Thus the Hamiltonian considered is

$$H-\mu N=\xi\sum_{\langle ij\rangle}(\psi_i^\dagger-\psi_j^\dagger)(\psi_i-\psi_j)+v\sum_{\langle ij\rangle}n_in_j-\mu\sum_i n_i.\tag{1.3}$$

We note here that the number v in the above model Hamiltonian should be considered as a matrix element of the two-particle interaction taken between states localized on neighboring sites.[6] It is therefore a functional of the interparticle potential and the particle mass. If v is positive, it is known that the classical lattice gas undergoes a transition to an ordered state in which every other site tends to be occupied. At a given density, the temperature of this transition scales with v. It is to be expected that the effect of quantum-mechanical tunneling will be to disorder the system and therefore to lower the transition temperature. A measure of the relative strengths of the tunneling and interaction terms is the quantity

$$\gamma \equiv \xi/v = \hbar^2/2md^2v. \tag{1.4}$$

If the interaction strength v is negative, the classical system undergoes a first-order transition into two phases of different densities. At the critical density, of course, the densities of the two phases are the same and the transition is of second order. Again it is to be expected that the quantum-mechanical tunneling term will lower the transition temperature. For completeness, we consider below both attractive and repulsive interactions.

II. ATTRACTIVE INTERACTIONS

Perhaps the simplest approximation that can be applied to the Hamiltonian of Eq. (1.3) is that of mean-field theory. In this approximation a cluster of one particle is considered to interact with the rest of the system via mean fields. The Hamiltonian of the one-particle cluster is

$$H_i - \mu n_i = -2\xi(\psi_i^\dagger \langle \psi_j \rangle + \langle \psi_j^\dagger \rangle \psi_i) + (4\xi + 2v\langle n_j \rangle - \mu) n_i \ , \tag{2.1}$$

where the angular brackets denote ensemble average. Because of the homogeneous nature of any phase of the system, this average is independent of the site index. We now observe that an exact calculation of the ensemble average of ψ_i must vanish for a fermion system, as there is no off-diagonal long-range order in the first reduced density matrix of such a system.[7] This average also vanishes for a two-dimensional boson system.[8] Even if this were not the case, the average would be nonzero only if the Bose system exhibited superfluidity, and this property is not of concern to us. We therefore set $\langle \psi_i \rangle$ to zero in Eq. (2.1). It is then seen from this equation that the kinetic energy makes no contribution to the cluster Hamiltonian other than a trivial shift in the chemical potential. We therefore recover the results of mean-field theory applied to a classical system and learn nothing of the quantum-mechanical effects. It is necessary then to turn to an approximation in which the effects of tunneling and statistics are included, such as the Bethe-Peierls approximation.[9,10]

In this scheme, we consider a cluster consisting of a "center" site and its four nearest neighbors. All terms in the total Hamiltonian which connect operators acting on sites within the cluster are treated exactly. Those terms which couple the cluster to the rest of the system are replaced by mean fields which are calculated self-consistently. Denoting the mean field which couples the edge sites of the cluster to the rest of the system by ϕ, the Hamiltonian of the cluster becomes

$$H_{cl} - \mu N_{cl} = \epsilon n_c - \xi \sum_\delta (\psi_c^\dagger \psi_\delta + \psi_\delta^\dagger \psi_c) + (v n_c - V) \sum_\delta n_\delta , \tag{2.2}$$

where

$$\epsilon \equiv 4\xi - \mu, \quad V \equiv \phi - \xi + \mu, \tag{2.3}$$

and c and δ denote center and edge sites, respectively. It should be noted that there are no terms in the above cluster Hamiltonian containing mean fields which couple to the edge-site field operators themselves (i.e., terms like $\bar{\phi} \sum_\delta \psi_\delta$). The reason is that a nonvanishing self-consistent field $\tilde{\phi}$ would imply a nonvanishing value of $\langle \psi \rangle$, which is contrary to the known exact results cited above. Therefore we set such fields $\tilde{\phi}$ to zero *ab initio*.

The self-consistency conditions are that the average occupation number of a center site and edge site should each be equal to the average density of the phase, liquid or gas, of the system, as there is no physical distinction between such sites. These conditions yield two equations, (2.6) and (2.7) below, which relate the following four quantities of the problem: the (dimensionless) temperature $(\beta v)^{-1}$, chemical potential $\beta\epsilon$, mean field βV, and density n. The quantity β is $(kT)^{-1}$. Upon specifying the density and temperature, the two self-consistent equations may be solved for the coupling field and chemical potential. The free energy per site of the system and pressure are then obtained from the relations

$$f(n, T) = \int_0^n \mu(n', T)\, dn', \tag{2.4}$$

$$\begin{aligned} p(n, T)d^2 &= -f(n, T) + \mu(n, T)n \\ &= \int_0^n [\epsilon(n', T) + 2v]\, dn' - [\epsilon(n, T) + 2v]\, n, \end{aligned} \tag{2.5}$$

where Eqs. (2.3) and (2.4) have been used.

In order to calculate the average occupation number of the center site or of an edge site, the cluster partition function is required or, equivalently, the eigenvalues of the cluster Hamiltonian, Eq. (2.2). As the cluster consists of a center site and four nearest neighbors, and each site can be occupied or empty, there are 2^5 basis states for the cluster. It is instructive to consider the form of the Hamiltonian matrix in the occupation-number representation. The diagonal elements are, apart from a shift in the chemical potential, the classical energies of the various configurations of the cluster. Because of the tunneling terms in the cluster Hamiltonian, there are off-diagonal elements of magnitude ξ. For a boson system, these terms are all negative, which stems from the fact that operators on different sites commute. For a fermion system, the off-diagonal terms are positive or negative as operators on different sites anticommute. It is therefore clear from the form of the Hamiltonian matrix that the effects of tunneling and statistics have been included in the Bethe-Peierls approximation.

The computation of the eigenvalues of the cluster Hamiltonian is simplified because the Hamiltonian of Eq. (2.2) conserves the number of particles in the cluster. Therefore the 32×32 matrix is block diagonal with submatrices of dimensionality 1, 5, 10, 10, 5, and 1 corresponding to states of the cluster with 0, 1, 2, 3, 4, and 5 particles, respectively. The eigenvalues are now found in a straightforward manner. They are listed in Table I for both sets of statistics.

Having obtained the eigenvalues and therefore the cluster partition function $Q(\beta\epsilon, \beta v, \beta V)$, we can now calculate the average occupation numbers of the center and edge sites, $\langle n_c\rangle$ and $\langle n_\delta\rangle$, and set them equal to the average density of the phase n. This yields the equations

$$\langle n_c\rangle = -\frac{\partial \ln Q(\beta\epsilon, \beta v, \beta V)}{\partial(\beta\epsilon)} = n , \tag{2.6}$$

$$\langle n_\delta\rangle = \frac{1}{4}\frac{\partial \ln Q(\beta\epsilon, \beta v, \beta V)}{\partial(\beta V)} = n . \tag{2.7}$$

We have solved these two equations for a given temperature $(\beta v)^{-1}$ for the complete range of densities zero to unity and obtained the chemical potential as a function of temperature and density. Thermodynamic instability of the system is signaled when the isothermal compressibility

TABLE I. Eigenvalues of cluster Hamiltonian. $R^{\pm}(l, m, n, p) \equiv \frac{1}{2}(\epsilon + lv - mV) \pm \frac{1}{2}[(\epsilon + lv + nV)^2 + p\xi^2]^{1/2}$.

Fermions		Bosons	
Root	Degeneracy	Root	Degeneracy
0	(1)	0	(1)
$-V$	(3)	$-V$	(3)
$-2V$	(3)	$-2V$	(2)
$-3V$	(1)	$\epsilon + 2(v - V)$	(2)
$\epsilon + v - V$	(1)	$\epsilon + 3(v - V)$	(3)
$\epsilon + 2(v - V)$	(3)	$\epsilon + 4(v - V)$	(1)
$\epsilon + 3(v - V)$	(3)	$R^+(2, 5, 1, 8)$	(3)
$\epsilon + 4(v - V)$	(1)	$R^-(2, 5, 1, 8)$	(3)
$R^+(0, 1, 1, 16)$	(1)	$R^+(1, 3, 1, 8)$	(3)
$R^-(0, 1, 1, 16)$	(1)	$R^-(1, 3, 1, 8)$	(3)
$R^+(1, 3, 1, 16)$	(3)	$R^+(2, 5, 1, 24)$	(1)
$R^-(1, 3, 1, 16)$	(3)	$R^-(2, 5, 1, 24)$	(1)
$R^+(2, 5, 1, 16)$	(3)	$R^+(1, 3, 1, 24)$	(1)
$R^-(2, 5, 1, 16)$	(3)	$R^-(1, 3, 1, 24)$	(1)
$R^+(3, 7, 1, 16)$	(1)	$R^+(0, 1, 1, 16)$	(1)
$R^-(3, 7, 1, 16)$	(1)	$R^-(0, 1, 1, 16)$	(1)
		$R^+(3, 7, 1, 16)$	(1)
		$R^-(3, 7, 1, 16)$	(1)

$\partial\mu(n, T)/\partial n$ becomes negative. The densities of the two phases coexisting in equilibrium can be found by a Maxwell construction in the chemical-potential–density plane. Rather than employ this construction, we have determined the phase diagram by exploiting the symmetry of the cluster Hamiltonian under the transformation $\psi_k \rightleftarrows \psi_k^\dagger$. Under this transformation $n_k \rightleftarrows 1 - n_k$ and $n \rightleftarrows 1 - n$ for both fermions and bosons because of the hard-core constraint. The cluster Hamiltonian itself becomes

$$H_{cl} - \mu N_{cl} = -(\epsilon + 4v)\, n_c \pm \xi \left(\psi_c^\dagger \sum_\delta \psi_\delta + \sum_\delta \psi_\delta{}^\dagger \psi_c \right) + (V - v + v n_c) \sum_\delta n_\delta + \epsilon + 4(v - V)\,,$$

where the upper (lower) sign is for fermions (bosons). By comparing with the original cluster Hamiltonian of Eq. (2.2), we see that this transformation could also be accomplished by making the following replacements in Eq. (2.2):

$$\epsilon \to -\epsilon - 4v, \quad \xi \to \pm\xi, \quad V \to -V + v,$$

and shifting all energies by $4v + \epsilon - 4V$. It therefore follows that for a given temperature

$$\epsilon\,(1 - n, T) = -\epsilon\,(n, T) - 4v\,,$$

$$V\,(1 - n, T) = -V(n, T) + v\,.$$

Equivalently, the functions $\epsilon\,(n, T) + 2v$ and $V\,(n, T) - \frac{1}{2}v$ are odd functions of $n - \frac{1}{2}$ and therefore vanish at a density n of $\frac{1}{2}$. The former of these two relations together with Eq. (2.5) for the pressure implies that the phase diagram is symmetric about the density $\frac{1}{2}$ and that everywhere on the phase boundary

$$\epsilon\,(n, T) + 2v = 0,$$

or, from Eq. (2.3),

$$\mu\,(n, T) = 4\xi + 2v. \tag{2.8}$$

This is most easily seen by considering the difference in pressures of two phases of density n_1, and n_2, which, from Eq. (2.5), is

$$[p\,(n_2, T) - p\,(n_1, T)\,]\, d^2 = \int_{n_1}^{n_2} [\epsilon(n', T) + 2v]\, dn' - [\epsilon(n_2, T) + 2v]\, n_2 + [\epsilon(n_1, T) + 2v]\, n_1\,.$$

As $\epsilon\,(n, T) + 2v$ is an odd function of $n - \frac{1}{2}$, the pressure of the two phases will be equal if n_1 and n_2 are symmetric about n of $\frac{1}{2}$ and Eq. (2.8) is satisfied. In addition, that equation implies that the chemical potentials of the two phases are equal. Thus the two phases are in fact in equilibrium. That Eq. (2.8) is satisfied everywhere on the phase boundary is completely analogous to the vanishing of the magnetic field on the phase boundary of a ferromagnet.

Solutions of Eqs. (2.6)–(2.8) are shown in Fig. 1 for values of γ equal to 0.0, 0.2, and 0.4. The expression for the phase boundary for the case of γ equals zero is simply the classical result[9]

$$kT/|v| = \{2 \ln[(x^4 - 1)/(x^3 - x)]\}^{-1},$$

$$x \equiv [n/(1 - n)]^{1/4}.$$

The difference between the phase diagram for Bose and Fermi systems is imperceptible on the scale of Fig. 1.

At a density of $\frac{1}{2}$, Eqs. (2.6)–(2.8) are not sufficient to determine the transition temperature. The reason is that at this density, Eq. (2.8) is satisfied at all temperatures. (The analogous statement for ferromagnets is that for zero magnetization, the magnetic field vanishes at all temperatures.) A limiting procedure is therefore employed. Equations (2.6) and (2.7) are expanded about a density of $\frac{1}{2}$ and subtracted. Because the transition temperature is a maximum at this density and Eq. (2.8) is satisfied at all temperatures there, the resulting equation takes the particularly simple form

$$\frac{\partial^2 \ln Q(\beta\epsilon, \beta v, \beta V)}{\partial(\beta\epsilon)\,\partial(\beta V)} + \frac{1}{4}\frac{\partial^2 \ln Q(\beta\epsilon, \beta v, \beta V)}{\partial(\beta V)^2} = 0\,.$$

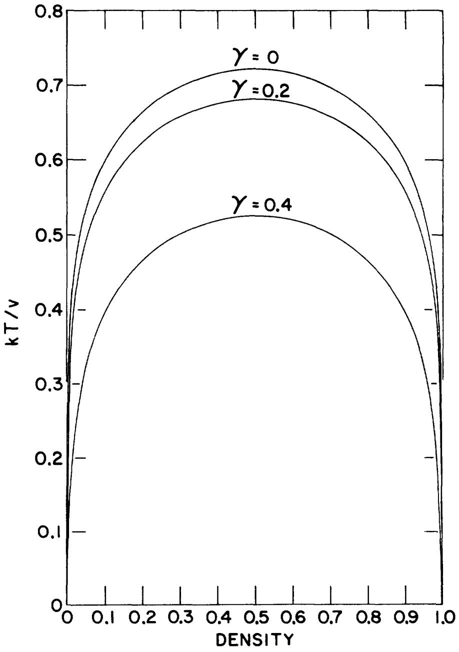

FIG. 1. Phase diagram for the case of attractive nearest-neighbor interactions.

This equation together with the fact that $V=\frac{1}{2}v$ and $\epsilon=-2v$ at density $\frac{1}{2}$ is sufficient to determine the maximum transition temperature. A series expansion for the maximum transition temperature as a function of γ for small γ can be obtained by expanding the cluster partition function in γ^2 and employing the above procedure. We obtain the result

$$T_M(\gamma, v)/T_M(0,v)=1-a\gamma^2-b\gamma^4-c\gamma^6+\cdots,$$

where

$$T_M(0,v)=|v|/2\ln 2, \quad a=1.32, \quad b=1.46$$

for bosons and fermions. The effect of statistics first occurs in the γ^6 term. It is found that the coefficient c is of order unity for both cases but is slightly larger for bosons. Thus, for equal masses and interaction strengths, the boson transition temperature is slightly lower than that of fermions. That the effect of particle statistics first occurs in order γ^6 within the Bethe-Peierls approximation is to be contrasted with the expectation that the difference in exchange effects will first appear in order γ^4 within perturbation theory.[11]

III. REPULSIVE INTERACTIONS

Because the repulsive nearest-neighbor interaction tends to cause the atoms to form an ordered array in which alternating sites are preferentially occupied, we further subdivide the area of adsorption into two interpenetrating sublattices of A and B sites in which A sites have B neighbors and vice versa. The cluster Hamiltonian of a cluster with an A center site is similar to that of Eq. (2.2). It is given by

$$H_{cl}^{A}-\mu N_{cl}^{A}=\epsilon n_c^A-\xi\left(\psi_c^{A\dagger}\sum_\delta \psi_\delta^B+\sum_\delta \psi_\delta^{B\dagger}\psi_c^A\right)+(vn_c^A-V^B)\sum_\delta n_\delta^B. \quad (3.1)$$

A similar expression for a cluster with a B center site is obtained from the above by interchanging A and B superscripts. The eigenvalues of the cluster Hamiltonian are obtained from Table I by affixing the appropriate superscript to V. The coupling fields V^A and V^B are calculated self-consistently by requiring that the average cell occupation density n^A of an A site be the same, irrespective of whether it is viewed as the center of an A cluster or the edge side of the B cluster, and similarly for the occupation n^B of a B site. Instead of the variables n^A and n^B we use as independent variables the density $n=\frac{1}{2}(n^A+n^B)$ and the order parameter $\eta=n^A-n^B$. This parameter is a measure of the difference in average occupation number of the two sublattices. From Eq. (3.1) the self-consistency conditions can be written in the form

$$-\frac{\partial \ln Q^A(\beta\epsilon,\beta v,\beta V^B)}{\partial\beta\epsilon}=n+\tfrac{1}{2}\eta, \quad (3.2)$$

$$\frac{1}{4}\,\frac{\partial \ln Q^A(\beta\epsilon,\beta v,\beta V^B)}{\partial\beta V^B}=n-\tfrac{1}{2}\eta, \quad (3.3)$$

$$-\frac{\partial \ln Q^B(\beta\epsilon,\beta v,\beta V^A)}{\partial\beta\epsilon}=n-\tfrac{1}{2}\eta, \quad (3.4)$$

$$\frac{1}{4}\,\frac{\partial \ln Q^B(\beta\epsilon,\beta v,\beta V^A)}{\partial\beta V^A}=n+\tfrac{1}{2}\eta. \quad (3.5)$$

This set of four nonlinear equations relates the six variables of the problem $\beta\epsilon$, βv, βV^A, βV^B, n, and η. At any temperature and density this set of equations admits a solution such that the order parameter vanishes and the two coupling fields are equal, corresponding to the disordered phase. In this phase, the chemical potential, and therefore the free energy, can be found by solving the two equations obtained from Eqs. (3.2)–(3.5) when η is set equal to zero and V_A to V_B. For all temperatures and densities, the disordered phase is found to be stable.

Within a restricted region of the temperature-density plane, the self-consistency equations allow a solution with a nonvanishing order parameter and unequal mean fields corresponding to an ordered phase. As in the classical case, it is found that this phase is stable and that its free energy is always lower than that of the disordered phase. The boundary of this phase is a line of second-order transitions on which the order parameter goes continuously to zero and the two mean fields are equal.

To determine this phase boundary, we expand Eqs. (3.2)–(3.5) about the values $\eta=0$ and $V^A=V^B$ and seek a solution for which the mean fields are infinitesimally different from one another. This yields the equation

$$-\frac{\partial^2 \ln Q(\beta\epsilon,\beta v,\beta V)}{\partial(\beta\epsilon)\partial(\beta V)}+\frac{1}{4}\,\frac{\partial^2 \ln Q(\beta\epsilon,\beta v,\beta V)}{\partial(\beta V)^2}=0, \quad (3.6)$$

which is true on the boundary itself. This equation, in addition to the self-consistency conditions which reduce to two equations on the phase boundary, is sufficient to determine the line of second-order transitions. The result of this calculation for fermions is shown in Fig. 2 for values of γ equal to 0.0, 0.1, and 0.3. When γ is set to zero, we recover the classical result[12]

$$kT/v=-\{\ln[(4n-1)(3-4n)/16n(1-n)]\}^{-1}.$$

The phase diagrams are symmetric about density $\frac{1}{2}$ as required by the symmetry of the cluster Hamiltonians under the transformation $n \rightleftarrows 1-n$. For nonzero γ, the ordering temperature is reduced at all densities, reflecting the disordering effects of quantum tunneling. Although the corresponding transition temperatures for bosons are lower than those for fermions for all values of γ and n, the difference is sufficiently small so as to be ignorable on the scale of Fig. 2.

An interesting unphysical result of the Bethe-Peierls approximation is shown in the presence of the lower (dashed) portion of the phase boundaries in Fig. 2. Accordingly, as the temperature is lowered, the system initially orders and the order parameter increases continuously from zero. However, as the temperature is lowered still further, the parameter reaches a maximum and then falls quickly, but continuously, to zero, with the system undergoing a second-order transition to the disordered phase. A similar behavior is encountered for attractive interactions. As this case is of less intrinsic interest to us, we have not calculated the dependence of this anomalous transition on density and temperature and it is therefore not shown in Fig. 1. Such anomalies were first noted by Anderson[13] and Li[14] for the case of the isotropic Heisenberg ferromagnet and antiferromagnet, respectively. Since the quantum lattice gas can, for bosons, be mapped onto an anisotropic Heisenberg spin model,[15] it is not surprising that these artifacts appear in the present problem also.

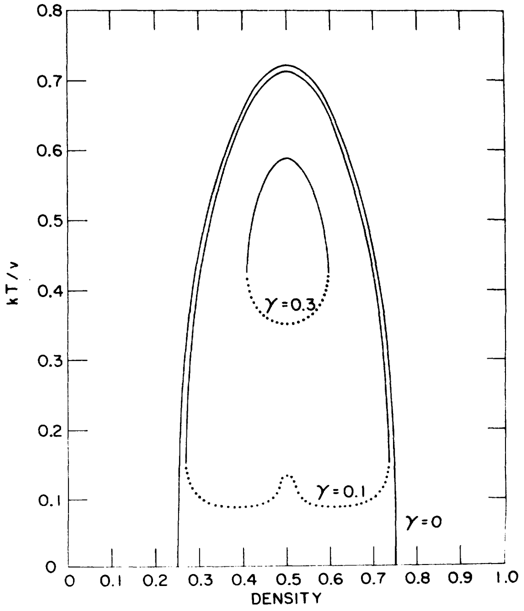

FIG. 2. Phase diagram for the case of repulsive nearest-neighbor interactions. Dotted lines indicate the anomalous transition.

As the value of γ increases, the region corresponding to the ordered phase shrinks and the transition temperature and anomalous transition temperature approach one another. The ordered phase vanishes entirely for γ approximately 0.33. For a density of $\frac{1}{2}$, a series expansion was carried out to determine the dependence of the maximum transition temperature on γ for small γ. This involves solving Eq. (3.6) together with the conditions $\epsilon = -2v$ and $V = \frac{1}{2}v$ which follow from the same symmetry conditions discussed in Sec. II. We find

$$T_M(\gamma,v)\,/\,T_M(0,v) = 1 - a'\gamma^2 - b'\gamma^4 - c'\gamma^6 + \dots, \tag{3.7}$$

where

$$T_M(0,v) = v\,/\,2\ln 2, \qquad a' = 1.37, \quad b' = 3.74 \tag{3.8}$$

for bosons and fermions. The effect of statistics again occurs first in the γ^6 term. As for the case of attractive interactions, the coefficient c' is of order unity for both cases but is slightly larger for bosons.

The anomalous ordering transition temperature was also calculated at a density of $\frac{1}{2}$, with the result

$$kT_A\,/\,v = -2/\ln[24\gamma^2 B(\gamma^2)],$$
$$B(\gamma^2) = \tfrac{1}{9} + 1/7(\ln 8\gamma^2 - \ln 3).$$

Thus the anomalous transition emerges from the Bethe-Peierls approximation for all finite values of γ and vanishes as $(\ln\gamma)^{-1}$ with vanishing γ.

IV. DISCUSSION

We have calculated the phase diagram of the two-dimensional quantum lattice gas in order to investigate the effects of tunneling and statistics on the order-disorder transitions of adsorbed systems. It was found that for all densities, the quantum effects decrease the transition temperature. Moreover, it was shown that the transition temperature depends, in order of decreasing importance, upon the interparticle interactions (order γ^0), quantum tunneling (order γ^2), and statistics (order γ^6). For the case of a square lattice and repulsive nearest-neighbor interactions, the values of γ for which a transition takes place are sufficiently small that the effects of statistics can be ignored. The difference in the maximum transition temperature of two isotopes of mass m_3 and m_4 ($m_3 < m_4$) is now easily calculated. As noted earlier, the parameter v is a functional of the particle mass, so that it will take different values in the two systems which we denote by v_3 and v_4. We assume for convenience that $\delta v \equiv v_3 - v_4$ is much less than $v \approx v_3 \approx v_4$. From Eqs. (3.7) and (3.8) we find

$$\delta T_M(\gamma, v) / T_M(0, v) = \delta v / v - a' \delta\gamma^2 + \ldots,$$

or

$$\delta T_M(\gamma, v) / T_M(0, v) = (1 + 2a'\gamma)\, \delta v / v + 2a'\gamma\, \delta m / m, \tag{4.1}$$

where the definition of γ

$$\gamma \equiv \hbar^2 / 2md^2 v$$

has been used. Note that if the interaction strengths were equal so that $\delta v = 0$, the lighter mass would have a lower transition temperature. This is what one might expect, as the lighter mass tunnels more easily and is therefore harder to order. However, δv will not vanish in general. Recall that v is the matrix element of the interparticle potential between wave functions which are localized at adjacent sites. The wave functions of the less massive particle will be somewhat less localized within a site than those of the heavier particles. This will be reflected in differing values of v_3 and v_4. Whether δv is positive or negative depends on the interparticle potential and the array of adsorption sites.

It is now seen that the difference in ordering temperatures of two isotopes has been related, via the quantum lattice gas, to two different manifestations of the kinetic energy corresponding to motion between cells and motion within a cell. The former effect appears explicitly in the tunneling term of the model Hamiltonian, contributes to the disorder of the system, and causes the difference in transition temperatures to vary directly with the difference in mass. The latter effect appears implicitly in the parameter $v(m)$ of the model, does not contribute to the disorder of the system, and causes the difference in transition temperatures to vary with the mass difference in a manner dependent upon the interparticle interaction and the array of adsorption sites. We now apply these results to the system of helium adsorbed on graphite. We expect that Eq. (4.1) remains valid for the system with coefficients a' which are appropriate to a triangular lattice. It is reasonable to assume that these coefficients will be of order unity as they are for the square array. To proceed further we need the distance d between the center of adsorption sites, which is 2.46 Å for graphite, and the matrix elements $v_3(m_3)$ and $v_4(m_4)$. Because the helium interparticle potential is strongly repulsive at 2.46 Å and has a positive second derivative there, it is to be expected that v_3 and v_4 will both be large and positive, with v_3 somewhat larger. In the calculation of these matrix elements it is clearly necessary to use a potential which is reasonably accurate in the repulsive region. The Beck potential,[16] whose form in this region is taken from theoretical calculations[17] of the helium interatomic potential, was chosen for this reason. Gaussian single-particle wave functions were assumed. The width of the Gaussian was taken as that value which, in the Hartree approximation, minimizes the energy of a two-dimensional system of helium atoms at a density corresponding to one particle per graphite site. Effects of the substrate potential are not included in the calculation of the width. Clearly the matrix elements calculated this way are not simply the interaction energy between two isolated atoms on adjacent sites but contain many-particle effects as well. However, we believe that it is entirely adequate for the qualitative understanding we seek.

The value of the matrix elements calculated by the above procedure are[18]

$$v_3 / k = 70.9 \text{ K}, \quad v_4 / k = 65.3 \text{ K}.$$

As expected, $\delta v = v_3 - v_4$ is positive. The corresponding values of $\gamma = \hbar^2 / 2md^2 v$ are

$$\gamma_3 = 0.019, \quad \gamma_4 = 0.015 .$$

With such small values of γ, it can be immediately concluded that effects of particle statistics can be completely ignored. Further, with a' assumed to be of order unity, it is seen from Eq. (4.1) that the major contribution to $\delta T / T$ arises from the term $\delta v / v$, which reflects the fact that, for small γ, the transition temperature scales with v. This circumstance is most fortunate because it permits a far greater confidence to be placed in the result for $\delta T / T$, which is independent of the particular scaling factor obtained by the Bethe-Peierls approximation, than in the results for δT or T which depend on this factor.

If a' is taken to be unity, Eq. (4.1) yields

$$\delta T / T \approx 0.082 .$$

This is to be compared with the experimental result[19]

$$\delta T / T \approx 0.027 .$$

The calculated fractional change is of the correct order of magnitude. Closer agreement is not expected, owing to the uncertainties associated with the calculation of v noted above. Most gratifying is the fact that the calculated fractional change has the correct sign; that is, the calculation yields a higher ordering temperature for He^3 than for He^4.

To summarize, the occurrence of a higher ordering temperature for He^3 can be understood as follows. Because the relative strength of the tunneling term is so small, the transition temperature of the adsorbed system essentially scales with the nearest-neighbor-interaction strength as in a classical system. The major quantum-mechanical effect is to cause this strength to be greater for He^3, as the less localized wave functions of the lighter atoms give greater weight to the repulsive part of the interatomic potential.

ACKNOWLEDGMENTS

The authors wish to thank A. D. Novaco for computing the relevant matrix elements and J. G. Dash and O. E. Vilches for useful discussions.

BFY02850 *PG PLRAA,00JUL3AB320003R020

*Work supported in part by the National Science Foundation.

[1] M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McLean, and O. E. Vilches, Phys. Rev. A (to be published).

[2] See, for example, C. Domb, Philos. Mag. Suppl. **9**, 149 (1960).

[3] C. E. Campbell and M. Schick, Phys. Rev. A **5**, 1919 (1972).

[4] This density range lies between 0.05 and 0.08 Å^{-2}.

[5] Y. C. Cheng and M. Schick, Phys. Rev. A 7, 1771 (1973).

[6] See, for example, W. J. Mullin, Phys. Rev. A **4**, 1247 (1971).

[7] C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962).

[8] P. C. Hohenberg, Phys. Rev. **158**, 383 (1967).

[9] H. A. Bethe, Proc. R. Soc. Lond. **150**, 552 (1935).

[10] R. E. Peierls, Proc. Camb. Philos. Soc. **32**, 471 (1935).

[11] See Ref. 6, wherein perturbation theory is carried out for the ground state to order γ^4.

[12] C. E. Easthope, Proc. Camb. Philos. Soc. **33**, 502 (1937).

[13] P. W. Anderson, Phys. Rev. **80**, 922 (1950).

[14] Y. -Y. Li, Phys. Rev. **84**, 721 (1951).

[15] T. Matsubara and H. Matsuda, Prog. Theor. Phys. **16**, 569 (1956).

[16] D. E. Beck, Mol. Phys. **14**, 311 (1969).

[17] P. E. Phillipson, Phys. Rev. **125**, 1981 (1962).

[18] A. D. Novaco (private communication).

[19] The experimental values of δT and T separately are 0.08 and 2.95 K.

PHYSICAL REVIEW A VOLUME 8, NUMBER 1 JULY 1973

Semiclassical Theory of Saturated Absorption in Gases

Jon H. Shirley
Quantum Electronics Division, National Bureau of Standards, Boulder, Colorado 80302

(Received 5 February 1973)

A three-dimensional theory for the resonant interaction of electromagnetic waves with a gas of two-level atoms is formulated in terms of macroscopic variables. The theory is utilized to find the steady-state attenuation of a plane wave in the presence of another plane wave running in the opposite direction with different amplitude. Contributions are included from the reflection of the oppositely running wave by an induced standing-wave inhomogeneity in the population inversion of the medium. The resulting attenuation and reflection coefficients are expressed as velocity integrals of continued fractions. Correspondence is made with existing gas-laser theories, yielding the formulation of a high-intensity ring-laser theory. Analytic approximations for the coefficients are presented for the Doppler-limit cases of both waves weak, one wave weak, and negligible reflection (rate-equation approximation). More-general cases have been calculated numerically. The attenuation coefficients exhibit a Lamb-dip feature. The relative depth of the dip increases rapidly with power at low saturation levels, slowly at high saturation, and is greater in the attenuation of the weaker wave. The width of the dip is nonlinearly power broadened. The shape of the dip is very nearly Lorentzian, except for one special case at high power in which the line splits. The propagation equations for the two waves are integrated over long absorption paths. A large resulting attenuation increases the relative size of the dip while decreasing the power broadening.

I. INTRODUCTION

Saturated absorption, or the nonlinear absorption of electromagnetic radiation at high power levels, was first observed in gases by microwave spectroscopy.[1] As the incident power was increased, the percent absorption decreased and the width of the absorption line increased. A theoretical explanation of these effects was given by Karplus and Schwinger[2] and independently by Snyder and Richards.[3] Actually such effects first appeared in the so-called Rabi transition probability[4] long used by workers in atomic and molecular beam resonance spectroscopy. Similar