(1958); A. Isihara, in Lectures in Theoretical Physics, edited by W. E. Brittin *et al*. (University of Colorado Press, Boulder, Colo., 1968), p. 329; E. W. Montroll, The Theory of Neutral and Ionized Gases, edited by C. DeWitt and J. Detoeuf (John Wiley & Sons, Inc., New York, 1960).

[7] D. J. Mitchell and B. W. Ninham, Phys. Rev. 174, 284 (1968).

[8] D. L. Bowers and E. E. Salpeter, Phys. Rev. 119, 1180 (1960); C. W. Hirt, Phys. Fluids 8, 693 (1965); E. E. Salpeter, Ann. Phys. (N.Y.) 5, 183 (1958); E. Meeron, Phys. Fluids 1, 139 (1958); H. E. DeWitt, J. Math. Phys. 7, 616 (1966).

[9] A. Isihara, Phys. Rev. 172, 166 (1968); and to be published.

[10] T. D. Lee and C. N. Yang, Phys. Rev. 105, 1119 (1957); 113, 1165 (1959); T. D. Lee, K. Huang, and C. N. Yang, Phys. Rev. 106, 1135 (1957); A. Isihara and D. D. H. Yee, Phys. Rev. 136, A618 (1964); C. J. Nisteruk and A. Isihara, Phys. Rev. 154, 150 (1967).

[11] A. Isihara and O. Aono, J. Chem. Phys. 48, 462 (1968); O. Aono and A. Isihara, J. Chem. Phys. 49, 1650 (1968).

[12] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959).

PHYSICAL REVIEW VOLUME 183, NUMBER 1 5 JULY 1969

Phase Transition in the Pair-Hamiltonian Model for Liquid Helium*

L. Reatto
Istituto di Fisica, Università di Milano
Gruppo Nazionale Struttura della Materia del Consiglio Nazionale della Ricerche Milano, Italy

and

J. P. Straley†
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 10 March 1969)

The thermodynamic properties of two models for degenerate Bose liquids have been investigated. The models are found to give a first-order phase transition. This aspect of the models is related to the collapse of the long-wavelength excitation spectrum as the condensate density vanishes.

I. INTRODUCTION

A number of models for the superfluid state of a Bose fluid have been proposed which are a version of the Bogoliubov model[1] generalized to include: (1) the Hartree-Fock part of the Hamiltonian, (2) Cooper pairing of particles in the nonzero momentum states, (3) the effect of temperature. In these models a phase transition takes place between a low-temperature state characterized by the presence of Bose-Einstein condensation and a normal state which is the ideal gas or the Hartree-Fock state, depending on the model. This transition has been compared[2] to the λ transition of liquid He^4, in spite of the fact that the reliability of these models decreases as the temperature increases and approaches the transition temperature. Such a comparison is tempting, however, because these models are among the few that are exactly soluble. Few numerical calculations have been attempted and thus some features of these models have been overlooked. In this paper we report numerical studies that have been made of the pair Hamiltonian of Luban[3] and of the closely related model of Shohno,[4] with particular emphasis on the phase transition.

It has been shown previously[5,6] that the condensate density for these models is multiple valued as a function of temperature; we have computed the relevant thermodynamic functions and find that the phase transition is of first order. This phenomenon is probably a general character of models of this sort; it can be traced directly to the behavior of the long-wavelength part of the single-particle excitation spectrum as the condensate vanishes.

II. THE MODELS

We have considered two models: The pair

Hamiltonian of Luban[3] and a simpler version in which the pairing of particles is disregarded for $k \neq 0$. This latter model was proposed by Shohno[4] and Luban and Grobman[2]; the motivation for using it is that it does not have a gap in the long-wavelength excitation spectrum. In each case we have used the Luban[3] "$T > T_c$" equations (the Hartree-Fock approximation) as the model for the uncondensed state.

These models are described by an effective Hamiltonian derived from the full Hamiltonian by replacement of a_0 by $(n_0\Omega)^{1/2}$ and linearization of the remainder with respect to the operators $n_k = a^\dagger_k a_k$ and $\chi_k = a_k a_{-k}$; it has the form

$$H_{\text{eff}} = U + \sum_{k\neq 0} [f_k n_k + \tfrac{1}{2} h_k (\chi_k + \chi^\dagger_k)]. \tag{1}$$

The coefficient f_k contains the Hartree-Fock approximation; h_k contains the equivalent contribution arising from the pairing $\langle \chi_k \rangle \neq 0$; U is a c number arising from the linearization. H_{eff} can be diagonalized by a Bogoliubov transformation; there results an excitation spectrum $\epsilon_k = (f_k^2 - h_k^2)^{1/2}$. For further details the reader is referred to Luban.[3]

The potential was chosen to be a repulsive δ shell for which

$$v(k) = v_0 [\sin(k\sigma)/k\sigma] = v_0 u(k\sigma).$$

The parameters chosen were

$$v_0 = 4\pi\sigma\hbar^2/m, \quad \sigma = 2.556\times 10^{-8} \text{ cm},$$

and $m = 6.6455\times 10^{-24}$ g, which are the pseudopotential, core radius, and mass appropriate to the helium atom. Since the angular average for fixed magnitudes k and p of this potential is

$$\int v(\vec{k} - \vec{q})\, d\Omega/4\pi = v_0 u(k\sigma) u(q\sigma),$$

there results an important simplification in the integral equations defining f_k and h_k: Luban's[3] Eqs. (45) – (47) for the condensed state and Eqs. (27) and (30) for the uncondensed state can be written

$$f_k = \hbar^2 k^2/2m + \gamma v_0 [u(k\sigma) - 1] + n_0 v_0 u(k\sigma) + \lambda v_0 + \Delta, \tag{2}$$

$$h_k = v_0 u(k\sigma)(n_0 - \lambda), \tag{3}$$

where for the condensed state $\Delta = 0$ and n_0, γ, λ (condensate density, Hartree parameter, and pairing parameter, respectively) are constants to be determined for given ρ and T:

$$\gamma = \int \frac{d^3k}{(2\pi)^3} u(k\sigma) \langle n_k \rangle = \int_0^\infty \frac{dk}{2\pi^2} k^2 u(k\sigma) \frac{1}{2} \left(\frac{f_k}{\epsilon_k} \coth \frac{\beta\epsilon_k}{2} - 1 \right), \tag{4}$$

$$\lambda = \int \frac{d^3k}{(2\pi)^3} u(k\sigma) \langle \chi_k \rangle = \int_0^\infty \frac{dk}{2\pi^2} k^2 u(k\sigma) \frac{1}{2} \frac{h_k}{\epsilon_k} \coth \frac{\beta\epsilon_k}{2}, \tag{5}$$

$$\rho = n_0 + \int \frac{d^3k}{(2\pi)^3} \langle n_k \rangle = n_0 + \int_0^\infty \frac{dk}{2\pi^2} k^2 \frac{1}{2} \left(\frac{f_k}{\epsilon_k} \coth \frac{\beta\epsilon_k}{2} - 1 \right), \tag{6}$$

$$\epsilon_k = (f_k^2 - h_k^2)^{1/2}. \tag{7}$$

For the uncondensed state Eqs. (2) – (7) hold with $\lambda = n_0 = 0$, and $\Delta = v_0(\rho + \gamma) - \mu$, where μ is the chemical potential. In this case γ and μ must be determined for given ρ and T. The model of Shohno is derived from the above equations by deleting all terms involving λ.

Equations (2) – (7) have been solved numerically for a variety of densities and temperatures; typical results are given in Figs. 1 and 2. For fixed density there is a temperature T_{c2} above which no solution with a condensate is available; there is a temperature T_{c1} below which no solution to the uncondensed Hartree-Fock model is possible. In every case $T_{c2} > T_{c1}$ and there is a range of temperatures for which three solutions are possible. The behavior of T_{c1} and T_{c2} as a

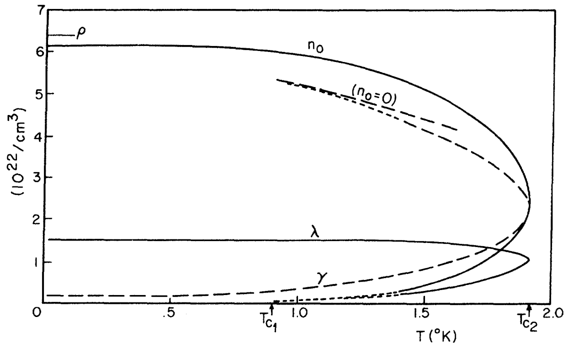

FIG. 1. Luban model: Condensate density n_0, Hartree parameter γ, and pairing parameter λ as a function of temperature for density 0.0423 g/cm^3. Above T_{c1} there is also available a solution with $n_0 = \lambda = 0$ and $\Delta \neq 0$.

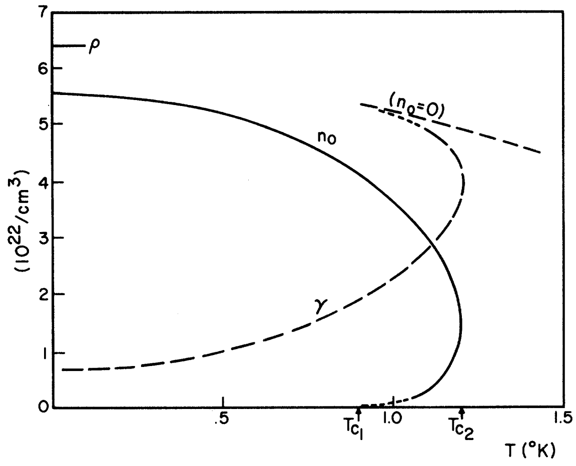

FIG. 2. Shohno model: Condensate density n_0 and Hartree parameter as a function of temperature for density 0.0423 g/cm^3.

function of density is shown in Fig. 3. We notice that $T_{c1} = 0$ for $\rho > 1.5\times10^{22}/\text{cm}^3$; therefore in this region an uncondensed solution is available at all temperatures (but not at $T = 0°\text{K}$).

It is clear that as the temperature is raised the system cannot continuously evolve from a condensed to an uncondensed state; at some temperature something discontinuous must take place. Luban and Grobman[2] took the point of view that the transition should take place at the highest possible temperature T_{c2}, at which point the condensate density drops discontinuously to zero. It should be possible, however, to locate the phase transition by means of a Maxwell construction.

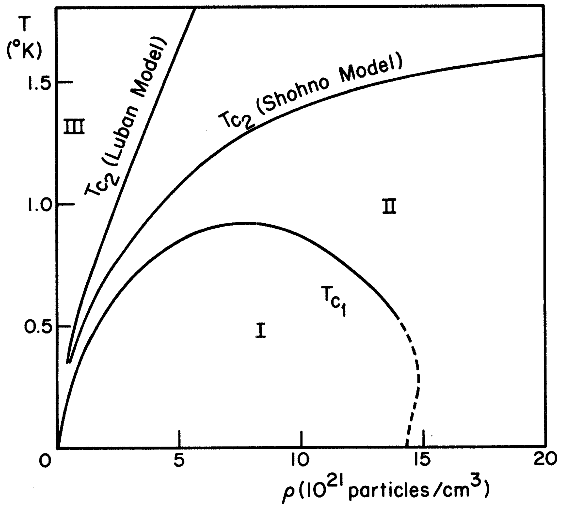

FIG. 3. Dependence of T_{c1} and T_{c2} on density for the Luban and Shohno models. In region I no uncondensed solution is possible; in region III no condensed solution is possible; in region II three solutions are available, one uncondensed and two condensed. (The short dashes indicate uncertainty due to poor convergence.)

Let us consider the behavior of the pressure and chemical potential in the two phases. Luban has given expressions for these thermodynamic functions [Eq. (44) for μ; Eqs. (7), (22), and (23) for p] which with our choice of potential become

$$\mu = (\rho + \gamma + \lambda)v_0, \tag{8}$$

$$p = \tfrac{1}{2}(\rho^2 + \gamma^2 + 2n_0\gamma - 2n_0\lambda)v_0 - \int \frac{d^3k}{(2\pi)^3}\left(\frac{1}{\beta}\ln(1 - e^{-\beta\epsilon_k}) + \frac{\epsilon_k - f_k}{2}\right) \tag{9}$$

in the condensed phase; for the uncondensed phase p is given by Eq. (9) with $\lambda = n_0 = 0$ and μ is given directly by the solution to Eqs. (2) – (7). We find that the pressure and chemical potential increase monotonically along the solution line (Fig. 4); since these quantities may not change discontinuously we conclude that Luban and Grobman's conjecture is not correct. We note that if the conjecture were correct, the Luban model would predict a phase transition in two dimensions (since there is a $n_0 \neq 0$ solution) although the gapless model would not. By comparison of the thermodynamic functions for the two phases (Fig. 5), we find that equilibrium exists between an uncondensed phase of density 0.0112 g/cm^3 and a condensed (Luban-model) phase of density 0.0196 g/cm^3 at $T = 0.85°\text{K}$ with $p = 2.74\times10^5$ dyne/cm^2 and $\mu = 1.38\times10^{-16}$ erg/particle. The phase transition is first order with a latent heat of 11.4 erg/mole.

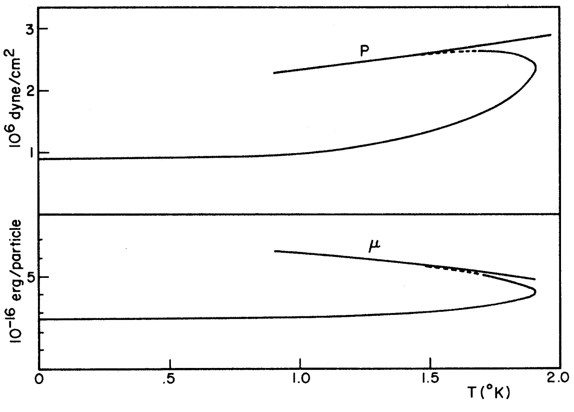

FIG. 4. Luban model: Pressure and chemical potential as a function of temperature for density 0.0423 g/cm^3. The corresponding figure for the Shohno model is qualitatively similar.

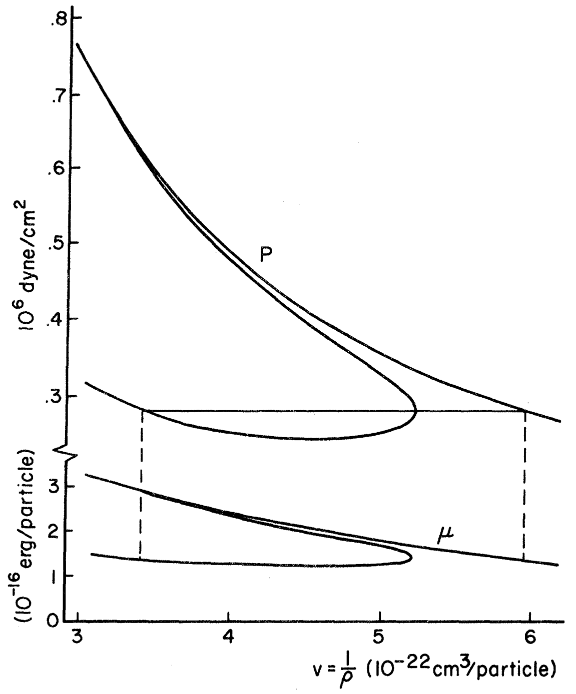

FIG. 5. Luban model: The isotherm $T = 0.85°$K as a function of volume per particle. The isobar drawn in connects phases in equilibrium and satisfies the Maxwell construction.

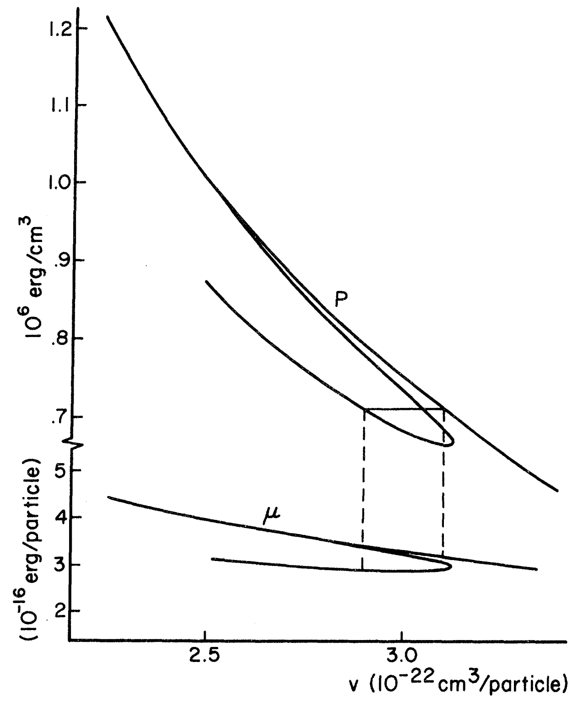

FIG. 6. Shohno model: The isotherm $T = 0.85°$K as a function of volume per particle. The isobar drawn in was determined by the Maxwell construction; however, the two phases have different chemical potentials.

The quantity μ given by Eq. (8) was determined by the condition $\langle [a_0^{+}, H] \rangle = 0$, which is necessary for the stability of the condensate. It is important to note that μ, defined this way, is also the energy per particle: This is the basis for its use in locating the phase transition. Hugenholtz and Pines[7] have given a proof that these two definitions should coincide for the solution of the full Hamiltonian; in the case of the Luban model it can be shown that $\partial p / \partial \mu |_T = \rho$: This equality guarantees the equivalence of the Maxwell construction to the prescription used above. However, the two definitions do not coincide in the Shohno model; this is a consequence of the fact that it is not based on a conserving approximation.[8] In this case $\partial p / \partial \mu |_T \neq \rho$ [where μ, p are given by Eqs. (8) and (9) with λ deleted] and the previous prescription for locating the phase transition fails disastrously: At $T = 0.85°$K, the two phases do not have p and μ equal for any choice of densities. We have illustrated this fact in Fig. 6, and have indicated the location of the phase transition as given by the Maxwell construction. We note that in this case μ is not the energy per particle.

Figure 4 gives a typical isochore for the model and Figs. 5 and 6 represent typical isotherms for $T < 0.92°$K (the maximum value of T_{c1} – see Fig. 3). In these figures we have not drawn a high-density – high-pressure branch of the isotherm which represents states unstable with respect to the states of the branch reproduced in the figures. At higher temperatures ($T > 0.92°$K), the isotherms take the shape sketched in Fig. 7. In this case a Maxwell construction is not possible; however, for the Luban model an isobar exists which connects two phases on the isotherm with the same chemical potential.

We have studied the effect of an attractive part in the potential by considering the Shohno model with a double δ-shell interaction for which

$$v(k) = v_0 u(k\sigma) - w_0 u(k\sigma') ,$$

where the parameters chosen were $\sigma' = \frac{5}{3}\sigma$ and $w_0 = \frac{10}{23} v_0$. The transition remains first order; we do not report here the solutions we have obtained because they differ from those we have reported only in a quantitative way.

III. THE LONG-WAVELENGTH SPECTRUM

We have seen above that for the models considered the function $n_0(T)$ is triple valued in the vicinity of the phase transition and that this gives rise to a first-order transition. In this section

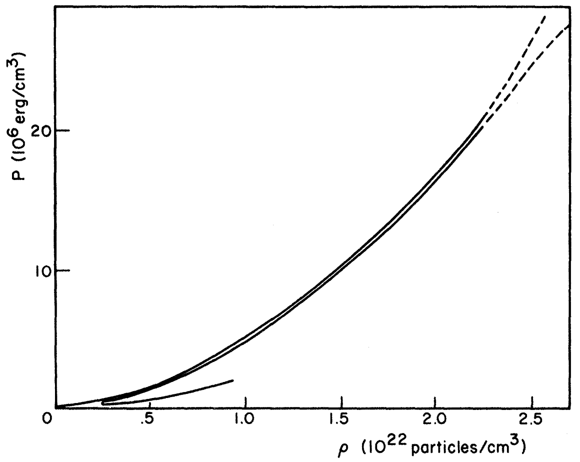

FIG. 7. Luban model: The isotherm $T = 1.0°$K as a function of number density. In the high-density–high-pressure region the uncondensed and condensed branches do not meet and will probably eventually diverge, although they are effectively coincident over a considerable range. Since there is no contour along which the uncondensed solution continuously transforms into the condensed solution, the Maxwell construction may not be applied.

we will attempt to establish which features of the models are responsible for this anomalous behavior and to determine whether this defect is endemic to models of this sort.

In Fig. 8 we show the function ϵ_k for the gapless model for a number of points on the solution curve. The spectrum in the Luban model would differ from this principally in that there would be a gap in the low k region which would decrease monotonically along the solution curve. We would like to point out the obvious feature that as the condensate density goes to zero, the spectrum transforms from an "initially linear" to an "initially quadratic" nature. This lowering of the excitation energy in the long-wavelength region causes anomalous contributions to the integrals in Eqs. (4) – (6). As an example, in Fig. 9 we show the right-hand side of Eq. (6) for fixed temperature as a function of n_0 (self-consistent values of γ have been inserted). The negative slope in the small n_0 region has its origin in the peculiar dependence of the long-wavelength part of the excitation spectrum on n_0 for small values of n_0; it is symptomatic of the existence of triple-valued solutions (observe that for some ρ there is more than one possible value of n_0; in such cases $n_0 = 0$ is also a solution). Approximations on the integrals which pressure this feature of the small k region indicate that the curve in Fig. 9 has the form $\rho(n_0) = A - B\sqrt{n_0} + Cn_0$ for small n_0. Analysis of the Luban model is on similar lines, except here it is the collapse of the gap, rather than the collapse of the linear part of the spectrum, that is of interest.

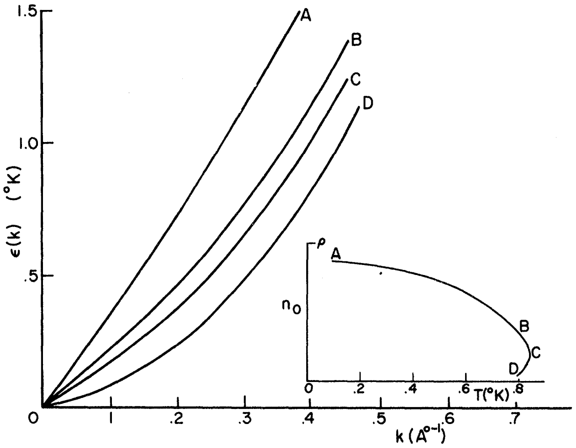

FIG. 8. Shohno model: The excitation spectrum at various temperatures for a system with density 0.021 g/cm^3. The inset shows how these spectra are related to the condensate density.

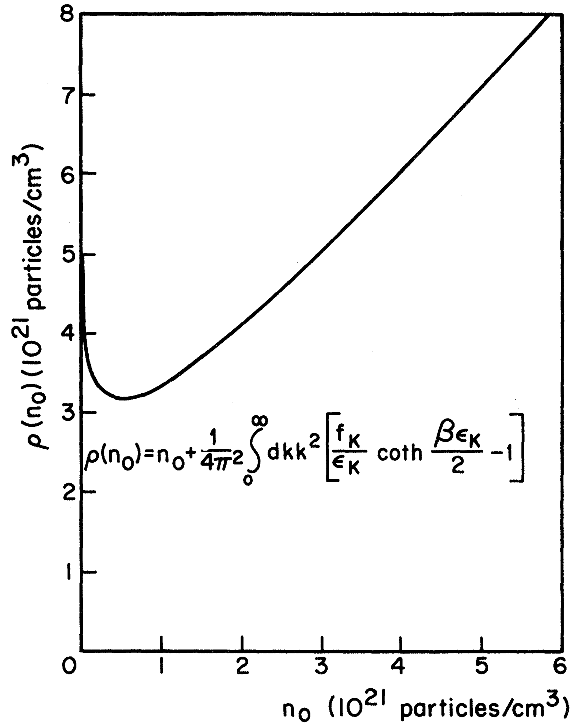

FIG. 9. Shohno model: The right-hand side of Eq. (7) for fixed $T = 0.85°$K as a function of the condensate density n_0 (self-consistent values of γ have been inserted).

An interesting question now arises: Does a collapse of the excitation spectrum, when $n_0 \to 0$, always imply a first-order phase transition? We can give a counter example: The Shohno model with a separable interaction so that for small k and q we have

$$v_{k,q} - v_0 \propto k^\epsilon q^\epsilon , \quad 0 < \epsilon < 2 \,;$$

in the condensed state the excitation spectrum has the following small k behavior:

$$\epsilon^2(k) = Dk^\epsilon(2n_0 v_0 + D_k^{\;\epsilon}) \,,$$

where D is a constant. In this case the spectrum has a collapse from a $k^{\epsilon/2}$ to a k^ϵ behavior, as $n_0 \to 0$. If $\epsilon > 1$ it is simple to study the small n_0 behavior of the right-hand side of Eq. (6) and we find that

$$\rho(n_0) - \rho(0) \sim n_0 - Bn_0^{\;3/\epsilon - 1} \,.$$

We conclude that $\rho(n_0)$ is an initially decreasing function of n_0 for $2 > \epsilon > \frac{3}{2}$ and the transition is of first order, whereas for $\frac{3}{2} > \epsilon > 1$ $\rho(n_0)$ is an increasing function and the system has a higher-order transition at the smallest temperature for which an uncondensed solution exists.

IV. IMPLICATIONS FOR MODEL BUILDING

The discussion above points out the danger that a model for which the excitation spectrum collapses as n_0 goes to zero will display a first-order phase transition. The models of Beliaev[9] and Brueckner and Sawada[10] display collapsing excitation spectra; this raises questions that should be answered before calculations on more complicated models are attempted: Is the first-order phase transition a serious defect? What features must a model incorporate to avoid it?

Since the model ignores lifetime effects, it fails at high temperature and inevitably before the phase transition; hence it might be argued that the predictions of the model are irrelevant in this region. It is reasonable to ask, however, that the model at least anticipate the transition to the extent that the condensate density be on its way to zero as the model's limits of validity are approached; furthermore, the collision broadening of the excitation spectrum would not seem to change the effects of the collapse. The first-order phase transition found above would thus seem to be a serious defect in the model.

The excitation spectrum discussed above has been the spectrum of the single-particle Green's function. It is not known whether this spectrum collapses at the λ point. An argument against such a collapse comes from the fact that the sound velocity does not collapse at the λ point. It has been proved theoretically[11,12] that the excitation spectrum discussed above, the spectrum of the single-particle Green function, and the spectrum of the density-density correlation function coincide in the long-wavelength limit and at zero temperature. This result seems to hold at higher temperatures and at higher wave vectors because the density fluctuation spectrum (as revealed by neutron scattering experiments) correctly reproduces the thermodynamics of helium below 1.9°K.[13] On the other hand, serious doubt in the conjecture that the spectra coincide is cast by the fact that in the theoretical proof[11,12] for small k a fundamental role is played by the existence of the condensate, which vanishes at the transition. A possible way out could consist in the coincidence of the two spectra at all temperatures only in the rather high k region, whereas in the small k region this coincidence depends on the presence of a condensate.

ACKNOWLEDGMENTS

The authors would like to thank Dr. G. V. Chester for his encouragement of this project and many useful discussions. The computer programming was done by William P. Francis and Mrs. R. C. Richardson.

---

[*] Work supported in part by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-3699, Technical Report No. NYO-3699-37, and by the Advanced Research Projects Agency through the Materials Science Center at Cornell, MSC Report No. 1111.

[†] National Science Foundation Graduate Fellow.

[1] N. Bogoliubov, J. Phys. (USSR) 11, 23 (1947).

[2] M. Luban and W. D. Grobman, Phys. Rev. Letters 17, 182 (1966).

[3] The zero-temperature case of this model was proposed by M. Girardeau and R. Arnowitt, Phys. Rev. 113, 755 (1959); finite temperature generalizations are due to D. N. Zubarev and Iu. A. Tserkovnikov, Doklady Acad. Nauk 120, 991 (1958) [English transl.: Soviet Phys. – Doklady 3, 603 (1958)]; G. Wentzel, Phys. Rev. 120, 1572 (1960). We shall use the formulation of M. Luban, Phys. Rev. 128, 965 (1962).

[4] N. Shohno, Progr. Theoret. Phys. (Kyoto) 31, 553 (1964); 32, 370 (1964).

[5] K. Huang, C. N. Yang, and J. M. Luttinger, Phys. Rev. 105, 776 (1957).

[6] W. D. Grobman and M. Luban, Phys. Rev. 147, 166 (1966).

[7] N. M. Hugenholtz and D. Pines, Phys. Rev. 116,

489 (1959).

[8] V. K. Wong Ph. D. thesis, Berkeley, 1966 (unpublished), p. 135.

[9] S. T. Beliaev, Zh. Eksperim. i Teor. Fiz. 34, 433 (1958) [English transl.: Soviet Phys. – JETP 7, 299 (1958)].

[10] K. A. Brueckner and K. Sawada, Phys. Rev. 106, 1117 (1957).

[11] J. Gavoret and P. Nozières, Ann. Phys. (N. Y.) 28, 349 (1964).

[12] K. Huang and A. Klein, Ann. Phys. (N. Y.) 30, 203 (1964).

[13] P. J. Bendt, R. D. Cowan, and J. L. Yarnell, Phys. Rev. 113, 1386 (1959).

PHYSICAL REVIEW VOLUME 183, NUMBER 1 5 JULY 1969

Third Sound and the Onset of Superfluidity in Unsaturated Helium Films

David Goodstein

Department of Physics, California Institute of Technology, Pasadena, California 91109

(Received 12 March 1969)

A simple model, commonly used for describing the behavior of the superfluid film is examined, and it is found to become spontaneously unstable when the partial molar entropy falls below a certain finite value for each temperature and film thickness. The instability is proposed as the cause of the onset curve for superfluidity in unsaturated films, and comparisons with experiment are made. In addition, the use of thermodynamic identities in the model leads to a new and more accurate expression for the velocity of third sound in terms of other measurable quantities.

I. INTRODUCTION

It is well known that liquid He^4 under its own vapor pressure undergoes a phase transition at $T_\lambda \cong 2.17°K$, below which temperature its properties are unusual enough to merit the term superfluid. It is also known that superfluidity exists in very thin films of helium (down to just a few atomic layers) but the nature of the transition to superfluidity in thin films is obscure. In bulk liquid He^4, the transition to superfluidity is accompanied by a logarithmic infinity in the heat capacity. In very thin films the heat capacity has a broad maximum at temperatures slightly lower than T_λ, but the onset of superflow occurs at temperatures considerably lower than the heat-capacity maximum.

If the equilibrium gas pressure, P, above a helium film is less than the liquid vapor pressure, P_0, the film is said to be unsaturated. The thickness of the film, d, or amount adsorbed per unit area, N, is a definite function of P and T for any given substrate. At each temperature below T_λ the superflow properties of the film are found to vanish if P/P_0 drops below some value. A plot of this value of P/P_0 against temperature is given in Fig. 1. Superflow is observed in the film at all lower temperatures and higher pressures. We shall refer to this curve as the onset curve.

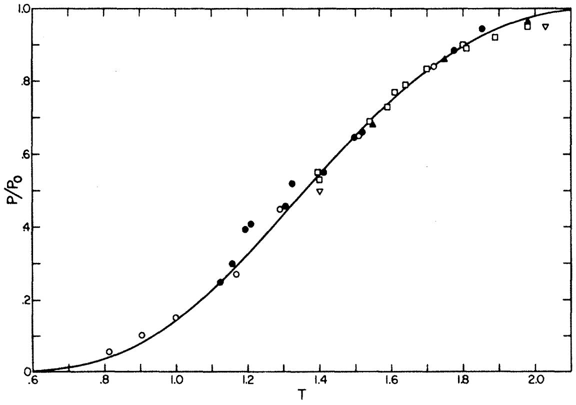

FIG. 1. The curve for the onset of superflow in unsaturated films: T in °K versus P/P_0 ∇ Long and Meyer, Phys. Rev. 79, 1031 (1950), mass transport; □ Brewer and Mendelssohn, Proc. Roy. Soc. (London) A260, 1 (1961), heat flow; ○ Fokkens, Taconis, and DeBruyn Ouboter, Physica 32, 2129 (1966), heat flow; ● Rudnick *et al.*, (Ref. 3), third sound; ▲ Henkel, Kukichi, and Reppy (Ref. 4), persistent currents. In the experiments by Long and Meyer, the film flowed under the influence of a pressure gradient. In some cases (the points shown) agreement with this curve was found. In others superflow all the way up to T_λ was detected even in very thin film. The discrepancy between these latter results and all other measurements has never been understood.