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Solid Layers in the Adsorbed Helium Film and Mobility of the Film at Low Coverages

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An examination is made of the evidence which led to the idea of the existence of solid layers in the adsorbed helium film at low temperatures. The experimental evidence from adsorption isotherm, specific heat, and flow measurements on the helium film is reviewed and the interpretation of this evidence as supporting the idea of a solid layer structure near the adsorbing surface is critically discussed. This discussion includes some evaluation of the applicability of the B.E.T. and other adsorption models used to describe helium adsorbed at very low temperatures. As a result of these considerations the author is of the opinion that the concept of a solid layer, or so, existing in an adsorbed helium film, is not nearly as well founded as is usually supposed. One particular inference from the solid layer picture; that the helium film at near monolayer coverages be considered immobilized is particularly questioned. The model of Dzyaloshinskii, Lifshitz, and Pitaevskii which considers no density variation with depth is discussed and a suggestion is also made for using some early calculations of Lennard-Jones and Devonshire to show that adsorbed helium at very low coverages should be quite mobile on the adsorbing surface.

I. INTRODUCTION

It has become customary when discussing the helium II film, to refer to the first layer or so near the wall as being of such high density that this corresponds to the helium being in the solid state. From time to time, this picture has been re-examined by various authors[1] but the idea still prevails that the film is solid near the wall, or, at very low thicknesses, solid throughout.[2] Whether the layers of the film near the wall are solid or not is a question of major importance when the mobility of very thin helium films is being discussed—that is, for the adsorbed film at low thicknesses. This question of mobility for very thin adsorbed helium films became of interest to the author in the course of investigations with adsorbed helium at temperatures below 1°K. Because, for such films, observed onset temperatures, for superfluid flow, extended to lower temperatures than had been reported before, and because previously reported onset temperatures were interpreted in a context[3] which viewed the first layer or so of adsorbed helium as being solid, it became of interest to examine the basis on which the solid layer picture was introduced. It was decided not only to evaluate the evidence for the existence of solid layers but also to see what evidence could be assembled for considering the adsorbed helium film to be mobile down to very low thicknesses. What follows is not a general discussion of the adsorbed helium film[4] but an examination of the evidence, presently available, of the way the film is held to the wall or substrate and in particular how this affects the mobility of those film layers closest to the wall. Throughout this article, the adsorbed helium film will mean the isotope, helium four, except where explicitly stated, and the "wall" will refer to the solid adsorbing surface to which the helium is attached.

II. ORIGIN OF THE SOLID-MONOLAYER PICTURE

It was first observed by Schaeffer, Smith, and Wendell[5] that the amount of helium adsorbed in a B.E.T.[6] monolayer was anomalously large at the temperature of 4.2°K. This quantity, usually denoted as v_m, is obtained from applying the B.E.T. equation to experimental plots of adsorption isotherm data. The B.E.T. isotherm equation may be written

$$v/v_m = cx/[(1-x)(1-x+cx)], \tag{1}$$

where v is the amount adsorbed, v_m the amount adsorbed in the first layer, and $x=p/p_0$ is the relative saturation pressure (p_0 is the saturation vapor pressure,

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[1] W. A. Steele, J. Chem. Phys. **25**, 819 (1956).

[2] M. H. Lambert, Phys. Rev. Letters **12**, 67 (1964).

[3] C. E. Hecht, Physica **24**, 1023 (1958).

[4] E. Long and L. Meyer, Advan. Phys. **2**, 1 (1953). This reference gives the only general review of the properties of the unsaturated helium film of which the writer is aware.

[5] W. D. Schaeffer, W. R. Smith, and C. B. Wendell, J. Am. Chem. Soc. **71**, 963 (1949).

[6] B.E.T. refers to the isotherm relation developed by S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).

TABLE I. Values of v_m for different gases on the same adsorbing surface, typical results from several investigations.

Surface	Helium		Nitrogen		Authors
	T°K	v_m	T°K	v_m	
Carbon black (1)	4.2	62.1 cm^3 S.T.P.	78	25.9 cm^3 S.T.P.	Schaeffer, Smith and Wendell (Ref. 5)
Carbon black (2)	4.2	113.9 cm^3 S.T.P.	78	52.1 cm^3 S.T.P.	
Glass	4.2	0.44 cm^3 S.T.P./m^2	78	0.22 cm^3 S.T.P./m^2	Keesome and Schweers[a]
Fe$_2$O$_3$ powder	<2	4000 cm^3 S.T.P.	77.3	1000 cm^3 S.T.P.	Frederikse and Gorter[b]

[a] W. Keesom and J. Schweers, Physica **8,** 1020 (1941).

[b] H. P. R. Frederikse and C. J. Gorter, Physica **16,** 402 (1950).

p the actual pressure in the system). The value of c is given by

$$c=j_1/j_{\text{liq}} \exp\{(E_1-E_{\text{liq}})/kT\}. \qquad (2)$$

In this equation; j_1 and j_{liq} are the partition functions for an atom in the first layer and in the liquid, respectively, while E_1 is the interaction energy between an atom in the first layer and the wall, and E_{liq} is the energy of interaction between the atoms in the bulk liquid. The B.E.T. equation may also be written in the form

$$[x/v(1-x)]=(v_mc)^{-1}+[(c-1)/v_mc]x \qquad (3)$$

so that if $x/v(1-x)$ is plotted against x the resulting straight line will give v_m and c from the values of its slope and intercept at $x=0$. Equation (1) is often referred to as the "∞-form" B.E.T. equation,[7] meaning that the number of adsorbed layers is not restricted. The value of v_m obtained in the above manner for helium, at temperatures of 4.2°K and below, is between two and four times as large as that for a gas such as nitrogen adsorbed on the same surface at temperatures near the nitrogen boiling point. Table I gives some values of v_m, typical of those available in the literature, for helium at 4.2°K or below, and also, in each case quoted, for nitrogen at about 78°K. Such values of v_m have also been compared[8] with the volume of helium required to give a surface coverage of a monolayer, assuming for it a density equal to that of bulk liquid helium, and on the basis of this simple view of a monolayer, the v_m value is two to three times greater than this monolayer volume.

Comparisons have also been made between the effective atomic diameter of helium in an adsorbed film, as given by the v_m value (assuming a simple close-packing of spheres) and the value for the bulk liquid and bulk solid. Table II presents some values of the atomic diameter, calculated from v_m, together with values of the atomic spacing obtained from diffraction experiments with bulk liquid and bulk solid. The picture of the adsorbed layer used in calculating these atomic diameters is a crude one[9] but they have, nevertheless, been compared with the atomic spacing for solid helium. It can be said that the atomic diameters calculated from adsorption information are considerably less, in most cases, than the interatomic distance obtained for liquid helium by Hurst and Henshaw[10] (compare however the values obtained by Hoffman, Edeskuty, and Hammel[11]).

Values of v_m and d, such as those displayed in Tables I and II, have been used as a basis for the view that the first layer of the adsorbed helium film, at temperatures of a few degrees absolute, is very dense; so dense that it could be regarded as a solid. The first suggestion of this, by Schaeffer, Smith, and Wendell,[5] was followed up, more forcefully, by Long and Meyer,[12] and by Band.[13] As a result of the considerations of these authors, the picture emerged that the first layer was solid-like and bound strongly to the wall and the higher layers, if present, were liquid-like. From this beginning, a picture has been developed that there is a continuous variation in the density of the film; from the highly compressed (solid) state next to the wall out to the bulk liquid density at large film thicknesses.[14,15]

Other experimental information which is available on adsorbed helium films has been used to support the above picture of the film's composition and these arguments are reviewed in Sec. IV. In Sec. III the limitations of the B.E.T. model will be examined as to their effect on the values that the model gives for such quantities as v_m.

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[7] D. M. Young and A. D. Crowell, *Physical Adsorption of Gases* (Butterworths Scientific Publications Ltd., London, 1962), p. 147.

[8] See Table I of Ref. 4.

[9] See, for instance, the discussion of this given by H. P. R. Frederikse and C. J. Gorter, Physica **16,** 402 (1950).

[10] D. G. Hurst and D. G. Henshaw, Phys. Rev. **100,** 994 (1955).

[11] C. J. Hoffman, F. J. Edeskuty, and E. F. Hammel, J. Chem. Phys. **24,** 124 (1956).

[12] E. Long and L. Meyer, Phys. Rev. **76,** 440 (1949).

[13] W. Band, Phys. Rev. **76,** 441 (1949).

[14] S. Franchetti, Nuovo Cimento (Ser. 10) **4,** 1504 (1956).

[15] K. R. Atkins, Can. J. Phys. **32,** 347 (1954).

TABLE II. Some values of atomic diameters for helium in adsorbed, bulk liquid, solid, and gaseous states.

State	d(A)	Temperature	Reference
Gaseous	2.1	Low temp. (down to 15°K)	Keesom[a] calculations from thermal conductivity data.
Liquid	3.7	4.2°K	Hurst and Henshaw (Ref. 10) experiments on neutron diffraction
Solid at 38 atm	3.55	1.45°K	Keesom and Taconis[b] experiments on x-ray diffraction
Adsorbed on carbon blacks	2.9 2.8	4.2°K	Schaeffer, Smith, and Wendell (Ref. 5) calculated from B.E.T. v_m value and assuming close packing of spheres
Adsorbed on Fe_2O_3	2.2	2.25°K and below	Long and Meyer (Ref. 12) calculated from v_m
Adsorbed on activated charcoal	3.1(He^4) 3.2(He^3)	3.95°K 3.0°K	Hoffman, Edeskuty, and Hammel (Ref. 11) calculated from v_m
Adsorbed on Fe_2O_3	2.7	4.2°K	Strauss (Ref. 22) calculated from v_m

[a] W. H. Keesom, *Helium* (Elsevier Publ. Co., Amsterdam, 1942), p. 110.

[b] W. H. Keesom and K. W. Taconis, Physica **5**, 161 (1938).

III. REVIEW OF THE EVIDENCE FROM ISOTHERMS

A. Limitations of the B.E.T. Model and Their Consequences When Applied to Helium

The B.E.T. isotherm relation was the first to give, in one equation, a description of an adsorption isotherm over a wide range of relative saturation pressures. To achieve this a number of simplifying assumptions were made and these are listed below:

(1) Adsorption is considered to take place on fixed sites, adsorption in higher layers on top of atoms already adsorbed and not on "in between positions."

(2) No lateral interaction between adsorbed atoms is considered.

(3) The first layer only to have an interaction with the surface. All further layers to have only interparticle interaction with the same energy as would apply in the liquid, and involving only nearest neighbors in the vertical stack of adsorbed atoms on each site.

(4) Classical statistics to apply. The shortcomings of such a list of assumptions has often been discussed[16] but the outcome of such discussions seems to be that is very hard to make modifications conveniently; as Gorter and Frederikse[17] remark "... B.E.T.—theory gives a simple and valuable first picture of the phenomenon of adsorption, but it seems difficult to correct its obvious shortcomings without destroying the simplicity which perhaps constitutes its chief attraction."

There seems to be no obvious single successor to the B.E.T. model but there has been progress in dealing more realistically with some aspects of the adsorption process. For instance, lateral interaction between adsorbed atoms can be allowed for, in some simple cases, by using an adaption of the Ising model, as has been done, in an exact calculation, by Ballentine and Betts.[18] However, such calculations still employ a classical description of the system and both this approach and that of the B.E.T. model fall short in this respect when applied to helium at temperatures of a few degrees absolute. At these temperatures the de Broglie wavelength of a helium atom is approximately 10 Å (much greater than the interatomic distance of an adsorbing surface) and the zero-point energy can be comparable to or greater than the classical value for the thermal energy. The large de Broglie wavelength compared to the probable interparticle distance on a set of sites means that quantum statistics must be applied; contrary to the statement made by Hecht[3] that classical statistics apply in the first layer as a result of localization on sites. Hecht further concluded that this meant there could be no quantum-statistical transition in the first layer (see Sec. IVC). Calculations which at least take the quantum-mechanical features of the system into account are discussed in Sec. VI.

Before going further it would be useful to summarize, briefly, the features of the adsorption process with which the B.E.T. theory has been successful. First of all, it gives an isotherm of the form which is typical of the type II (as classified by Braunauer[19]) and covers the full range of p/p_0 from zero to saturation. Although for any given situation the agreement with experiment

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[16] See Ref. 7, p. 159.

[17] C. J. Gorter and H. P. R. Frederikse, Physica **15**, 891 (1949).

[18] L. E. Ballentine and D. D. Betts, Physica **28**, 1077 (1962).

[19] S. Brunauer, *The Adsorption of Gases and Vapors* (Clarendon Press, Oxford, England, and Princeton University Press, Princeton, N.J., 1945).

is not likely to be very close for more than a small part of the range, the qualitative features of the isotherm are represented. Next, the B.E.T. plot (see Sec. II) gives values for v_m, the amount adsorbed in the first B.E.T. layer, and c, the constant related to the adsorption interaction energy [Eq. (2)]. The experimentally obtained values of v_m are very often used to determine surface areas of adsorbents; the area obtained using nitrogen at the temperature of its boiling point, and assuming an area of 16.2 $(\text{Å})^2$ for the nitrogen molecule, being often referred to as a "standard B.E.T. area." Checks of this value for the adsorbing area have been made by such methods as the direct measurement of the area of a metal foil, and, electronmicroscope or x-ray methods of determining the mean particle size of a powder. These give values for the ratio: (B.E.T. area)/(apparent geometrical area) which vary with the method used for direct measurement and with the adsorbing surface, but which have an average value of about 1.3 (often expressed as a roughness factor). This agreement is sufficiently close, considering the uncertainties in the adsorption measurement and the area check, that the standard B.E.T. area has come to be considered as good as any other measure of the adsorption area, and it also has the advantage of being much more convenient for powder adsorbents. From the experimental value of c the value of E_1 can be obtained if the ratio j_1/j_{liq} [see Eq. (2)] is known for the particular situation. Often this ratio is taken as unity, merely for convenience, but attempts to evaluate it explicitly for particular situations have not been very illuminating either.[20] Assuming some value for j_1/j_{liq}, the value obtained for E_1 should bear some relation to the heat of adsorption per molecule obtained in other ways, but the agreement is not very good, even for the case of nitrogen.

With the foregoing in mind, we now look at the application of the B.E.T. relation to the adsorption of helium for temperatures at or below its boiling point. When adsorption data for helium became available it was natural to compare them with the B.E.T. model and this led to the finding of anomalously large v_m values (Table I). Further examination of these v_m values, however, shows them to be temperature-dependent[21,22] and this question has been taken up by Steele.[1] Using an isotherm relation introduced by Dole,[23] one which reduces to the B.E.T. relation under assumption (3) listed at the beginning of this section, Steele considered the less restricted case in which a molecule in the second adsorbed layer has an energy between the value it would have in the first layer and that which it would have in the bulk liquid. Steele introduces a quantity, z, which is, for the second layer, what c is for the first layer in the B.E.T. model. This quantity z increases with decreasing temperature and, as Steele shows, isotherms of helium adsorbed at 4.2°K can be fitted with z having values between e^3 and e^5. Steele also shows that the greater the value of z in this isotherm relation, the greater the apparent value of v_m obtained if the experimental data are analysed according to standard B.E.T. theory. Thus, if z increases with decreasing temperature, the B.E.T. value for v_m would also increase, and this has been found experimentally as mentioned above. From Steele's study it seems clear that the error involved in neglecting the heat of adsorption for the higher layers becomes more serious as the temperature of the system is lowered and one of the situations which would show this most would be the comparison of results on the same adsorbent at liquid-nitrogen and liquid-helium temperatures. Steele concludes that adsorbed helium is compressed but not to the large values generally reported; he also refers to some calculations made by Singh and Band[24] who conclude that adsorbed helium would be thermodynamically unstable if it had the density attributed to it from application of B.E.T. theory. These considerations of Steele's, while they do not give a complete remedy for assumption (3), given at the beginning of this section, do show that if a less restricted assumption is used it can point up how v_m data from a B.E.T. analysis are biased. There is therefore much less ground for retaining the solid structure idea for the helium monolayer; the helium may possibly be denser than bulk liquid (see Sec. VI) but there is no compelling reason for deciding that it is solid.

There is a further point raised by Steele's analysis concerning the pressure at which the first layer is completed. This is usually loosely associated with the pressure at which the "knee" appears on the isotherm (see Fig. 1). The isotherm relation of Steele and Dole gives

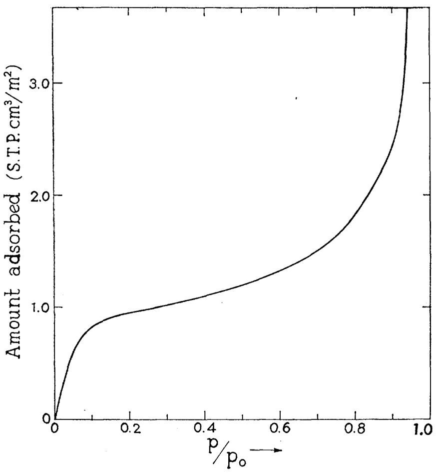

FIG. 1. Illustration of the form of an isotherm for physical adsorption on a nonporous adsorbent—the Type II of the classification given by Brunauer (Ref. 19).

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[20] See Ref. 7, p. 164.

[21] See Fig. 5 of the paper by C. J. Hoffman, F. J. Edeskuty, and E. F. Hammel, J. Chem. Phys. **24**, 124 (1956).

[22] A. J. Strauss, thesis, University of Chicago (1956) quoted in E. Long and L. Meyer, Ref. 4 (see Fig. 2, of their paper).

[23] M. Dole, J. Chem. Phys. **16**, 25 (1948).

[24] R. P. Singh and W. Band, J. Phys. Chem. **59**, 663 (1955).

the knee as occurring at $p/p_0 \approx 10^{-15}$ for values of c and z consistent with reasonable experimental findings for helium at 4.2°K. [Steele's Eq. (5).] Hobson[25] has compared his experimental isotherm data for helium on Pyrex glass at 4.2°K with this isotherm relation. He concludes that in following the adsorption down to p/p_0 values of 10^{-12} he could not find clear indication that he was dealing with less than monolayer coverage. Thus this is not inconsistent with the Steele–Dole relation. Meyer[26] concluded from some adsorption experiments on gold that at 4.2°K the first layer was completed at $p/p_0 < 10^{-7}$ which is also much lower than the values usually quoted and not in conflict with Hobson's findings. Thus we see that there are indications that the monolayer is formed at much lower pressures than would be expected from the B.E.T. theory and this also points to the monolayer containing less helium than would be given by the B.E.T. model.

B. Other Forms of Isotherm Used for Adsorbed Helium at Low Temperatures

Up to this point the discussion has been concerned with the influence of the limitations of the B.E.T. model on the derived quantity, v_m, particularly. It should also be mentioned that several attempts to modify the simple B.E.T. picture have been made for the special case of helium. The first of these was suggested by Aston and Mastrangelo[27] who considered the first B.E.T. layer as really more than one layer. They expressed this by taking the energy of an atom in a layer to be greater than that in the bulk liquid for more than just the one layer considered in the simple B.E.T. model, but they took these inner layers to each have the same energy even though different from the liquid. Steele, in his later discussion of this same feature, took the energy in the second layer to be intermediate between that of the first layer and that for the bulk liquid; a more realistic representation, although still an approximation. Brewer and Champeney[28] have used the isotherm of Steele, with the additional assumption that the first two layers have the solid density, in discussing their results for adsorption in Vycor glass. Ross and Steele[29] have derived a very general B.E.T.-type isotherm relation which can be particularized to give different forms, some of them previously suggested by other authors. Such an isotherm relation it seems, however, does not give as good agreement with their experimental data as the one proposed earlier by Steele.[1] Ross and Steele conclude that no B.E.T.-type isotherm gives a completely satisfactory agreement with experiment.

In a series of papers, Steele and Ross[30] developed a monolayer adsorption isotherm in the form of a power series, the terms of which involve integrals giving the interactions between the adsorbed atoms and the wall, and between the adsorbed atoms themselves. This approach is applied to the particular case of the adsorption of helium on argon, where the interactions are evaluated using an explicit form for the helium–argon potential. From this they calculated that the net energy of an adsorbed helium atom in its ground state was -187 cal/mole and they obtained an experimental value about 15% greater for the heat of adsorption of helium on argon (i.e., argon pre-adsorbed on titanium dioxide crystals). The theoretical work was extended to the case of multilayer adsorption of helium and used to estimate the amounts of helium per layer and the energy per layer in the first two or three layers. These findings too, they compared with their own experimental values for the layer energies and layer capacities. The experimental values were obtained from measurements of the heat of desorption (q_{st}) as a function of the amount adsorbed (v). From a plot of q_{st} vs v they obtained an estimate of the completion of the first and the second layers as corresponding to coverages where q_{st} dropped more rapidly with increasing v. Such an interpretation then gives directly the amount of gas in the layer and the magnitude of the adsorption energy for the layer. Ross and Steele find agreement between these experimental values and calculations based on their description of the helium–argon adsorption system. The amount of helium in the first layer, according to the above criterion, is about 70% of the amount corresponding to the B.E.T. v_m value, obtained from isotherms for the same system. Though less than the B.E.T. value, this monolayer capacity is still equivalent to 2.2 times the liquid density which at 4.2°K corresponds to the helium being solid. Thus this estimate of the layer density, which is independent of an isotherm model, also gives the first layer as being solid. However, the interpretation of the curve of q_{st} vs amount adsorbed is possibly not as simple as these authors suggest, in view of the work of Drain and Morrison[31] on argon, nitrogen, and oxygen adsorbed on titanium dioxide. Drain and Morrison view the shape of such curves as being governed by the nonuniformity of the adsorbing surface, at least for low coverages. It is not clear that there will be uniformity of the adsorbing surface comprising argon on titanium dioxide when nonuniformity appears to be important for the adsorption of argon on bare titanium dioxide. (The amount of argon used by Ross and Steele was "slightly in excess" of one B.E.T. monolayer while Drain and Morrison made their measurements and analysis for coverages just under one monolayer). However this matter is resolved by

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[25] J. P. Hobson, Can. J. Phys. **37**, 300 (1959).

[26] L. Meyer, Phys. Rev. **103**, 1593 (1956).

[27] J. G. Aston and S. V. R. Mastrangelo, J. Chem. Phys. **19**, 1067 (1951).

[28] D. F. Brewer and D. C. Champeney, Proc. Phys. Soc. (London) **79**, 855 (1962).

[29] M. Ross and W. A. Steele, J. Chem. Phys. **35**, 871 (1961).

[30] W. A. Steele and M. Ross, J. Chem. Phys. **33**, 464 (1960); **35**, 850 (1961); **35**, 862 (1961); **35**, 871 (1961).

[31] L. E. Drain and J. A. Morrison, Trans. Faraday Soc. **48**, 316 (1952); **48**, 840 (1952); **49**, 654 (1953).

further work, the approach used by Steele and Ross in considering the details of the atomic interactions for the adsorption system under consideration is obviously much better than trying to fit a very general model (such as B.E.T.) to specific circumstances. There is a parallel here in the study of specific heats of crystalline solids.

IV. REVIEW OF OTHER EVIDENCE FOR SOLID LAYERS

A. The Specific Heat of Adsorbed Helium

The first measurements of the specific heat of adsorbed helium were made by Frederikse[32] using Fe_2O_3 powder as an adsorbing surface. Subsequently, these experimental results were subjected to interpretations which were used to support the idea of there being a solid layer next to the wall in the helium film. The first of these suggestions, made by Band,[13] was that the specific heat curve obtained by Frederikse at a relative pressure of $p/p_0=0.11$ (which Frederikse took as corresponding to a monolayer coverage) was "... consistent with that of a two-dimensional Debye solid with a characteristic temperature of about 18°K. It is therefore reasonable to consider the film at low pressure as immobilized...." This inference was repeated more recently.[3,33] There is no real justification for making such a statement; for one thing the experimental points obtained by Frederikse (see the review paper by Long and Meyer[4] rather than Frederikse's original paper for the curves) are badly scattered at these low coverages and there are considerable gaps between the points. In addition, a T^2 dependence of the specific heat could indicate that one was dealing with a two-dimensional Debye elastic continuum but not necessarily with a solid. In fact, a two-dimensional Debye continuum has been used (together with an appropriate dispersion relation) to represent the modes of oscillation of the free surface of a body of liquid helium in order to estimate their contribution to the free energy. The surface tension, calculated from the free energy thus obtained, seems to give a reasonable description[34–36] of the temperature dependence of the surface tension of liquid He^4 and He^3. Again, the specific heat of He^4 liquid can be accounted for by considering only phonon excitation up to 0.6°K and this corresponds to a T^3 dependence for the specific heat, the same as that of a three-dimensional Debye continuum; which is most often thought of as describing a solid at very low temperatures. There is therefore no simple correspondence between the form of the temperature dependence of the specific heat of a system and whether the system is in the liquid or solid state, particularly in the case of He^4.

The next inference from the specific heat results of Frederikse was made by Mastrangelo and Aston[37]: that there was no observed lambda transition for a coverage of one statistical layer and that this meant that the film was solid. In making such an observation one should bear in mind that there is a general decrease in sensitivity of the specific heat measurements with decreasing amount of helium adsorbed (as shown by the increased scatter of the points), and also that Frederikse did not allow a correction for the heat of desorption in his measurements, a factor that would become increasingly important as the coverage decreased. There have also been measurements of the specific heat of adsorbed helium, by Mastrangelo and Aston,[37] but not at low coverages, and some specific heat measurements on helium contained in the pores of Vycor glass have been made by Brewer *et al.*[33,38] These latter measurements are reported as going to low coverages and the authors report finding no specific heat anomaly at the lowest coverage, but details are not available at present. Even if it is established that there is no specific heat anomaly at very low coverages this does not mean automatically that the film is solid; some theoretical models relevant to this consideration will be discussed in Sec. IVC.

B. High "Effective" Pressure in the Film as an Explanation of the Variation of the Lambda Temperature With Thickness

It was at one time suggested[39,37] that the shift of the lambda point for adsorbed helium films to lower temperatures for decreasing thickness of the film could be explained on the basis of there being large effective pressures for the helium in the layers close to the wall. According to this view the lambda temperature in the film is lowered by the effect of the increasing density of the helium as the film becomes thinner, in a similar manner to the decrease of the lambda temperature for the bulk liquid as the pressure is increased (the lambda line in the helium phase diagram). This suggestion was taken sufficiently seriously that even the lambda temperature at which the lambda line met the solid–liquid equilibrium line (i.e., at which the lambda line ended) was thought to correspond to the temperature below which there were only a few solid layers in the adsorbed film and, on the basis of Frederikse's specific heat results, for which there was no specific heat anomaly detected below this thickness.

The above concept has been criticized by Atkins[40] on the basis of an expression that Atkins obtained for

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[32] H. P. R. Frederikse, Physica **15**, 860 (1949).

[33] D. F. Brewer, A. J. Symonds, and A. L. Thomson, Phys. Rev. Letters **15**, 182 (1965).

[34] K. R. Atkins, Can. J. Phys. **31**, 1165 (1953).

[35] R. G. Arkhipov, Zh. Eksperim. i Teor. Fiz. **33**, 822 (1957) [English transl.: Soviet Phys.—JETP **6**, 634 (1958)].

[36] K. R. Atkins and Y. Narahara, Phys. Rev. **138A**, 437 (1965).

[37] S. V. R. Mastrangelo and J. G. Aston, J. Chem. Phys. **19**, 1370 (1951).

[38] D. F. Brewer, D. C. Champeney, and K. Mendelssohn, Cryogenics **1**, 108 (1960).

[39] S. V. R. Mastrangelo, J. Chem. Phys. **18**, 896 (1950).

[40] K. R. Atkins, *Liquid Helium* (Cambridge University Press, London, 1959), p. 228.

the density of the helium film. Atkins' expression for the density in the film is based on a high density for the innermost layers, in fact, this concept is built into his model of a film. Even so, his film model does not give a density increase which is great enough, by a factor of ten, to correspond to a pressure giving the observed lambda temperature decrease. Also, as Atkins points out, the end of the lambda line corresponds to a temperature of 1.75°K whereas superfluid onset temperatures (see Sec. IVC) had been observed down to 1.3°K at the time Atkins wrote (since then they have been observed down to about 0.7°K[41]). More criticism of this pressure effect explanation of the shift of the lambda temperature is given by Long and Meyer.[42] Morrison and Drain[43] also found that the application of Mastrangelo's idea to the melting transition in adsorbed argon films leads to a pressure dependence of the melting point which is opposite in sign to that found in their experiments. Thus on the basis of the above observations and criticisms it does not seem likely that the decrease in the lambda temperature for thin films is caused by pressure effects in the film.

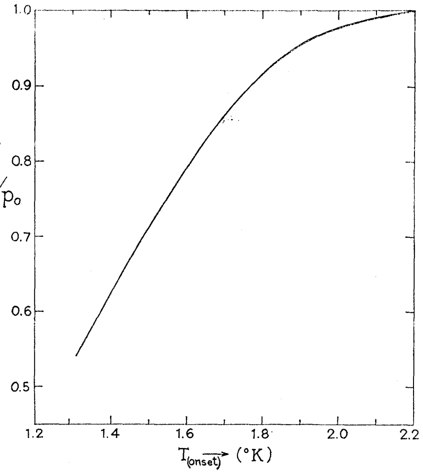

FIG. 2. The dependence of T(onset) on relative saturation pressure for the helium film. The curve has been plotted from the data of Long and Meyer (Ref. 44).

C. Flow Experiments in the Adsorbed Helium Film

It was demonstrated in a series of experiments by Long and Meyer[44] and by Bowers, Brewer, and Mendelssohn[45,46] that a large flow of heat could take place in an adsorbed helium film and that the observations were consistent with superfluid flow occurring below an onset temperature which is characteristic of a given degree of saturation in the film; this temperature always being lower, for unsaturated conditions, than the lambda temperature corresponding to the appearance of superfluid behavior in the bulk liquid. The variation of onset temperature with degree of saturation was investigated by the above authors for the range $p/p_0=1$ to $p/p_0=0.45$ corresponding to onset temperatures from 2.2°K down to 1.3°K (See Fig. 2). Further data on onset temperatures for superfluid flow have been obtained by Manchester[41] showing that they occur down to at least 0.75°K. The measurements of Frederikse[32] on the specific heat of adsorbed helium gave lambda temperatures which did not agree very well with onset temperatures observed for ostensibly the same degree of relative saturation; the specific heat maxima being apparently as much as 0.4°K higher than the onset temperature for the same nominal relative saturation.[47] Brewer, Symonds, and Thomson,[33] in the work already referred to on helium absorbed in Vycor make a comparison between onset temperatures and the temperatures of the specific heat anomalies for films of the same nominal thickness. For the specific heat values they combine their own results on Vycor with those of Frederikse on Fe_2O_3, and for the onset temperatures they use the results obtained by themselves[45,46] and others[44] on the helium film flowing on glass and metal surfaces. Their presentation of these results gives the difference between the two "critical" temperatures to be as large as about 0.7°K. A major difficulty when considering such a comparison is the uncertainty in the value of the nominal film thickness. This value of the film thickness has been obtained from adsorption isotherm information in all of the experiments just referred to, and in the view of the writer there is not yet an isotherm relation available which will enable a film thickness to be estimated with sufficient confidence that comparisons of the absolute value of the thickness can be made for different experiments. Irrespective of whether there is a real difference between the temperature of the specific heat anomaly and the onset temperature for an adsorbed helium film, the important thing for the purposes of the present discussion is that the onset temperature drops with decreasing p/p_0 and therefore with decreasing film thickness (even though the absolute value of that thickness cannot be very well specified at the present time) and the available indications point to the film being still able to transform to superfluid behavior as its thickness is progressively lowered. The existence of an onset temperature means that the film is mobile at that particular

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[41] F. D. Manchester, *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio* (Plenum Press, New York, 1965), p. 202.

[42] Reference 4, p. 24.

[43] J. A. Morrison and L. E. Drain, J. Chem. Phys. **19**, 1063 (1950).

[44] E. A. Long and L. Meyer, Phys. Rev. **98**, 1616 (1955).

[45] R. Bowers, D. F. Brewer, and K. Mendelssohn, Phil. Mag. **42**, 1445 (1951).

[46] D. F. Brewer and K. Mendelssohn, Proc. Roy. Soc. (London) **A260**, 1 (1961).

[47] T_λ and T_{onset} are not thought to be different for the bulk liquid, see for instance, B. Smith and H. A. Boorse, Phys. Rev. **99**, 367 (1955).

thickness, and the interesting thing about recent measurements of the onset temperatures[41] is that they are lower than those thought to correspond to the film having close to monolayer thickness in earlier work. Long and Meyer,[44] for instance, estimate that for an onset temperature of 1.3°K the coverage is close to two statistical layers and they regarded the layers as being immobile just below this coverage. This seems to have led to the inference that the films would become immobile at coverages for which the onset temperature approaches 1°K.[3] The observance of transition temperatures well below 1°K tends to call the above picture of the immobile layers into question—it is also of interest that the onset transitions are reasonably sharp ($\approx 10^{-3}$ °K in "width") and do not show any trend comparable with the broadening of the λ-anomalies in the specific heat measurements of Frederikse.

While the study of the onset temperatures can be useful for giving information on the mobility of the film at low coverages it is also of considerable interest to find out what would happen to the transition if the film did not become solid but remained liquid down to the lowest coverages. Eventually, the transition should disappear as the body of helium in the film changes to a collection of independent particles. If one thinks in terms of Bose–Einstein condensation of an ideal Bose gas (an analog that has been used extensively in discussing the lambda-transition in bulk liquid helium) it can be shown that there is no finite condensation temperature for the case of a two-dimensional gas of infinite extent.[48] However, if the size of the assembly is restricted, then there will be a "transition region" of temperature which is analogous to the transition for an infinite system and this transition region will occur at different temperatures as the thickness of the assembly is increased; the form of this variation depending on the thermodynamic quantity used to monitor the transition region.[49] There is, at present, no known mechanism for keeping helium atoms in a film in assemblies of a particular size, so that no unambiguous designation can be made from this model of how a transition temperature varies as the film thickness is decreased. Another physical model is applicable to the variation of transition temperature with film thickness is that discussed by Ginzburg and Pitaevskii.[50] These authors have examined the case of an isolated, parallel-sided, film of helium, applying to it the order-parameter approach used successfully by Ginzburg and Landau in their description of superconductivity.[51] Ginzburg and Pitaevskii show that the order parameter ψ (in this application, the theory gives $\rho_s = m\,|\,\psi\,|^2$, where m is the mass of the helium atom, ρ_s is the density of the superfluid fraction) goes to zero throughout the film when the film still has a finite thickness (see Fig. 3). Thus, on this picture, the film is viewed as still being liquid but not retaining its superfluid properties a situation which would be very hard to check directly when dealing with extremely thin helium films. Nevertheless, it would be interesting to see if any indication of such behavior could be found from a study of the thickness dependence of the onset temperature and it is also interesting to note that this model of a helium film provides for the disappearance of superfluidity without invoking that the film be solid.

V. THE USE OF SOLID BOUNDARY LAYERS IN THE INTERPRETATION OF OTHER THAN ADSORPTION PROCESSES

Challis, Dransfeld, and Wilks,[52] in a paper describing some experiments carried out to investigate the Kapitza boundary resistance, in particular, the temperature and pressure dependence of the resistance, applied the solid layer picture to an analysis of heat transport across the interface between the bulk liquid helium and a metal surface. Taking over the idea that there is an increase in the density of the helium very close to the wall, from the work on adsorption isotherms (see Sec. III), they introduce this density increase into the Khalatnikov[53] model of the thermal boundary resistance, a model which views the resistance as arising from an impedance mismatch for transmission of phonons across the boundary. Challis *et al.* view the region of high density as playing the role of a matching region between the acoustic impedance of the solid and that of the liquid, and they recalculate the heat flow across the boundary

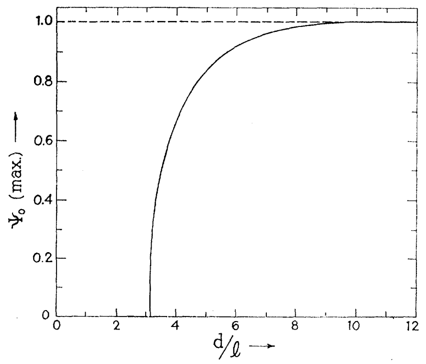

FIG. 3. Plot of the relative order parameter, ψ_0, at its maximum value, against relative film thickness for a film of thickness d between two solid walls; l is the characteristic length of the Ginzburg–Pitaevskii (Ref. 50) theory.

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[48] M. F. M. Osborne, Phys. Rev. **76**, 396 (1949).

[49] D. F. Goble and L. E. H. Trainor, Phys. Letters **18**, 122 (1965).

[50] V. L. Ginzburg and L. P. Pitaevskii, Zh. Eksperim. i Teor. Fiz. **34**, 1240 (1958) [English transl.: Soviet Phys.—JETP **7**, 858 (1958)].

[51] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

[52] L. J. Challis, K. Dransfeld, and J. Wilks, Proc. Roy. Soc. (London) **A260**, 31 (1961).

[53] I. M. Khalatnikov, Zh. Eksperim. i Teor. Fiz. **22**, 687 (1952).

in terms of this changed "input impedance" to the liquid, obtaining a revised value for the resistance at the boundary. In a comparison with their own experimental results there is an improvement over the agreement obtained by using the original Khalatnikov theory but still a considerable discrepancy in absolute magnitude. The picture of acoustical impedance mismatch as worked out by Little[54] gives reasonable agreement with experiment for the boundary between copper and tin,[55] when the tin is in the superconducting state, although there is a change in magnitude and temperature dependence for the case of a superconducting lead–copper boundary, and this, together with other indications, suggests that while the acoustical impedance mismatch seems to play an important part, the theory needs further refinement or there may be other mechanisms still not taken into account. For the purposes of the present discussion however, one is only interested in whether the idea of an increase in density near the boundary (so that the first layer or so is solid) plays any decisive role in improving the model of the boundary resistance and the answer seems to be that it does not.

VI. MORE GENERAL DISCUSSION OF MODELS OF THE ADSORBED HELIUM FILM

A. The Density Variation and the Helium Atom–Wall Interaction in Models of a Thick Film

The background physical picture which is usually given in advocating that the first layer or so of adsorbed helium is solid, is that the attractive forces between the helium atoms and the wall are stronger than the distending effect of zero point energy, and thus the helium atoms near the wall may be bound strongly enough to form a solid (see, for instance, the discussion of this view given by Daunt and Smith[56]). There are models of the thick helium film[57] which regard the attractive force of the wall as acting throughout the thickness of the film and varying at t^{-3}, where t is the distance from the wall, and assuming the pressure does not change appreciably over a distance equal to an interatomic separation. On the other hand, the observation of the anomalously large values of v_m in the first B.E.T. layer (see Sec. IIIA), which leads to the picture of a high density in this layer, comes from a theory which does not treat the film as having an energy of adsorption for anything above the first layer, i.e., no interaction forces between the wall and helium for any layers above the first. There is thus a contradiction here; the view of the film which tends to favor the attribution of the solid density to the innermost layers is not compatible with a smoothly varying helium–wall interaction extending well into the film. The idea of the wall–helium interaction varying as t^{-3} seems to have been taken over from the calculations of Van der Waals forces made by F. London (see the review by T. L. Hill[58] for an illustration of this calculation). The approach used is to take the $1/r^6$ Van der Waals interaction between two atoms and consider this as applying between an adsorbed atom and each of the adsorbent atoms in its neighborhood. The integration over all of these contributions gives a resultant interaction which varies as t^{-3}.

This method of regarding the problem is objected to by Dzyaloshinskii, Lifshitz, and Pitaevskii[59] who point out that this is making use of a relation applying to isolated atoms for describing a case where a solid body is interacting with a liquid. Their view, amplified in other publications,[60] is that for a complete description of the forces between atoms over a wide range of separations, the electromagnetic interaction, that is the effect of the radiation field of one atom on the other, and vice versa, must be considered. This is an extension beyond the solely electrostatic interaction considered by London.[61] Such an approach requires a knowledge of the dielectric constant for instance, over a wide frequency range, and this, in most cases, will be very different for atoms in the gas phase (i.e., essentially isolated atoms) compared with those in a solid. These authors point out that it is inappropriate to use calculations for pairs of isolated atoms in a simple additive way and that the radiation field of an atom and hence its interaction will be strongly modified by the presence of its neighbors in a solid or a liquid. The original calculation of the electromagnetic interaction was made by Lifshitz[62] and applied by Dzyaloshinskii, Lifshitz, and Pitaevskii[59] to the case of liquid films and the helium film as one particular case. They obtain a thickness vs height relation for the helium film which has the same form as that given by Schiff,[63] viz.: $t \propto z^{-1/3}$ (where t is the thickness of the film at a height z above the bulk liquid) although they are only able to make a rough comparison with the experimental value of the constant in the equation. It is interesting to note that with the above description of the film, Dzyaloshinskii, Lifshitz, and Pitaevskii take the density to be constant throughout the film and obtain a film profile relation which agrees with experiment as well as any other relation

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[54] W. A. Little, Can. J. Phys. **37**, 334 (1959).

[55] L. J. Barnes and J. R. Dillinger, Phys. Rev. Letters **10**, 287 (1963).

[56] J. G. Daunt and R. S. Smith, Rev. Mod. Phys. **26**, 209 (1954).

[57] K. R. Atkins, Can. J. Phys. **32**, 347 (1954).

[58] T. L. Hill, *Advances in Catalysis and Related Subjects* (Academic Press Inc., New York, 1952), Vol. IV, p. 211.

[59] I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Zh. Eksperim. i Teor. Fiz. **37**, 229 (1959) [English transl.: Soviet Phys.—JETP **10**, 161 (1960)].

[60] B. V. Derjaguin, I. I. Abrikosova, and E. M. Lifshitz, Quart. Rev. Chem. Soc. (London) **10**, 295 (1956).

[61] F. London, Z. Physik **63**, 245 (1930); Z. Phys. Chem. **B11**, 222 (1930).

[62] E. M. Lifshitz, Doklady. Akad. Nauk. SSSR **97**, 643 (1954); **100**, 879 (1955); Zh. Eksperim. Teor. Fiz. **29**, 94 (1955).

[63] L. I. Schiff, Phys. Rev. **59**, 839 (1941).

presently available. The same basic theory applied to the attraction between macroscopic solid bodies separated by a gap of 10^{-4}–10^{-5} cm gives very good agreement with experiment.[60]

As mentioned at the beginning of this section, it is often stated that the attractive forces of the wall are strong enough to overcome the effect of zero-point energy and thus to hold the film to the wall with a much greater density than that of the bulk liquid. In the theory of the helium film given by Dzyaloshinskii, Lifshitz, and Pitaevskii the zero-point energy is automatically included as the contribution to the fluctuating radiation field at zero temperature. Thus a reasonable form for the film profile relation can be obtained from a theory which treats the film as having a constant density and which also takes account of the zero-point energy. It is shown later in this section that for values which it is reasonable to assume for the zero-point energy, this energy can make possible (in another model) the mobility of the helium atoms across a crystalline adsorbing surface—even for a film of very low thickness, which is the case where the helium is most often regarded as being solid and therefore immobile.

B. A Description of a Very Thin Adsorbed Helium Film Which can be Mobile at Very Low Temperatures

The simplest case to discuss in dealing with an adsorbed film is that of a sparsely occupied monolayer in which there is essentially no interaction between the adsorbed atoms, and where only the interaction with the atoms of the adsorbing surface need be considered. Beside being a model which is restricted enough to give some explicit answers this situation also corresponds to the case of very low partial pressures over a film. One is interested then, in an independent particle model calculation of the interaction between a single atom and a crystal surface of simple but known structure. Such a calculation has been made by Lennard-Jones and Devonshire[64] for a helium atom in the neighborhood of the (100) surface of a lithium fluoride crystal. This calculation was part of an extensive investigation on the interaction of atoms with surfaces, principally in connection with the atomic beam experiments of Stern and his collaborators[65] in the early nineteen thirties.

Lennard-Jones and Devonshire concluded that, apart from an increase in the effective mass (approximately eight percent in one example they considered), the helium atom can migrate over the crystal surface, even at very low temperatures. It is very interesting to read the conclusion of their paper (written in 1936, before any of the work on adsorbed helium films had been started), in part they remark:

> "... seeing that three-dimensional arrays of helium atoms are liquid at very low temperatures, it seems reasonable to infer that two-dimensional films would have similar properties. In that case an adsorbed film of helium atoms should remain mobile even at very low temperatures. It would be interesting if this property could be demonstrated experimentally."

The calculation of Lennard-Jones and Devonshire will be briefly outlined here,[66] particularly with emphasis on what it can tell us about the mobility of adsorbed helium atoms at low temperatures. Lennard-Jones and Devonshire put the description of the helium atom outside a (100) surface of a lithium fluoride crystal (one of the crystals actually used in the experiments of Stern's group) in the following terms. The interaction was only considered as taking place between helium atoms and the fluorine atoms, a conclusion arrived at from a comparison of other calculations with the experimental results for the diffraction of an atomic beam of helium atoms at a cleavage plane surface (100) of a lithium fluoride crystal. This choice of Lennard-Jones and Devonshire is not fully explained but it does not affect the essentials of their analysis. A Morse potential was used to represent the interaction in the following fashion:

$$V(x,y,z)=D\{\exp[-2\kappa(z-b)]-2\exp[-\kappa(z-b)]\}$$
$$-2\beta D\exp[-2\kappa(z-b)](\cos ax+\cos ay).$$

The crystal surface is in the x, y plane and the depth of the potential well at its minimum ($z=b$) is given by D; D is modified in the second term of the expression by the factor β which is taken to have the value of 0.038 for the helium atom on a LiF (100) surface. The rate at which the field falls off at large distances from the surface is given by κ. Thus for each value of x and y, V is a Morse function with the depth of the potential minimum varying from a value of $D(1-4\beta)$ over a lattice point (x, $y=\pi/a$) to $D(1+4\beta)$ over the centre of a lattice cell (x, $y=0$); in this the lattice spacing has been taken as $2\pi/a$. The value of D was determined from an associated calculation[67] to be -175 cal/mole of helium. This value, which depends only on experimental information from atomic beam diffraction experiments, is of the same magnitude as the heat of adsorption for helium determined by other methods as is shown in Table III (compare, particularly, the value given by Ross and Steele, which is probably the best of those listed).

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[64] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A158,** 242 (1937).

[65] See, for example, H. Massey and E. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, Oxford, England, 1952), Chap. IX.

[66] The author would like to thank Mrs. A. Buckley for helpful discussions concerning the Lennard-Jones and Devonshire model.

[67] A. F. Devonshire, Proc. Roy. Soc. (London) **A156,** 37 (1936).

The expression $V(x, y, z)$ for the potential energy of the helium atom, is actually an approximation, being only the first two terms of what should in principle be an infinite, doubly periodic, Fourier series in x and y. Using the approximation to the full series enables the Schrödinger equation for the problem to be treated as separable and it does not affect the physical conclusions drawn from the calculation, for present purposes. The periodic potential, using the notation of Lennard-Jones and Devonshire is given as

$$(\hbar^2/2m)2U_1^{(n)}(\cos ax+\cos ay).$$

If this is expressed as a Fourier series in x and y it may be written:

$$V=\sum_{m_1m_2} V_{m_1m_2}\exp[-ai(m_1x+m_2y)],$$

where $|V_{\pm1,0}|=|V_{0,\pm1}|=\hbar^2/2m|U_1^{(n)}|$, with all other $V_{m_1m_2}$ set equal to zero. With a potential function that has the periodicity of the lattice of the crystal surface, Lennard-Jones and Devonshire obtain, as would be expected, a solution for the appropriate Schrödinger equation in terms of allowed energy bands for the helium atom, separated by gaps of forbidden energies, as shown in Fig. 4. The calculation also gives the appropriate wave functions for the particles in the bands. In effect, the case considered by Lennard-Jones and Devonshire is one for which the height of the potential barrier between adsorption sites is not large. Thus, while their calculation gives the details of a band structure having energy gaps which decrease with increasing particle energy, the magnitude of the first energy gap

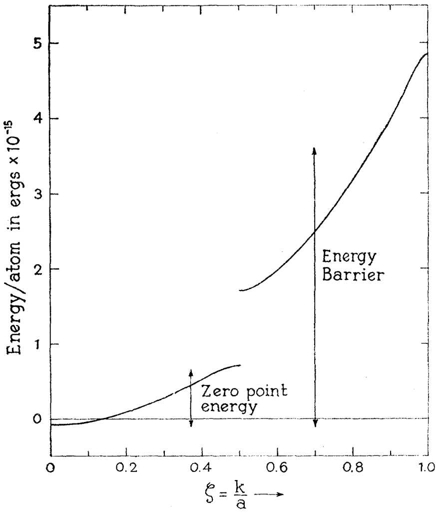

FIG. 4. Form of the energy bands for the case of a helium atom on the 100 surface of lithium fluoride (k is the wave number and $2\pi/a$ is the lattice spacing) based on the calculations of Lennard-Jones and Devonshire (Ref. 64). The magnitudes of the zero-point energy and the height of the potential barrier between neighboring potential minima are indicated on the same energy scale.

TABLE III. Heats of adsorption at low coverages (q_{st}=isosteric heat of adsorption).

Surface	Method	Temp.	Heat of adsorption at lowest coverage	Heat of adsorption at B.E.T. v_m coverage	Author	Remarks
Fe_2O_3 powder	Adsorption isosteres	2.4°K	$q_{st}=38$ cal/mole	$q_{st}=38$ cal/mole	Strauss (Ref. 22)	
Glass	Adsorption isosteres	2–4°K	$q_{st}=100$ cal/mole	$q_{st}=68$ cal/mole	Keesom and Schweers	Quoted values in paper are differential heats.
Charcoal	Using c value from B.E.T. plot (modified form)	3.95°K 3.00°K	He^4: $E_1=71.2$ cal/mole He^3: $E_1=45.3$ cal/mole		Hoffman, Edeskuty, and Hammel (Ref. 11)	This value for E_1 involves crude assumptions in using relation for c.
TiO_2 crystals	Calorimetric measurements and adsorption isosteres	13–20°K	$q_{cal}=675$ cal/mole	...	Aston, Mastrangelo, and Tykodi[a]	
Argon on TiO_2 crystals	Calorimetric and isostere measurements	14°K	Energy of a single adsorbed atom estimated from limiting value of q_{st}; $E=-220\pm20$ cal/mole.		Ross and Steele (Ref. 30)	

[a] J. G. Aston, S. V. R. Mastrangelo, and R. J. Tykodi, J. Chem. Phys. **23**, 1633 (1955).

is that given by the nearly free-particle approximation, viz:

$$\Delta E = 2 \mid V_{m_1 m_2} \mid .$$

The form of the bands and the magnitude of the energy gaps will depend on the expression used for the potential, including the well width and depth, as well as how fully the periodic nature of the potential is represented. Nevertheless, the interest in the present case is in the region of energies about the first band, and for this case the solutions obtained by Lennard-Jones and Devonshire appear to be satisfactory for discussing the behaviour of a helium atom in this potential field at low temperatures.

In Fig. 4 the $E(k)$ relation is plotted for the x direction showing the first two energy bands. Also shown on the same scale is the difference in energy between the value of D over the position of a lattice site and that over the centre of a lattice cell. This is the barrier which must be surmounted by a particle moving classically from one adsorption site to another. It can be seen that the first energy band is located well below the top of the potential barrier and that if a particle has energy enough to enter this band it can move across the crystal surface (although with an increase in effective mass). A small amount of energy has to be supplied to the helium atom in order for it to enter the first band, and this energy is available as the zero point energy of the helium atom. An estimate of the available zero point energy is shown in Fig. 4, the estimate being obtained from applying the Heisenberg uncertainty principle for the case where the helium atom was regarded as having an uncertainty in position of about half a lattice spacing distance—anything much greater than this not being consistent with the atom being located on a site. Thus the picture given by these considerations is that there is an energy band structure for the helium atom in the neighborhood of an ideal crystal surface and that the helium atom can easily enter at least the lowest of these energy bands. Extending the discussion to cover the case of large numbers of helium atoms requires that the occupancy of these bands by bosons be considered. This will be different from the more common case of discussing "filling up" the band to a given energy level with fermions and in the boson case only the bottom of a band has to be energetically accessible for numbers of atoms to be able to migrate across the crystal surface. The manner in which the bands of energy states of the system are occupied will depend on the nature of the interaction between the particles and on the temperature. There is then, a definite physical mechanism available by means of which helium atoms may move across an ideal crystal surface and which is compatible with the mechanisms already known to work well for particle transport through crystalline solids. Although the above discussion ignores such matters as crystal imperfections and we do not at present know the details of how the energy bands are occupied, it is in principle a more satisfactory approach than to regard the attachment of an adsorbed atom to its site in an essentially classical manner as has so often been done in the past.[68]

It seems likely that a separation should be maintained between the treatment of the very thin film as discussed above, and that involving longer range forces in the thick film, as treated by Lifshitz.[62] For both of these cases, as described by the models reviewed in this section, there is no restriction on mobility of the helium atoms and for the thick film there is no density variation.

CONCLUSION

The aim of this review has been to assemble evidence, both from experiment and from theoretical models, to show that the concept of a solid inner layer or so existing in an adsorbed helium film, at low temperatures, is not nearly as well founded as is usually supposed. The accumulation of more certain evidence is required and it should help such evidence to emerge if the limitations of the present picture of the structure of the adsorbed helium film are more clearly and widely recognized.

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[68] See Ref. 58, p. 215.