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**THERMODYNAMICS OF DILUTE GASES:
APPLICATION TO SUBMOLEOLAYER HE FILMS**

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PONTIFÍCIA UNIVERSIDADE CATÓLICA DO RIO DE JANEIRO

DEPARTAMENTO DE FÍSICA

Av. Marquês de São Vicente, 225

Cidade Universitária - Rio de Janeiro - RJ

22451-1 - Caixa Postal - 20121

THEMODYNAMICS OF DILUTE GASES:
APPLICATION TO SUBMONOLAYER He FILMS

M. B. Vetrovec* and G. M. Carneiro
Departamento de Física, Pontifícia Universidade Católica
Cx.P. 38071, Rio de Janeiro, RJ, Brasil

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ABSTRACT. In this paper we calculate the thermodynamic properties of submonolayer He films. We first obtain expressions for the thermodynamic properties of dilute systems of particles interacting through a short range potential taking into account binary interactions between the particles. These expressions are exact in the limit $n \rightarrow 0$, n being the particle number density, and are valid at all temperatures. At high temperatures our expressions reduce to those obtained using the virial expansion truncated after the second term. Next we apply these expressions to He in two dimensions and compare our results with experiment and with previous calculations.

RESUMO. Neste trabalho nós calculamos as propriedades termodinâmicas de filmes de He a densidades correspondentes a submonocamadas. Primeiramente ~~nós~~ obtemos expressões para as propriedades termodinâmicas de um sistema diluído de partículas que interagem através de um potencial de curto alcance levando em consideração interações binárias entre as partículas. Essas expressões são exatas no limite $n \rightarrow 0$, n sendo a densidade do número de partículas, e são válidas a qualquer temperatura. Para altas temperaturas nossas expressões são idênticas àquelas obtidas utilizando a expansão do virial truncada a partir do segundo termo. Em seguida, nós aplicamos estas expressões para He em duas dimensões e comparamos nossos resultados com os dados experimentais e com cálculos realizados anteriormente.

*Permanent Address: Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela.

I. INTRODUCTION

Recent measurements of the thermodynamic properties of submonolayer He films adsorbed on Grafoil¹ suggest that these systems behave, over a wide range of temperatures and densities, as two-dimensional non-ideal gases. Theoretical calculations of the thermodynamics of He films have, so far, been carried out based on the virial expansion of the equation of state truncated after the second term^{2,3} (referred to here as second order virial expansion). The specific heat obtained in these calculations reproduce well most of the experimental data if it is assumed that the interaction potential between two adsorbed He atoms is a two-dimensional 6-12 Lennard-Jones potential or a two-dimensional Beck potential.³ Such good agreement between this theory and experiment is somewhat surprising because most of the experimental data is taken at temperatures and densities at which the second order virial expansion is not expected to be valid. As well know, this approximation treats the particles as obeying Boltzmann's statistics and thus neglects the effects of quantum statistics. These are expected to become important at temperatures and densities for which the thermal De Broglie wavelength $\lambda = (2\pi\hbar^2/Mk_B T)^{1/2}$ is greater than the average interparticle distance $\sim n^{-1/2}$, n being the areal number density. For the existing He data $n\lambda^2 \gtrsim 0.6$. Thus this problem needs further theoretical investigation.

The way to improve upon the second order virial expansion of the equation of state is suggested by results which have been derived in the so called generalized Hartree calculations of the thermodynamic properties of interacting quantum systems.⁴⁻⁶ These results show that the equilibrium thermodynamic properties of the system at all temperatures can be expressed in terms of "statistical quasiparticles" by formulas analogous to those proposed phenomenologically by Landau in his theory of Fermi liquids.⁷ In these calculations the thermodynamic potential is expressed as a functional of the quasiparticle distribution function and the equilibrium distribution function is obtained by minimizing the thermodynamic potential, just as in Landau's phenomenological theory. It follows that the entropy and particle number are given by the same expressions as those for a non-interacting gas of quasiparticles. The role of the quasiparticle energy in these expressions is played by the statistical quasiparticle energy, defined as the functional derivative of the total energy with respect to the quasiparticle distribution function. These results show that in the expressions for the thermodynamic properties there is a clear separation between statistics and dynamics. The statistics enter through the entropy and particle number expressions whereas the dynamics of the interacting particles enter only through the statistical quasiparticle energy (this quantity being given by its perturbation theory expansion⁴⁻⁶).

We therefore expect that the corrections of lowest order in the density to the thermodynamic properties at any temperature follow by taking into account the same dynamics as that entering the second order virial expansion - the dynamics of two - particle scattering - and by considering that the particles obey the correct quantum statistics (Fermi-Dirac or Bose-Einstein), instead of Boltzmann's statistics.

Following these ideas we derive in Sec. II expressions for the thermodynamic properties of a system of particles interacting through a short range potential which are exact to leading order in density and which are valid at all temperatures. First we write the total energy as a functional of the distribution function taking into account binary interactions between the particles. From this expression we obtain the statistical quasiparticle energy from which we derive the entropy, particle number and the equation of state. At high temperatures our expressions are identical to those obtained in the second order virial expansion and at low temperature they agree with the results obtained by Yand and Leo⁸, by Galitzkii⁹ and by Bloom¹⁰ for the imperfect Fermi gas, to lowest order in the density.

Using these expressions we calculate in Sec. III the thermodynamic potential of two-dimensional He gases assuming that two He atoms interact through a 6-12 Lennard-Jones potential identical to that used in Ref. 2. We compare our results with experiment and with previous

calculations.² Our results support the belief that submonolayer He films, at densities covered by experiment ($0.025 \text{ \AA}^{-2} \lesssim n \lesssim 0.050 \text{ \AA}^{-2}$), behave as non-ideal gases, except at the lowest temperatures. We find that there are sizeable differences between our results and those predicted by the second order virial expansion which indicate that this expansion is not justified in this temperature and density range. Our specific heat curves lie systematically above experiment.

II. THERMODYNAMICS OF DILUTE GASES

Consider a system of N identical particles in d dimensions ($d = 2, 3$) interacting through a short range potential. We assume that the potential is such that there are no two-particle bound states. At low densities the mean interparticle distance is large compared to the range of the potential and therefore binary interactions between the particles are the most important ones. Thus, the functional dependence of the total energy, E , on the distribution function, $n_{p\sigma}$, can be approximated by its linear and quadratic terms, that is

$$E[n_{p\sigma}] = \sum_{p\sigma} \epsilon_p^0 n_{p\sigma} + \frac{1}{2} \sum_{p\sigma} \sum_{p'\sigma'} f_{pp'\sigma\sigma'} n_{p\sigma} n_{p'\sigma'} + \dots \quad (1)$$

In Eq. (1) $\epsilon_p^0 = p^2/2M$, M being the mass of the particles, $f_{pp'\sigma\sigma'}$ is the energy of interaction of a particle of momentum p and spin projection σ with a particle of

momentum \underline{p}' and spin projection σ' . Here we consider only spin 1/2 fermions for which $\sigma = \pm 1/2$, and spinless bosons for which $\sigma = 0$.

The energy of interaction, f , which is identical to the shift in the energy levels of two-particles produced by the potential, follow from well known results of two-body scattering theory. For two distinguishable particles of spin zero $f_{\underline{p}\underline{p}'}$, is given in three dimensions (3D) by¹¹

$$f_{\underline{p}\underline{p}'} = - \frac{4\pi}{MkV} \sum_{\ell=0}^{\infty} (2\ell+1) \delta_{\ell}(k) \quad (\underline{k} = \frac{1}{2}(\underline{p}-\underline{p}')) \quad (3D) \quad (2)$$

and in two dimensions (2D) by

$$f_{\underline{p}\underline{p}'} = - \frac{4}{MA} \sum_{m=-\infty}^{\infty} \delta_m(k) \quad (\underline{k} = \frac{1}{2}(\underline{p}-\underline{p}')) \quad (2D) \quad (3)$$

In Eqs. (2) and (3) δ_{ℓ} and δ_m are, respectively, the scattering phase shifts for the partial waves of relative angular momentum ℓ and m , V is the volume of the 3D system and A is the area of the 2D system. For two indistinguishable particles f also follows from Eqs. (2) and (3) by considering the symmetry or anti-symmetry of the two-particle wave function. For spinless bosons only even angular momentum states lead to symmetric wave functions. Thus

$$f_{\underline{p}\underline{p}'}^B = \begin{cases} - \frac{8\pi}{MkV} \sum_{\ell=0 (\ell \text{ even})}^{\infty} (2\ell+1) \delta_{\ell}(k) & (3D) \quad (4) \\ \underline{k} = \frac{1}{2}(\underline{p}-\underline{p}') \\ - \frac{8}{MA} \sum_{m=-\infty (m \text{ even})}^{\infty} \delta_m(k) & (2D) \quad (5) \end{cases}$$

An extra factor of two in Eqs. (4) and (5) results from the indistinguishability of the particles. For spin 1/2 fermions (assuming that the potential is spin independent) an anti-symmetric wave function results from the combination of even angular momentum states with the singlet spin state or from the combination of odd angular momentum states with the triplet spin state. Now since the spin state $|\sigma\sigma'\rangle$ has probability $\frac{1}{2} \delta_{\sigma,-\sigma'}$ of being the singlet state and probability $(\frac{1}{2} \delta_{\sigma,-\sigma'} + \delta_{\sigma,\sigma'})$ of being the triplet state, $f_{\underline{p}\sigma, \underline{p}'\sigma'}$ is given by

$$f_{\underline{p}\sigma, \underline{p}'\sigma'}^F = \begin{cases} -\frac{4\pi}{MkV} \left\{ \delta_{\sigma,-\sigma'} \sum_{l=0}^{\infty} (l \text{ even}) (2l+1) \delta_l(k) + \right. \\ \left. + (2\delta_{\sigma,\sigma'} + \delta_{\sigma,-\sigma'}) \sum_{l=0}^{\infty} (l \text{ odd}) (2l+1) \delta_l(k) \right\} & (3D) \quad (6) \\ k = \frac{1}{2} (\underline{p} - \underline{p}') \\ -\frac{4}{MA} \left\{ \delta_{\sigma,-\sigma'} \sum_{m=-\infty}^{\infty} (m \text{ even}) \delta_m(k) + \right. \\ \left. + (2\delta_{\sigma,\sigma'} + \delta_{\sigma,-\sigma'}) \sum_{m=-\infty}^{\infty} (m \text{ odd}) \delta_m(k) \right\} & (2D) \quad (7) \end{cases}$$

Next we obtain the thermodynamic potential, Ω . As well known Ω is given by

$$\Omega = E - TS - \mu N \quad (8)$$

where T is the temperature, S is the entropy, μ is the chemical potential and N is the particle number. According to the results mentioned in Sec. I, S and N are given by

the non-interacting gas expressions⁴

$$S = -k_B \sum_{\underline{p}\sigma} \{ n_{\underline{p}\sigma} \ln n_{\underline{p}\sigma} \pm (1 \mp n_{\underline{p}\sigma}) \ln(1 \mp n_{\underline{p}\sigma}) \} \quad (9)$$

and

$$N = \sum_{\underline{p}\sigma} n_{\underline{p}\sigma} \quad (10)$$

In Eq. (9) k_B is Boltzmann's constant, the upper sign is for fermions and the lower sign is for bosons. The equilibrium distribution function, $\bar{n}_{\underline{p}\sigma}$, is obtained by minimizing Ω with respect to $n_{\underline{p}\sigma}$ one finds

$$\bar{n}_{\underline{p}\sigma} = \frac{1}{e^{(\epsilon_{\underline{p}\sigma} - \mu)/k_B T} \pm 1} \quad (11)$$

where $\epsilon_{\underline{p}\sigma} \equiv \delta E / \delta n_{\underline{p}\sigma}$ is the statistical quasiparticle energy. At low densities we find, using Eq. (1), that

$$\epsilon_{\underline{p}\sigma} = \epsilon_p^0 + \sum_{\underline{p}'\sigma'} f_{\underline{p}\sigma\underline{p}'\sigma'} n_{\underline{p}'\sigma'} \quad (12)$$

This result has been derived by Balian and De Dominicis⁵ by summation of terms in perturbation theory. The equilibrium thermodynamic properties of the system follow from Ω , Eq. (8), evaluated at $n = \bar{n}$. This requires the evaluation of E , S and N , Eqs. (1), (9) and (10) at $n = \bar{n}$. Substituting Eqs. (11) and (12) in Eqs. (1), (9) and (10) and expanding to lowest order in density we find

$$E(\mu T) = \sum_{p\sigma} \epsilon_p^0 n_p^0 + \sum_{p\sigma p'\sigma'} \epsilon_p^0 \frac{\partial n_p^0}{\partial \epsilon_p^0} f_{p\sigma p'\sigma'} n_{p'}^0 + \frac{1}{2} \sum_{p\sigma p'\sigma'} f_{p\sigma p'\sigma'} n_p^0 n_{p'}^0 \quad (13)$$

$$S(\mu T) = -k_B \sum_{p\sigma} \{ n_p^0 \ln n_p^0 + (1 \mp n_p^0) \ln(1 \mp n_p^0) \} + - \sum_{p\sigma p'\sigma'} \frac{\partial n_p^0}{\partial T} f_{p\sigma p'\sigma'} n_{p'}^0 \quad (14)$$

and

$$N(\mu T) = \sum_{p\sigma} n_p^0 + \sum_{p\sigma p'\sigma'} \frac{\partial n_p^0}{\partial \epsilon_p^0} f_{p\sigma p'\sigma'} n_{p'}^0 \quad (15)$$

In Eqs. (13)-(15)

$$n_p^0 = \frac{1}{e^{(\epsilon_p^0 - \mu)/k_B T} \pm 1} \quad (16)$$

Substituting Eqs. (13)-(15) in Eq. (8) we find

$$\Omega(\mu T) = \Omega^0(\mu T) + \frac{1}{2} \sum_{p\sigma p'\sigma'} f_{p\sigma p'\sigma'} n_p^0 n_{p'}^0 \quad (17)$$

where

$$\Omega^0(\mu T) = \mp k_B T \sum_{p\sigma} \ln(1 \pm e^{-(\epsilon_p^0 - \mu)/k_B T}) \quad (18)$$

is the thermodynamic potential of the non-interacting system.

Next we obtain the equation of state and the specific heat. First we eliminate μ from Eqs. (17) and (14). For this purpose it is necessary to find μ as a

function of the density, n ($= N/V$ in 3D or $= N/A$ in 2D), and of the temperature. Here we need only μ to lowest order, so let

$$\mu(nT) = \mu^0(nT) + \Delta\mu(nT) , \quad (19)$$

where $\mu^0(nT)$ is the chemical potential of the non-interacting system and $\Delta\mu(nT)$ is the correction of lowest order in density. Now, $\Delta\mu(nT)$ follows from the requirement that the non-interacting system and the interacting system have the same number of particles, that is from

$$N = \sum_{p\sigma} n_p^0(\mu^0T) = \sum_{p\sigma} \tilde{n}_{p\sigma}(\mu T) . \quad (20)$$

In Eqs. (20) we display the explicit dependence of n_p^0 , Eq. (16), and of $\tilde{n}_{p\sigma}$, Eq. (11), on the thermodynamic variables, for obvious reasons. Substituting Eqs. (11), (12) and (19) in Eq. (20), and expanding to lowest order we find

$$\sum_{p\sigma} \frac{\partial n_p^0(\mu^0T)}{\partial \epsilon_p^0} \left(\sum_{p'\sigma'} f_{p\sigma p'\sigma'} n_{p'}^0(\mu^0T) - \Delta\mu(nT) \right) = 0 . \quad (21)$$

Thus

$$\Delta\mu(nT) = \frac{\sum_{p\sigma p'\sigma'} f_{p\sigma p'\sigma'} \frac{\partial n_p^0}{\partial \epsilon_p^0} n_{p'}^0}{\sum_{p\sigma} \frac{\partial n_p^0}{\partial \epsilon_p^0}} . \quad (22)$$

In Eq. (22) n_p^0 stands for $n_p^0(\mu^0T)$. From here on we adopt this notation, unless stated otherwise.

To find $\Omega(nT)$ we substitute Eq. (19) in Eq. (17). The second term in the right hand side of Eq. (17) is already of first order and may be evaluated at $\mu = \mu^0$. Expanding the Ω^0 term in Eq. (17) to first order in $\delta\mu$ we obtain

$$\Omega(nT) = \Omega^0 - N\delta\mu + \frac{1}{2} \sum_{p, p'} f_{pp'} \frac{\partial n_p^0}{\partial T} \frac{\partial n_{p'}^0}{\partial T}, \quad (23)$$

where Ω^0 is $\Omega^0(\mu^0, T)$. The equation of state follows from the relationship between Ω and the pressure which is usually written in 2D and 3D as

$$\Omega = \begin{cases} -PV & (3D) \\ -\phi A & (2D) \end{cases} \quad (24)$$

where P is the pressure and ϕ is the spreading pressure.

The specific heat at constant volume, in 3D, or at constant area in 2D is

$$C = T \frac{\partial S(nT)}{\partial T} \quad (25)$$

Following the same procedure as before and using Eq. (14) we find that $S(nT)$ is given by

$$S(nT) = S^0 - \sum_p \frac{\partial n_p^0}{\partial T} \left(\sum_{p'} f_{pp'} \frac{\partial n_{p'}^0}{\partial T} - \delta\mu \right), \quad (26)$$

where S^0 is $S^0(\mu^0, T)$.

Thus

$$\begin{aligned}
C = C^0 - T \sum_{p\sigma} \frac{\partial^2 n_p^0}{\partial T^2} \left(\sum_{p'\sigma'} f_{p\sigma p'\sigma'} n_{p'}^0 - \Delta u \right) \\
- T \sum_{p\sigma} \frac{\partial n_p^0}{\partial T} \left(\sum_{p'\sigma'} f_{p\sigma p'\sigma'} \frac{\partial n_{p'}^0}{\partial T} - \frac{\partial \Delta u}{\partial T} \right) \quad (27)
\end{aligned}$$

These are the desired expressions. They do not apply to bosons below the Bose condensation temperature. However in 2D the Bose condensation temperature is zero¹² so they apply to any finite temperature.

Next let us show that at high temperatures above results reduce to the second order virial expansion and that at low temperatures they reduce to the imperfect Fermi gas results. Consider $\Omega(nT)$, Eqs. (23). At high temperatures $-\mu^0/k_B T \gg 1$ and we may approximate n_p^0 , Eq. (16), by the Boltzmann distribution, that is

$$n_p^0 = e^{-(\epsilon_p^0 - \mu^0)/k_B T} \quad (28)$$

Substituting Eq. (28) in Eq. (23) and using the high temperature expansion of Ω^0 (c.f. Eq. (18)),

$$\Omega^0 = -k_B T \sum_{p\sigma} e^{-(\epsilon_p^0 - \mu^0)/k_B T} \pm \frac{k_B T}{2} \sum_{p\sigma} e^{-2(\epsilon_p^0 - \mu^0)/k_B T} + \dots$$

we find

$$\begin{aligned}
\Omega(\mu T) &= -k_B T \sum_{p\sigma} e^{-(\epsilon_p^0 - \mu^0)/k_B T} \pm \frac{k_B T}{2} \sum_{p\sigma} e^{-2(\epsilon_p^0 - \mu^0)/k_B T} \\
&= -N \Delta_\mu + \frac{1}{2} \sum_{p\sigma p'\sigma'} f_{p\sigma p'\sigma'} e^{-(\epsilon_p^0 + \epsilon_{p'}^0 - 2\mu^0)/k_B T} + \dots \quad (29)
\end{aligned}$$

At high temperatures μ^0 is, according to Eqs. (22) and (28), given by

$$\Delta u = e^{\mu^0/k_B T} \frac{\sum_{p\sigma p'\sigma'} f_{pp'\sigma\sigma'} e^{-(\epsilon_p^0 + \epsilon_{p'}^0)/k_B T}}{\sum_{p\sigma} e^{-\epsilon_p^0/k_B T}} \quad (30)$$

To eliminate μ^0 we use Eq. (20), which at high temperatures reduces to

$$N = e^{\mu^0/k_B T} \sum_{p\sigma} e^{-\epsilon_p^0/k_B T} + e^{2\mu/k_B T} \sum_{p\sigma} e^{-2\epsilon_p^0/k_B T} \quad (31)$$

Substituting Eq. (31) in Eqs. (29) and (30) we find

$$\Omega(\mu T) = -Nk_B T(1 + B(T)N) \quad (32)$$

where

$$B(T) = \frac{1}{2} \frac{\sum_{p\sigma} e^{-2\epsilon_p^0/k_B T}}{(\sum_{p\sigma} e^{-\epsilon_p^0/k_B T})^2} + \frac{1}{2k_B T} \times$$

$$\times \frac{\sum_{p\sigma p'\sigma'} f_{pp'\sigma\sigma'} e^{-(\epsilon_p^0 + \epsilon_{p'}^0)/k_B T}}{(\sum_{p\sigma} e^{-\epsilon_p^0/k_B T})^2} \quad (33)$$

is the second virial coefficient. This can easily be verified by substituting Eqs. (4)-(7) in Eq. (33) and comparing the results with the well known formula for the second virial coefficient.¹³ At low temperatures the characteristic wavelength of the particles is large compared to the range

of the potential and $f_{p\sigma p'\sigma'}$ Eqs. (4)-(7) is dominated by the s-wave contribution. For fermions interacting through a hard-sphere potential of radius a $\delta_0 = -ka$ in 3D and $\delta_0 = \pi/2 \ln ka$ in 2D, and f is given by

$$f_{p\sigma p'\sigma'}^F = \frac{4\pi a}{MV} \delta_{\sigma, -\sigma'}$$

in 3D, and

$$f_{p\sigma p'\sigma'}^F = -\frac{4\pi}{MA} \frac{1}{\ln ka} \delta_{\sigma, -\sigma'}$$

in 2D. Using Eqs. (22), (23), (26) and (27) we see that at low T (neglecting the weak T dependence in 2D) there is only a shift in μ by $\Delta\mu = \frac{2\pi na}{M}$ in 3D and $\Delta\mu = -\frac{\pi n}{M} \frac{1}{\ln k_F a}$ in 2D, k_F being the Fermi momentum. The entropy and specific heat reduce to those of the ideal gas. These results are just those obtained for the imperfect Fermi gas to lowest order in density by Yang and Lee⁸ and Galitzkii⁹ in 3D and by Bloom¹⁰ in 2D.

We have just obtained expressions for the thermodynamic properties of a system of interacting particles valid at all temperatures and which are exact in the limit $n \rightarrow 0$. Before these results can be applied to predict the behavior of real systems, it necessary to answer the question of how low n must be in order that the higher order corrections to them can be neglected. This requires the calculation of higher order contributions in n to the statistical quasiparticle energy. The perturbation expansion for this quantity can be represented in terms of

diagrams which are topologically identical to self-energy diagrams but with rules for evaluating the contribution from a diagram so complicated that, so far, results have only been published for particles interacting with random impurities.^{5,6} To the best of our knowledge and except in the case discussed here, which corresponds to the summation of the so called ladder diagrams, the explicit calculation of the statistical quasiparticle energy has not been attempted. We have estimated the contributions of higher order in density to the statistical quasiparticle energy by assuming that these are roughly of the same order of magnitude as the corresponding self-energy diagrams. Our results indicate that the higher order corrections are at least of the order $\eta \equiv n\bar{\epsilon}/\bar{\epsilon}$, where $\bar{\epsilon}$ is of the order of the average interaction energy between two particles, that is

$$\bar{\epsilon} \sim \frac{\sum_{\underline{p}\underline{p}'\sigma'} f_{\underline{p}\underline{p}'\sigma'} n_{\underline{p}}^0 n_{\underline{p}'}^0}{\sum_{\underline{p}\sigma} n_{\underline{p}}^0 \sum_{\underline{p}'\sigma'} n_{\underline{p}'}^0},$$

and $\bar{\epsilon}$ is of the order of the typical particle energy at temperature T . Note that, for fixed n , η depends on the temperature. For particles interacting through a hard sphere potential of radius a , for instance, η reduces at low temperatures to $\eta \sim n^{1/3} a$ for fermions in 3D, $\eta \sim 1/\ln na$ for fermions in 2D and $\eta \sim 1/\ln(a/\lambda)$ for bosons in 2D. This is in agreement with the results obtained by Yang and Lee⁸, by Galitzkii⁹ and by Bloom¹⁰ for the imperfect Fermi gas. At high temperatures

$\eta \sim na^3$ in 3D and $\eta \sim na^2$ in 2D, in agreement with the classical virial expansion.¹³

From this analysis we conclude that for a low density system - low density meaning that the interparticle distance, $\sim n^{-1/d}$, is much greater than the range of the potential - we may distinguish three regions, characterized by the relationship between the De Broglie wavelength λ ($\lambda = 2\pi\hbar^2/Mk_B T$) and the interparticle distance $\sim n^{-1/d}$. First there is semi-classical region where $\lambda \ll n^{-1/d}$ in which our results are identical to those of the second order virial expansion. Second there is the intermediate region where $\lambda \sim n^{-1/d}$. There the effects of quantum statistics become important and the second order virial expansion is not adequate. The results of numerical calculations in 2D systems, to be discussed shortly, show that in this region η is small and that there are considerable differences between our results and the second order virial expansion. Finally there is the region $\lambda \gg n^{-1/d}$. There the second order virial expansion breaks down completely, of course, but our results become trivial, and higher order corrections become important, particularly in 2D.¹⁴

Next we discuss numerical calculations in 2D using the results of this section.

III THERMODYNAMICS OF SUBMONOLAYER He FILMS

In this section we apply the expressions derived earlier to calculate the thermodynamic properties of submonolayer He films and compare the results with experiments performed on He films adsorbed on Grafoil.¹

We assume, following the work of Siddon and Schick², that two He atoms bound to a plane surface interact through the 6-12 Lennard-Jones potential

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (34)$$

where r is the 2D distance between the atoms, $\epsilon/k_B = 10.22$ K and $\sigma = 2.556$ Å. We obtain $f_{pp\sigma}$, Eqs. (5) and (7), corresponding to $V(r)$, Eq. (34), using the phase shifts calculated by Siddon.¹⁵

In calculating the thermodynamic properties of submonolayer He films, to be discussed shortly, we have, just as in the previous section, neglected the contribution from bound states of two He atoms. However, in 2D, two He atoms interacting through $V(r)$, Eq. (34), have one bound state at energies $E_B/k_B = -4.63 \times 10^{-2}$ K for He³ and $E_B/k_B = -2.36 \times 10^{-2}$ K for He⁴ and at relative angular momentum $m = 0$. There are three ways in which these bound states contribute to the thermodynamic properties. First there will be a separate contribution to Ω from bound He atoms which in the present approximation is of the form of an ideal gas of He₂ molecules. Second the phase shift $\delta_0(n)$ in Eqs. (4)-(7) must be replaced by $[\delta_0(k) - \delta_0(0)]$;

$\delta_0(0) = \pi$ according to Levinson's theorem. It can be shown that for $T \gg -E_B/k_B T$ the contribution from the bound state is cancelled out by the $\delta_0(0)$ term in f .² Third there is a change in $\delta_0(k)$ itself which $\rightarrow \pi$ as $k \rightarrow 0$. This affects $\delta_0(k)$ appreciably only for values of $k \lesssim \sqrt{2mE_B/\hbar^2}$. For the E_B given above this represents a very small region of the phase space which will play a role only at very low temperatures ($T \lesssim -E_B/k_B$) which are of no interest here. Thus we can use the expressions derived in the previous section.

Now let us discuss the thermodynamic properties. First consider the equation of state which according to Eqs. (23) and (24) is

$$\beta(nT) = \phi^0(nT) + n\Delta\mu - \frac{1}{2A} \sum_{p\sigma p'\sigma'} f_{p\sigma p'\sigma'} n_p^0 n_{p'}^0$$

where ϕ^0 is the spreading pressure of the non-interacting gas. The results of our numerical calculations are shown in the isotherms of Figs. 1 (a)-(e). Also shown are the isotherms predicted by the second order virial expansion (ϕ_v) and the non-interacting gas isotherms (ϕ^0).

For close comparison between our results and the second order virial expansion we write ϕ as

$$\phi(nT) = \phi^0(nT) + nk_B T \beta(nT)N \quad (35)$$

where

$$\beta(nT) = \frac{\Delta\mu}{Nk_B T} - \frac{1}{2k_B T} \frac{\sum_{p\sigma p'\sigma'} f_{p\sigma p'\sigma'} n_p^0 n_{p'}^0}{\sum_{p\sigma} n_p^0 \sum_{p'\sigma'} n_{p'}^0} \quad (36)$$

We recall that the second order virial expansion of ϕ is

$$\phi_v = nk_B T(1 + B_0(T)N) + nk_B T B_{int}(T)N \quad (37)$$

In Eq. (37) B_0 , given by the first term in the right hand side of Eq. (33), is the non-interacting gas contribution to the second virial coefficient and $B_{int}(T)$, given by the second term in the right hand side of Eq. (33), is the part of the second virial coefficient due to interaction between the particles. For $n \lesssim 0.05 \text{ \AA}^{-2}$ the differences between ϕ and ϕ_v seen in Figs. 1(a)-(e) are mostly due to the difference between $\beta(nT)$ and $B_{int}(T)$, and not to the difference between ϕ_0 and $nk_B T(1 + B_0(T)N)$. We see from these figures that, as expected, ϕ and ϕ_v are equal only for $n\lambda^2 \ll 1$.

Our equation of state predicts regions of instability, where $(\partial\phi/\partial n)_T < 0$, for both He^3 and He^4 . For He^3 we predict that it is unstable for $T < 0.5 \text{ K}$ and $n > 0.025 \text{ \AA}^{-2}$ and that it is stable for $T > 0.5 \text{ K}$ at all densities. For He^4 we predict that it is unstable for $n < 0.05 \text{ \AA}^{-2}$ and $T < 2\text{K}$. This supports the idea that He^4 becomes liquid below 1.5 K for $n \lesssim 0.05 \text{ \AA}^{-2}$.

As discussed in Sec. II higher order corrections to our results are expected to be of order n . For $n \lesssim 0.05 \text{ \AA}^{-2}$, $n \lesssim 1$ for $T \gtrsim 1\text{K}$ in He^3 , and for $T \gtrsim 1.5$ in He^4 . Below these temperatures higher order corrections become important.

Next we consider the specific heat, C , Eq. (27). The results of our numerical calculations are shown in Figs. 2(a)-(d) (full curve) compared with the specific

heat obtained in the second order virial expansion², C_v , (dashed curve) and with the experimental points. First we note that our results differ substantially from C_v , except at higher temperatures. These differences are significant only for $T \gtrsim 1.0$ K for He^3 and for $T \gtrsim 1.5$ K for He^4 , for below these temperatures the higher order corrections to our results cannot be neglected. Above these temperatures the differences are large enough to support the conclusion that the second order virial expansion is not justified at these densities and temperatures. Second we see that our results for both He^3 and He^4 lie systematically above the experimental points. This discrepancy may be interpreted, not considering band structure effects or other complications, as indicating that the Lennard-Jones potential is not adequate.

We see from Figs. 2(b) and 2(d) that C for He^4 has a peak ($C/Nk_B \sim 4$) at $T \approx 1$ K. It is not possible, however, to attach any physical meaning to this peak because He^4 is unstable in this region. It is interesting to note that our expressions also give a peak in C for a system of hard disk bosons. This peak in C has been predicted by Siddon and Schick² on the basis of the second order virial expansion.

One feature of the specific heat data which has been interpreted as supporting the validity of the second order virial expansion down to temperatures where $n\lambda^2 > 1$ is the fact that $(CNk_B - 1)/n$ obtained experimentally is nearly independent of $n^{1/2}$ (the second order virial expansion

predicts that $(C_V/Nk_B - 1)/n$ is independent of n). In our calculation $(C/Nk_B - 1)/n$ depends rather weakly on n , as shown in Figs. 3(a)-(b). Our results for He^3 are in qualitative agreement with the data (Figs. 3(a)-(b)) and for He^4 they are in better qualitative agreement with the data than the second order virial expansion for they predict that for $T < 4\text{K}$ $(C/Nk_B - 1)/n$ increases with n in accordance with the behavior observed experimentally between 1.5 K and 4K. Thus this support further our conclusion that the second order virial expansion is not fully justified at the temperatures and densities investigated experimentally.

To summarize then, our calculation predicts that for $n < 0.05 \text{ \AA}^{-2}$ He^3 behaves as a non-ideal quantum gas for $T \gtrsim 1\text{K}$ and that He^4 behaves as a non-ideal quantum gas for $T \gtrsim 2\text{K}$ and becomes unstable below this temperature. The specific heat obtained by us differs by as much as 20% from experiment. We interpret this as evidence that the Lennard-Jones potential is not adequate to describe the interaction between two He atoms bound to the surface.

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- 14 This is expected for in our calculation the two particle scattering problem was treated neglecting the fact that the intermediate states are occupied by particles distributed according to $n_{p\sigma}$. It is known from the work on the imperfect Fermi gas that occupation of intermediate states is responsible, to lowest order in n , to an effective mass different from the bare mass and consequently to a non trivial specific heat at low temperatures. In the present context this could correspond to considering f in Eq. (1) also a functional of $n_{p\sigma}$.
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FIGURE CAPTIONS

- Fig. 1 Isotherms for He^3 and He^4 obtained in the present calculation (ϕ , full lines) compared to the second order virial expansion isotherms (ϕ_v , dashed lines) and with the non-interacting gas isotherms (ϕ_0 , dash-dotted lines).
- Fig. 2 Specific heat of He^3 and He^4 obtained in the present calculation (C/Nk_B , full line) compared to experiment (circles), to the second order virial expansion specific heat (C_v/Nk_B , dashed line) and to the non-interacting gas specific heat (C_0/Nk_B , dash-lotted line).
- Fig. 3 $(C/Nk_B - 1)/n \times T$ for He^3 and He^4 obtained in the present calculation (full lines) compared to experimental points and to the prediction of the second order virial expansion (dashed line).

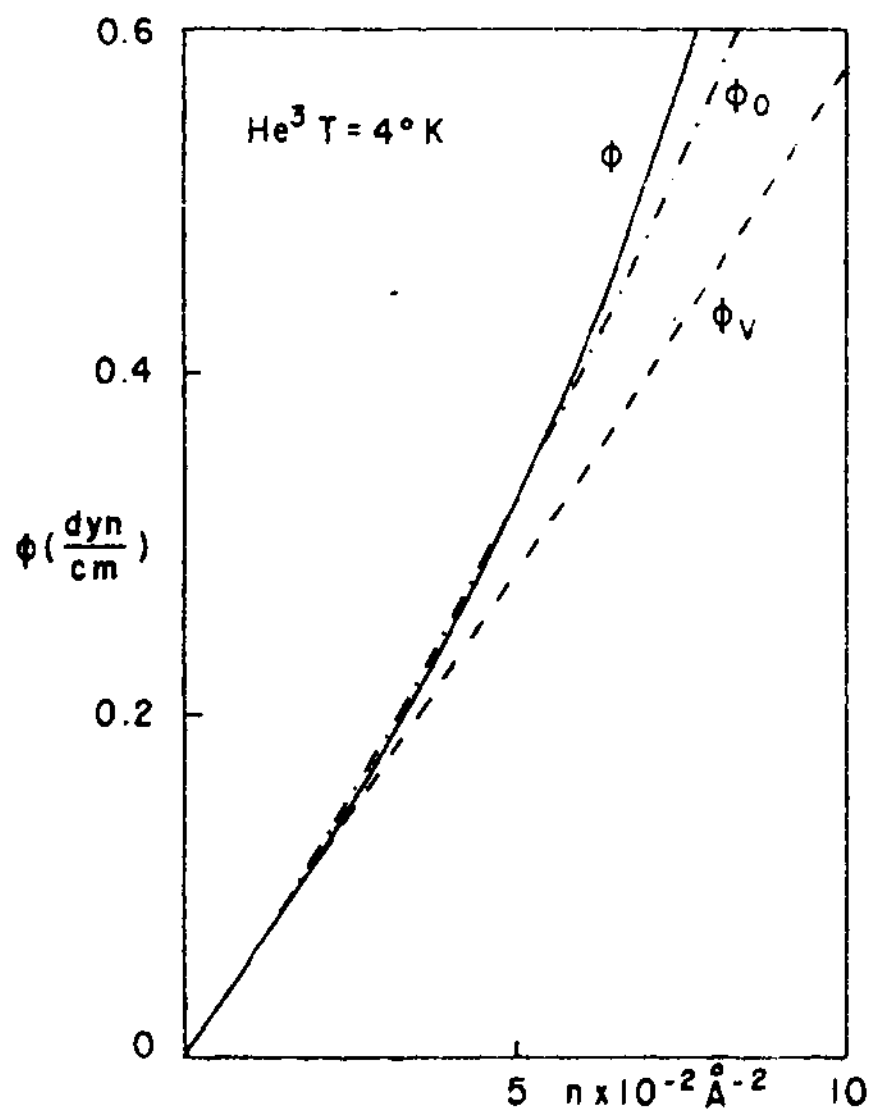


Fig. 1(a)

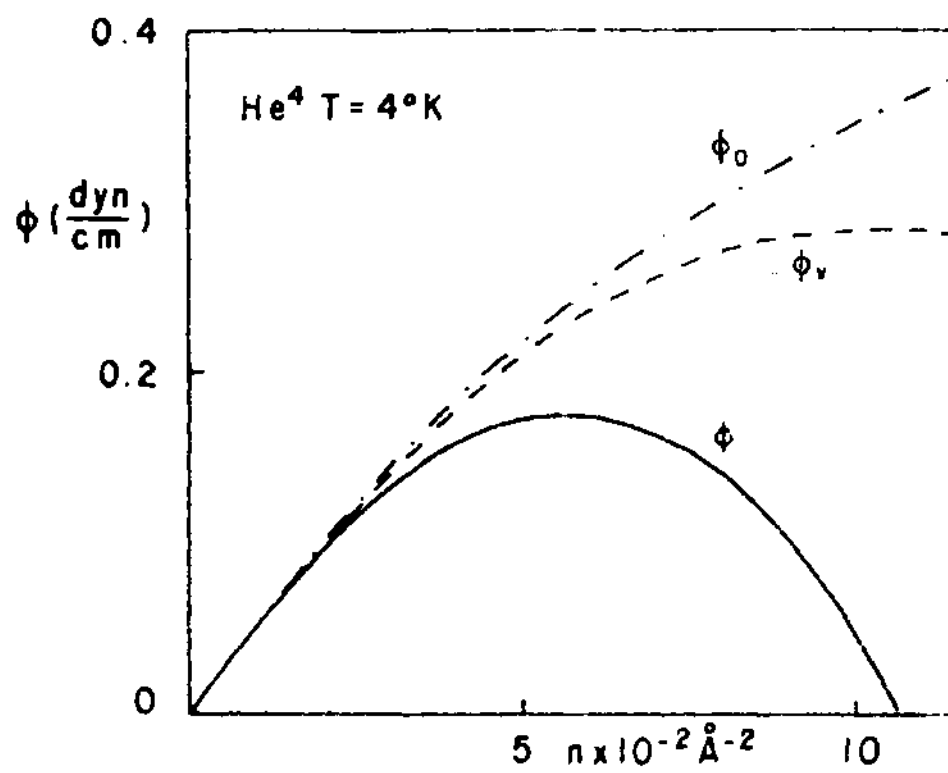


Fig. 1(b)

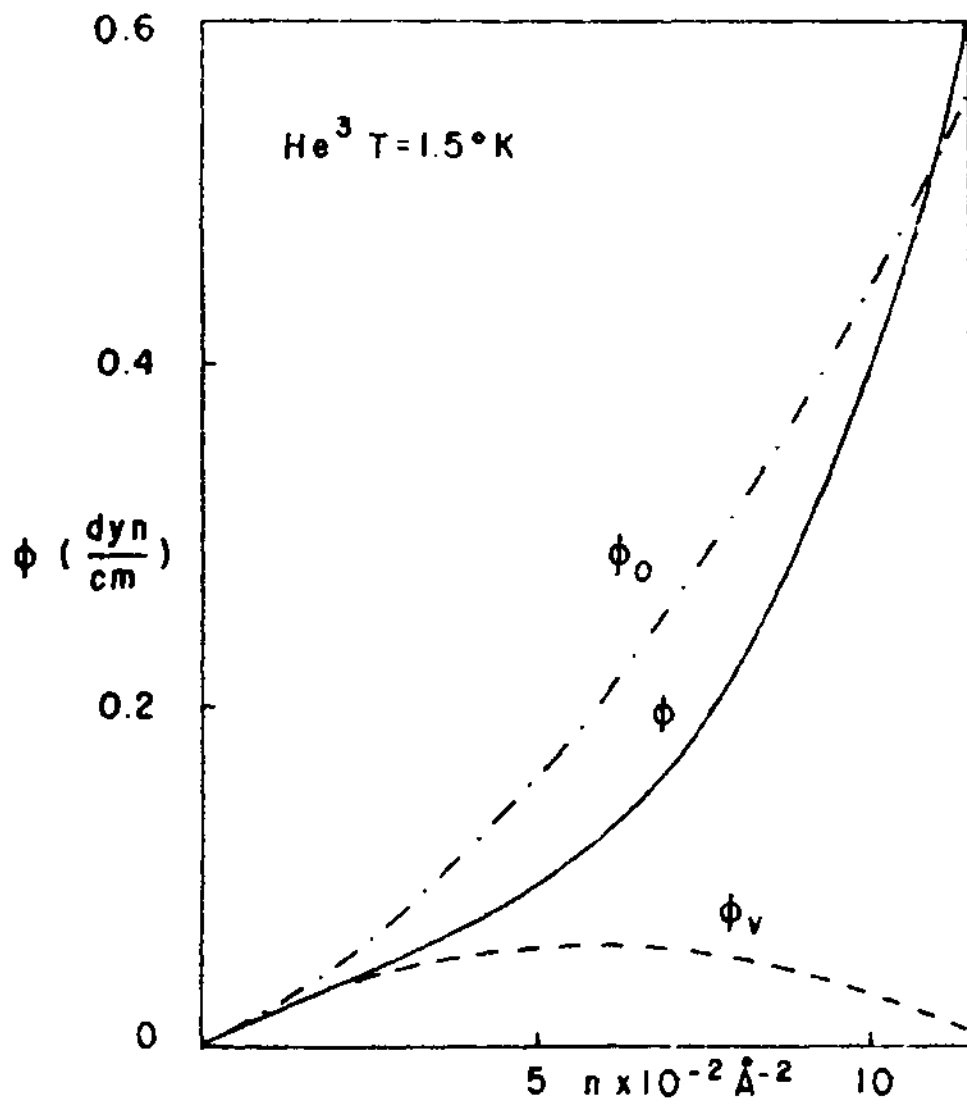


Fig. 1(c)

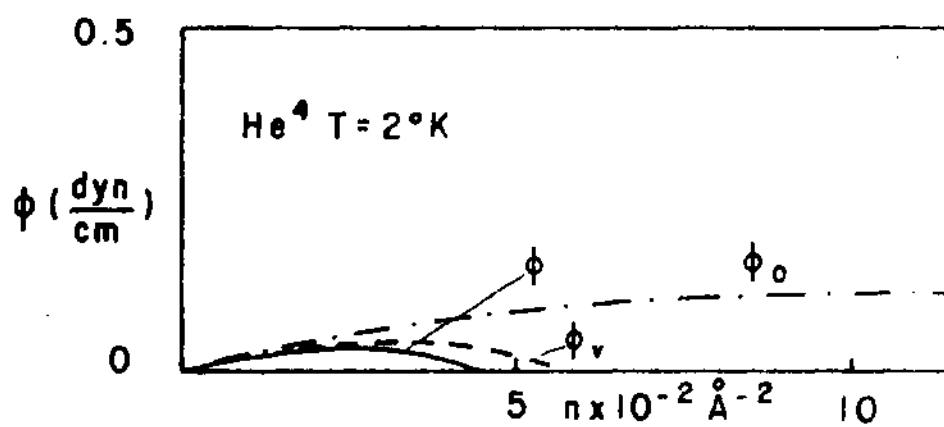


Fig. 1(d)

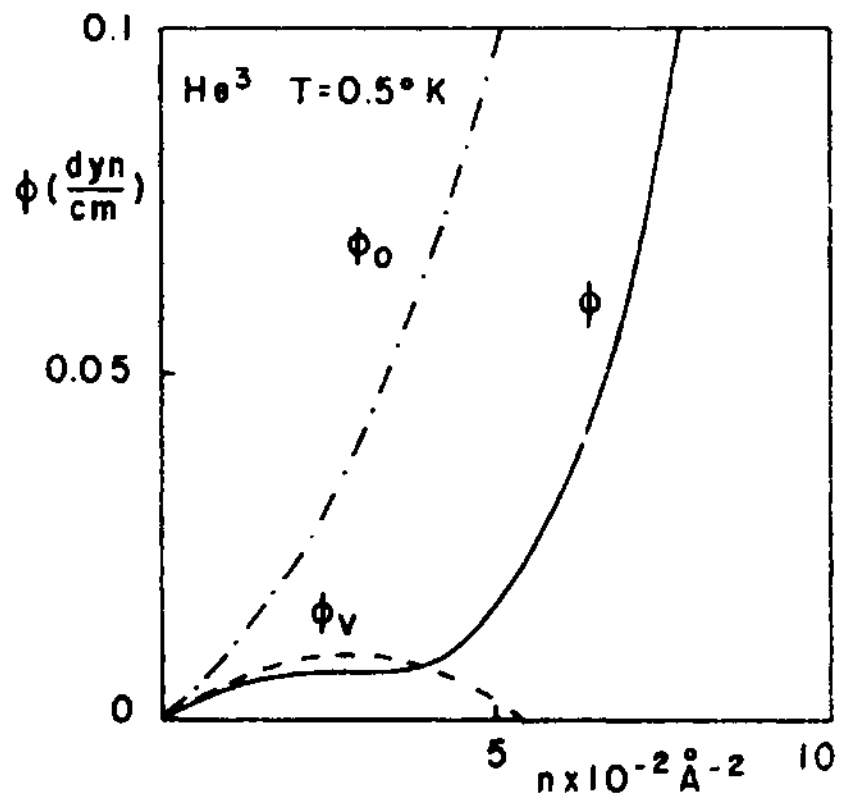


Fig. 1(e)

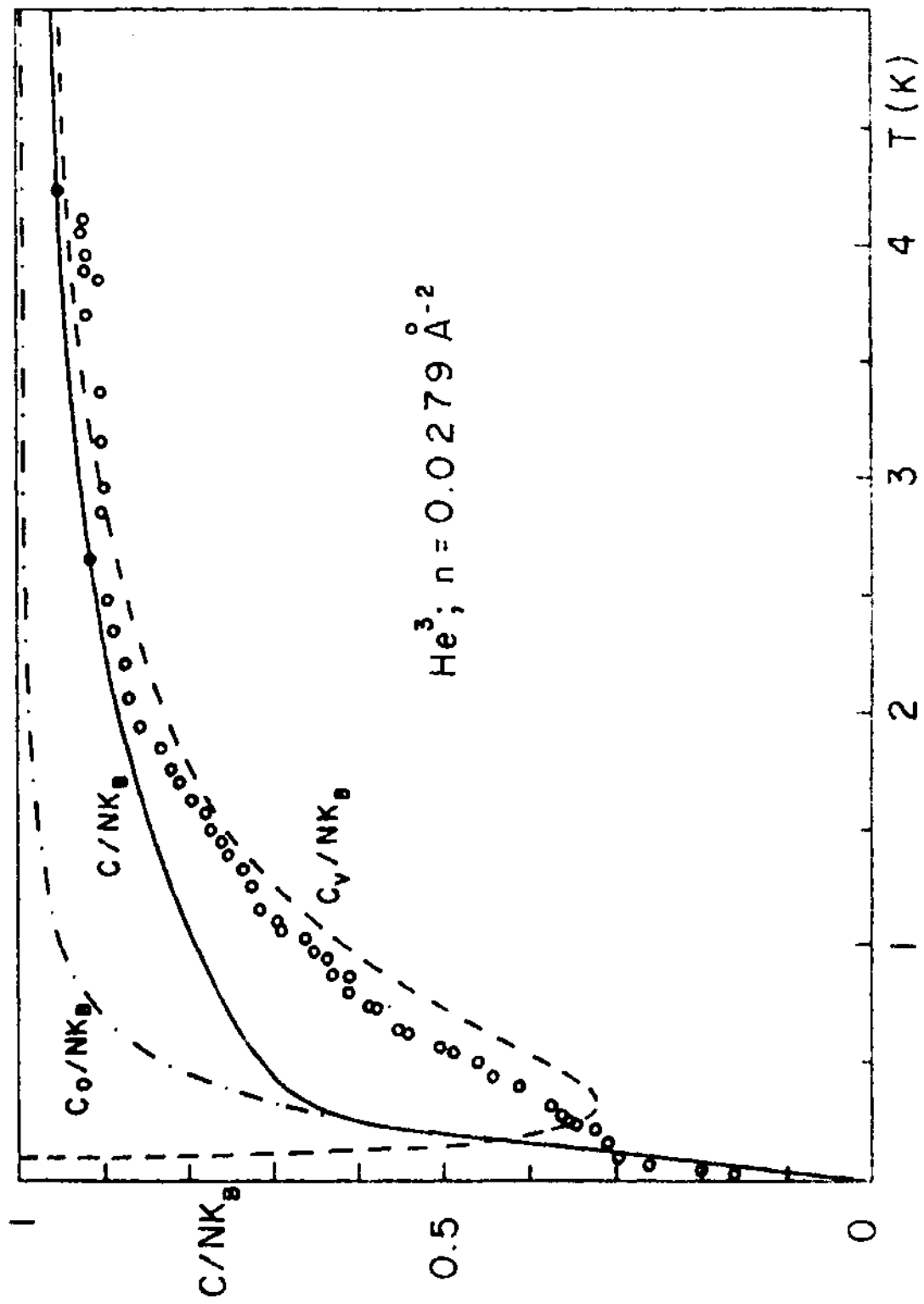


Fig. 2a

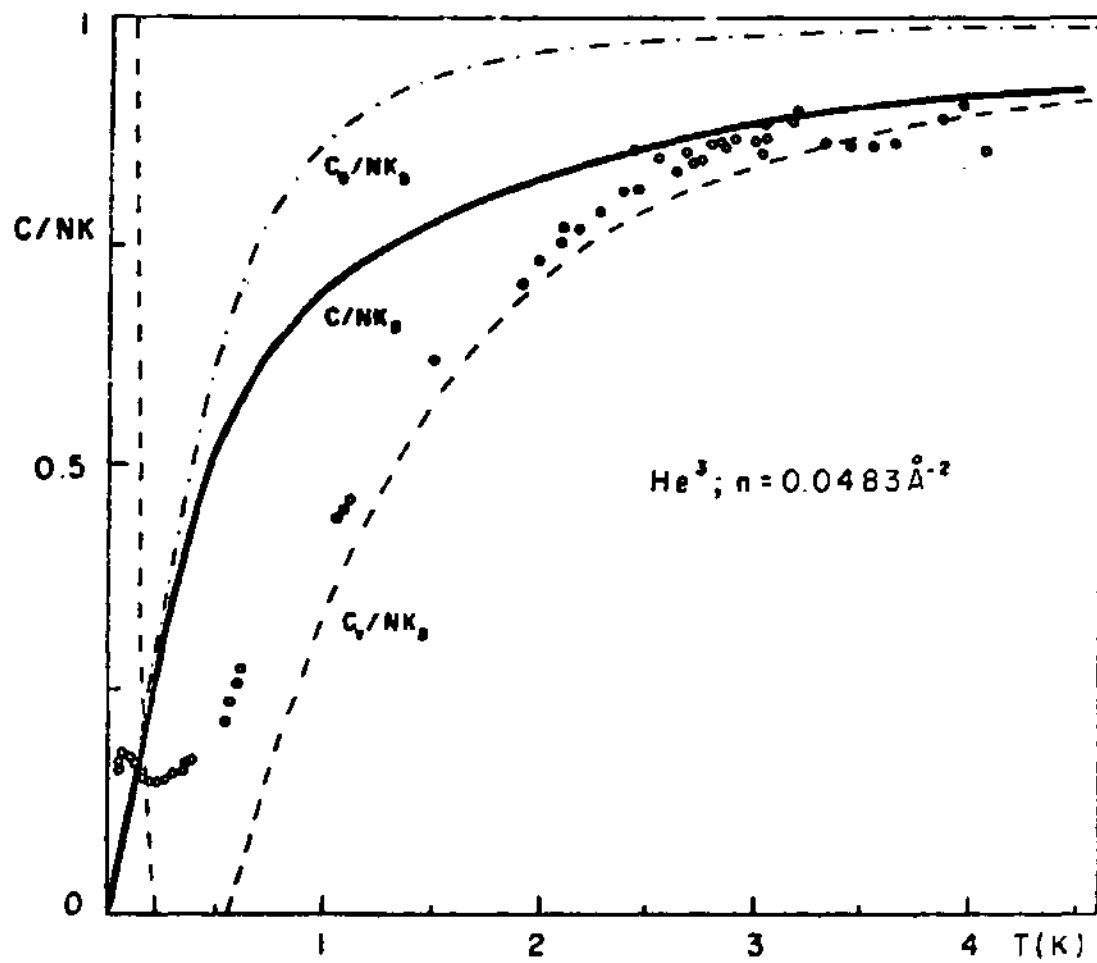


FIG. 2b

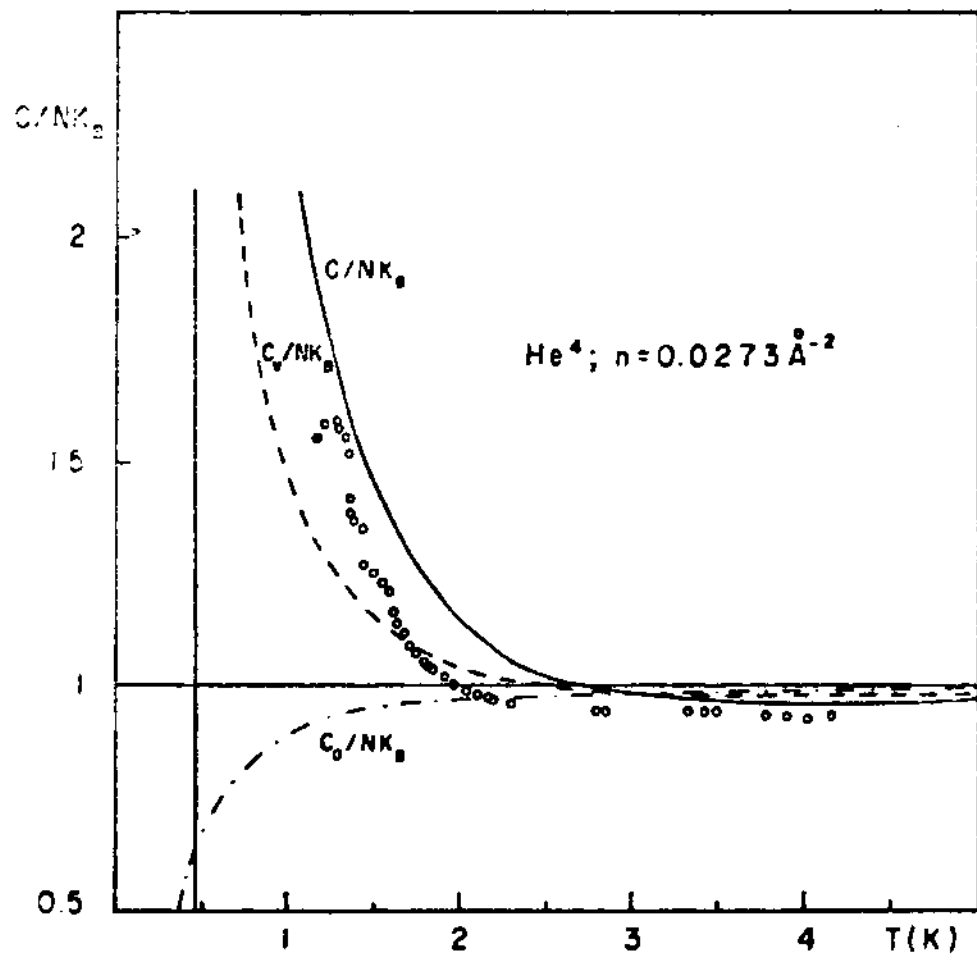


Fig. 2c

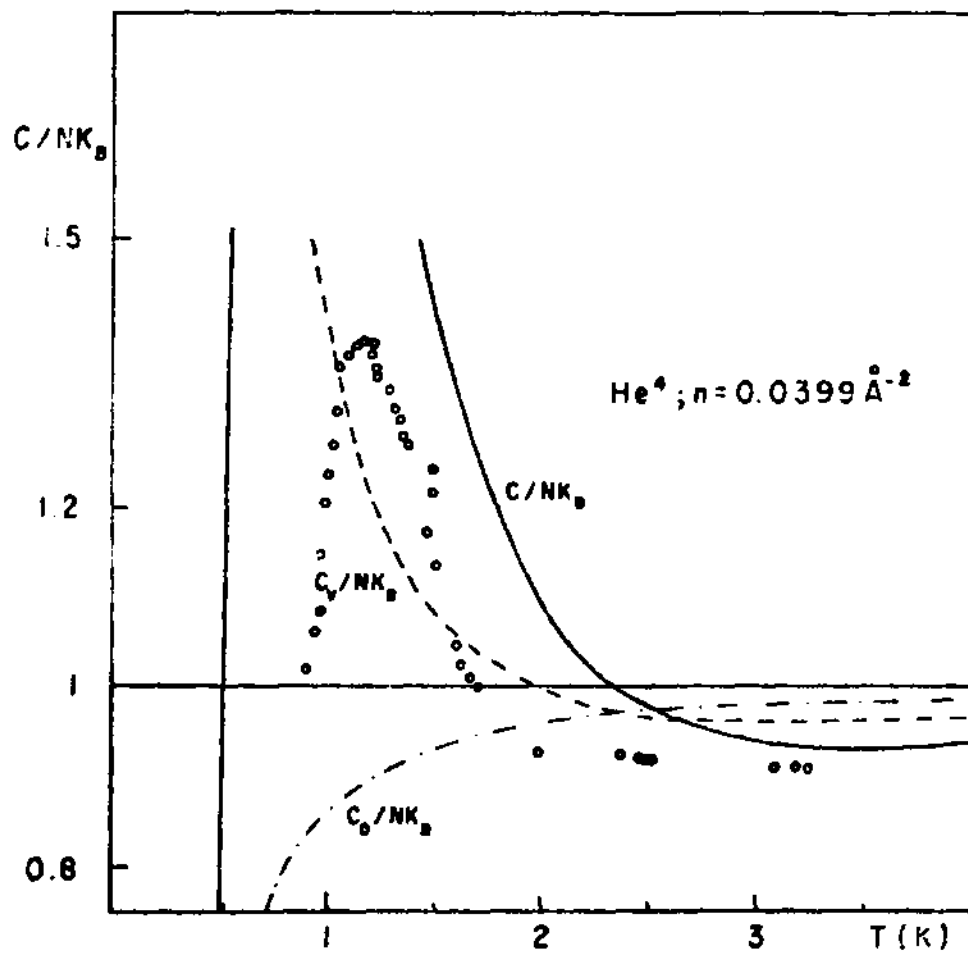


Fig. 2d

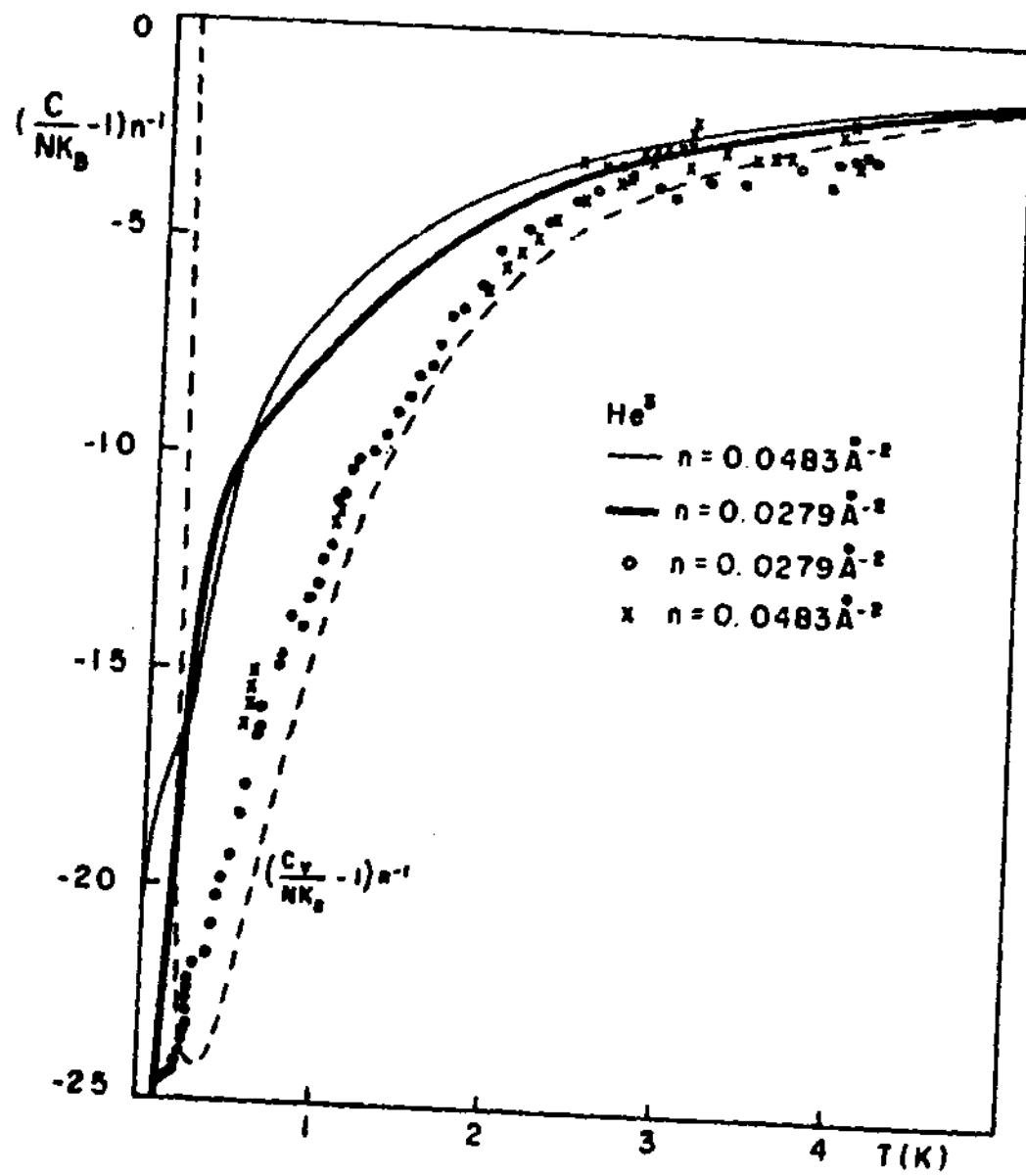


Fig. 3a

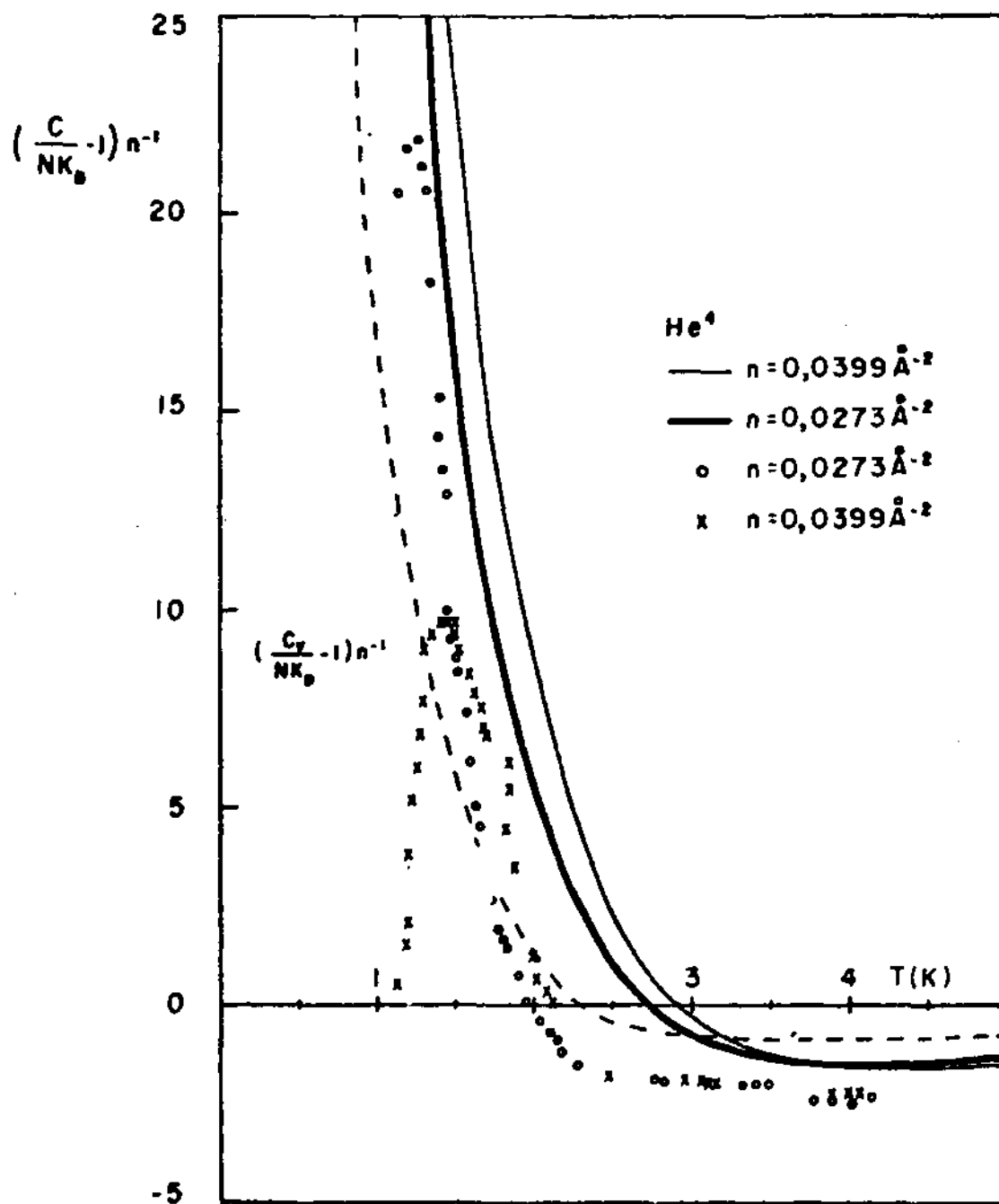


Fig. 3b