However, we would like to suggest that this effect may result from a residual interference effect arising at the inner crossing.[2]

The results presented here have stimulated considerable efforts to understand the detailed interactions occurring in low-energy ion-atom collisions. The theory recently developed by Rosenthal and Foley has been remarkably successful in leading to an understanding of those results. Some unanswered questions remain, however, and further theoretical efforts will be needed to answer them. It is clear that the full elucidation of the detailed structure of the excitation functions will provide a powerful test of our understanding of the dynamics of the unbound molecular state formed during these inelastic collisions.

The authors are most indebted to Professor W. W. Smith and Dr. N. Tolk for their extensive aid in obtaining these results and in discussing their interpretation. We are also indebted to Dr. H. Foley and Mr. H. Rosenthal for extensive discussions on their new theoretical model. This work would not have been possible without the enthusiastic support of the members of the Physics Department Machine Shop and Electronics Shop.

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VARIATIONAL CALCULATION OF THE PROPERTIES OF LIQUID He³-He⁴ MIXTURES AT 0°K

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The properties of liquid He³-He⁴ mixtures at 0°K are studied by a variational method using a Jastrow-Slater trial wave function and the Wu-Feenberg expansion of the energy expectation value: The system of mass-3 boson + mass-4 boson shows complete phase separation; the system of mass-3 fermion + mass-4 boson and the system of mass-3 boson + mass-4 fermion mixtures separate incompletely; and the system of mass-3 fermion + mass-4 fermion mixes completely. The limiting solubility of the mass-3 fermion in the mass-4 boson solvent is found to increase with pressure.

In this Letter we present the results of a variational calculation of the ground-state properties and phase equilibrium of liquid He³-He⁴ mixtures. The properties of such mixtures at zero and nonzero temperatures have already been investigated by Cohen and Van Leeuwen[1,2] (CVL). These authors, using a Fermi-Bose hard-sphere model and the Huang-Yang-Lee pseudopotential method up to first[1] and second[2] order in the hard-sphere diameter, were able to show that such a system has a phase diagram which is in excellent agreement with the experimentally observed He³-He⁴ phase diagram; in particular CVL predicted the existence of an incomplete phase separation at

0°K, which was later confirmed by experiment. The main purpose of our work is to show that this incomplete phase separation remains in a treatment which is not limited to low densities. This can be done by a variational calculation which has, however, the drawback of providing information only on the ground-state properties of the mixture. A variational calculation has already been made by Massey and Woo[3,4], who investigated only the properties of the dilute (less than 7%) solutions of He³ in He⁴ and did not attempt to describe the phase separation.

We assume that the system of n_4 He⁴ (mass m_4) and n_3 He³ (mass m_3) atoms, in a volume v (n_3

$+n_4 = n$, concentration $x = n_3/n$, density $\rho = n/v$), is described by the Hamiltonian

$$H = -\frac{\hbar^2}{2m_3}\sum_{i=1}^{n_3}\Delta_i - \frac{\hbar^2}{2m_4}\sum_{i=n_3+1}^{n}\Delta_i$$

$$+ \sum_{i<j=2}^{n} V(|\vec{r}_i - \vec{r}_j|),$$

where $V(r)$ is the Lennard-Jones 12-6 potential

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

with

$$\epsilon = 10.22°K, \quad \sigma = 2.556 \text{ Å}.$$

We choose a Jastrow-Slater type trial wave function

$$\Psi(\vec{r}_1, \cdots, \vec{r}_N) = \Psi_B(\vec{r}_1, \cdots, \vec{r}_N)$$

$$\times \Phi_F(\vec{r}_1, \cdots, \vec{r}_{n_3}) \qquad (1)$$

with

$$\Psi_B(\vec{r}_1, \cdots, \vec{r}_N) = \prod_{i<j=2}^{n} f(|\vec{r}_i - \vec{r}_j|).$$

We assume that the short-range correlation factor is the same for the three types of pairs and is characterized by one variational parameter b:

$$f(r) = \exp\{-(b\sigma/r)^5\}.$$

A more refined treatment of the mixture would be to introduce three different parameters for the three types of pairs, a procedure similar to that used by Massey and Woo.[4]

The antisymmetry of the wave function with respect to the interchange of two He[3] atoms is accounted for by a Slater determinant

$$\Phi_F(\vec{r}_1, \cdots, \vec{r}_{n_3}) = \text{Det}\{e^{i\vec{k}_i \cdot \vec{r}_j}\chi_i(\sigma_j)\}_{i,j \le n_3}$$

of plane waves of wave vector $\vec{k}_i$ in the spin state χ_i, filling up two Fermi spheres of equal radius

$$k_F = (3\pi^2\rho x)^{1/3}.$$

Although trial wave functions analogous to (1) yield, in the case of pure liquid He[3] and He[4],[5,6] values of the energy and density in reasonable

agreement with the experimental values, no such agreement can be expected for the ground-state excess energy of the mixture

$$E^e(x) = E(x) - xE(1) - (1-x)E(0)$$

which is roughly 10^3 times smaller than the ground-state energy of the pure liquids. The use of the variational method to compute the ground-state excess energy is thus, we feel, the main approximation of our treatment which should therefore be regarded as describing a model Jastrow-Slater fluid of wave function (1) whose properties bear only qualitative resemblance to those of true He[3]-He[4] mixtures.

Two other approximations, introduced already by Wu and Feenberg[7] (WF) in their treatment of pure liquid He[3], are necessary to deal with the Slater determinant: The first one is to assume that the optimum wave function $\Psi_B(\vec{r}_1, \cdots, \vec{r}_N)$, obtained by minimizing $\langle\Psi_B|H|\Psi_B\rangle/\langle\Psi_B|\Psi_B\rangle$, is the true ground-state wave function for the mixture of mass-3 boson + mass-4 boson of concentration x, i.e., to assume

$$H\Psi_B(\vec{r}_1, \cdots, \vec{r}_N) = E_B\Psi_B(\vec{r}_1, \cdots, \vec{r}_N).$$

The second one is to expand the exchange effects described by Φ_F, by use of the WF cluster expansion, and to keep only the first two terms, i.e., those in which the Pauli principle acts only on pairs and triplets of particles. A justification for the use of such an expansion is that it seems to converge rapidly: The second-order correction to the ground-state excess energy is typically 10 times smaller than the first one.

The WF zeroth order consists in neglecting completely the Pauli principle and treating the academic mass-3 boson + mass-4 boson mixture. The ground-state energy of such a mixture of concentration x can be deduced in a straightforward way from the average values $f_6(b) = \langle(\sigma/r)^6\rangle$, $f_7(b) = \langle(\sigma/r)^7\rangle$, and $f_{12}(b) = \langle(\sigma/r)^{12}\rangle$, computed in Ref. 5 for several values of b at a given density by the molecular-dynamics method. Indeed the scaling trick of McMillan[6] enables one to express the energy expectation value of the mixture for a value b' of the parameter and at a density ρ' as

$$E^B(b', \rho') = 4\epsilon\{S^{12}f_{12}(b) - S^6 f_6(b)\} + \frac{\hbar^2}{4m_3}20b^5 S^2 f_7(b)\left\{x + \frac{m_3}{m_4}(1-x)\right\}, \qquad (2)$$

where $S = (\rho'/\rho)^{1/3}$ and $b' = b/S$. The ground-state energy and equilibrium density of the mixture for each concentration x are then obtained by minimizing (2) with respect to b' and ρ'. The resulting excess energy is shown in Fig. 1 as a function of x; its second derivative is everywhere negative, indicating that a mass-3 boson + mass-4 boson mixture separates completely at 0°K. Such a result was already obtained in the CVL model and is a consequence of the difference in density and compressibility

Table I. Experimental He³-He⁴ mixture properties compared with the results of the variational calculation. η is the initial slope of the ground-state excess energy as a function of the concentration x (in °K), ϵ_3 is the binding energy of one He³ atom in liquid He⁴ (in °K), x_m is the maximun solubility of He³ in He⁴, α is the dilatation parameter defined by (4), and π_0 is the osmotic pressure at three He³ concentrations.

	η (°K)	η (°K)	x_m (%)	α	π_0 (mm of Hg) 2%	4%	6%
Results of variational calculation	−0.67	1.92	12.6	0.29	3.	11.	23.
Experimental	−0.312	2.78	6.4	0.284	2.5	7.7	13.5

of the two components, due to their difference in zero-point energy.[8]

For the system of mass-3 fermion + mass-4 boson, the WF first- and second-order approximants to the energy expectation value $\langle \Psi_B \Phi_F | H | \Psi_B \Phi_F \rangle / \langle \Psi | \Psi \rangle$ are[3]

$$E^{(1)}(b',\rho') = E^B(b',\rho') + \frac{\hbar^2}{2m_3}\frac{3}{5}xS^2 k_F^2 + 24x^2\frac{\hbar^2 k_F^2}{2m_3}S^2 \int_0^1 S_B(2k_F r)(1 - \tfrac{3}{2}r + \tfrac{1}{2}r^3)r^4 dr,$$

$$E^{(2)}(b',\rho') = E^{(1)}(b',\rho') - \left(\frac{3}{8\pi}\right)^3 \frac{\hbar^2}{2m_3}k_F^2 S^2 x^3 \underset{|\vec{r}_1|,|\vec{r}_2|,|\vec{r}_3| < 1}{\int\int\int} S_B(k_F r_{12})[S_B(k_F r_{23}) - 1]$$

$$\times [S_B(k_F r_{31}) - 1]r_{12}^2 d^3r_1 d^3r_2 d^3r_3, \qquad (3)$$

where $S_B(k)$ is the structure factor corresponding to the pure mass-4 boson fluid of variational pa-
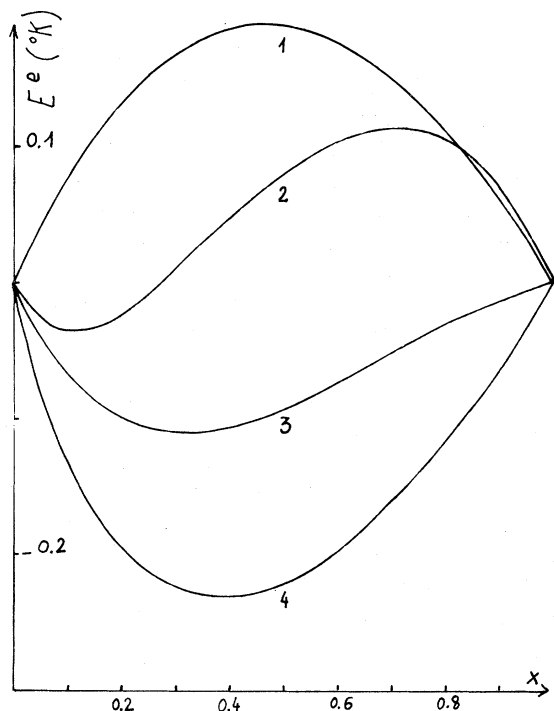

FIG. 1. Excess energy E^e (in °K) versus concentration x of the first component of the following mixtures: curve 1, mass-3 boson + mass-4 boson; curve 2, mass-3 fermion + mass-4 boson (physical case); curve 3, mass-4 fermion + mass-3 boson; curve 4, mass-3 fermion + mass-4 fermion. The regions of negative curvature ($d^2E^e/dx^2 < 0$) are unstable.

rameter b, at the density ρ, taken from Ref. 5. Minimization of (3) with respect to b' and ρ' leads to the ground-state excess energy shown in Fig. 1, which indicates an incomplete phase separation. This result is a consequence of two competing tendencies: a tendency to complete separation, as in the boson-boson case, due to difference in density and in compressibility, and a tendency for the fermion species to mix completely with the boson species in order to minimize its Fermi energy.

The maximum solubility of He³ in He⁴ is obtained by solving

$$E^e(x) + (1-x)\frac{dE^e(x)}{dx} = 0.$$

The dilatation parameter α is defined by relating the molar volume $v(x)$ of a solution of concentration x in He³ to the molar volume of pure He⁴,

$$v(x) = v_4[1 + \alpha x]. \qquad (4)$$

As expected, the agreement with experiment[9] is only qualitative: The values of the initial slope η of the ground-state excess energy, the binding energy of one He³ atom in liquid He⁴, $\epsilon_3 = -\eta - E_3^0$ (where E_3^0 = ground-state energy of pure He³, cf. Ref. 9), the maximum solubility x_m, the dilatation parameter α, and the osmotic pressure π_0, shown in Table I, are seen to differ appreciably from the experimental values.

The sensitivity of the incomplete phase separation to both the mass ratio and the statistics was

investigated by considering two other (academic) cases: The system of mass-3 boson + mass-4 fermion separates incompletely (with a pure mass-4 fermion phase) and the mass-3 fermion + mass-4 fermion mixture mixes completely as shown in Fig. 1 [note that in the CVL treatment, Ref. 1, the fermion-fermion system shows incomplete phase separation].

Lastly, the effect of an external pressure was studied by minimizing the enthalpy. We find that, as the pressure is varied from 0 to 25 atm, the dilatation coefficient α decreases monotonically from 0.29 to 0.19 and the maximum solubility increases monotonically from 12.6 to 31% with a negative second derivative. This last result is due to the fact that, because of the greater compressibility of liquid He^3, the volume difference of the pure liquids decreases with increasing pressure, lowering the tendency to phase separation. A similar, though nonmonotonic, increase of the maximum solubility with increasing pressure was already predicted by Edwards.[10] The predicted effect has been very recently observed experimentally.[11]

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NUCLEATION OF QUANTIZED VORTEX RINGS BY IONS IN HELIUM II *

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We suggest that a quantized vortex ring is formed when a roton, localized near a moving ion, is expanded by stochastic processes to become a small ring, attached to the ion. Calculations based on this notion are compared with experiment.

The purpose of this Letter is to suggest that quantized vortex rings are nucleated from moving ions by stochastic processes. It is easy to show that conservation of energy and momentum lead to estimates for the critical velocity far too high to agree with experiment.[1] We adopt the view, first advanced by Iordanskii, that there exists a Maxwell distribution of vortex rings in He II.[2] We suppose further that there exists a smallest ring (proto-ring) and that higher states are filled by thermal collisions.

Suppose that proto-rings are somehow located near the equator of an ion moving with velocity v_I. The effect of collisions of other quasiparticles with the ion–proto-ring complex will be, on occasion, to make one of these rings grow to finite size. In this case we know that the natural attraction felt by an ion near the core of a vortex

(which has been extensively studied by the authors[3]) will cause the ring to attach to the ion. If the ring grows to be of such radius that its forward velocity is equal to that of the ion it will be a "critical fluctuation" in the sense that further growth will be at the expense of the electric field, and will continue until the drag on the ring is equal and opposite to the electric force. A possible sequence of events is pictured in Fig. 1(a); the advantage of this view is that estimates may be made of the shape, energy, momentum, and velocity of the critical fluctuation which allow calculation of the free energy difference ΔF between the proto-ring and the critical fluctuation. While we cannot specify how the critical fluctuation is formed, ergodic arguments tell us that it will occur with a probability P proportional to $\exp(-\Delta F/kT)$.