

An alternative statistical analysis of the fluctuations was tried by calculating  $\langle \Delta I^3 \rangle$  and  $\langle \Delta I^4 \rangle$  in addition to  $\langle \Delta I^2 \rangle$ . The ratio  $\langle \Delta I^4 \rangle / \langle \Delta I^2 \rangle^2$  was calculated with the hope of finding a high value in the periodic regime.<sup>5</sup> The actual values found were always close to 3, as expected for a Gaussian distribution of fluctuations.

It should be noticed that we have left out a few data points, some of which do not fit to our curve for  $\langle \Delta I^2 \rangle$ . Some of them were left out because of high values for the third moment. Others were left out because they did not represent the final, stationary state to which the system passed when waiting long enough (several hours). These points evidently correspond to local minima of the thermodynamic potential and some of them have autocorrelation functions that display a very clear damped-harmonic-oscillator behavior.

The experiments will be continued with the aim of presenting more quantitative data. At present we know only qualitatively how the data of Fig. 1 are connected with the order parameters that have been defined for convection<sup>2</sup> and for periodic<sup>5</sup> and strongly turbulent flow.<sup>4</sup> This work represents a novel application of neutron scattering and of neutron-data analysis. We know of no other case where the neutron intensity oscillates on a time scale longer than the period of measurement. An effect of this is that the problem of energy resolution is converted to one of time and patience.

We first observed such instabilities when investigating the nematic-isotropic transition of PAA. The complicated time behavior and field dependence of the intensities caused us initially to draw some unjustified conclusions about the nature of this transition.<sup>15</sup> The instability at this transition, where two phases coexist, is probably of the type found in binary mixtures.<sup>1</sup>

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## Antonoff's Rule and the Structure of Interfaces near Tricritical Points\*

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The Van der Waals theory of surface tension and interface structure is extended to three-phase equilibrium. The theory predicts that near a tricritical point the three interfacial tensions will satisfy "Antonoff's rule" in the form  $\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ , where  $\beta$  is the distinguished phase, and that the composition profile of the  $\alpha\gamma$  interface will be qualitatively different from that of the  $\alpha\beta$  and  $\beta\gamma$  interfaces.

Van der Waals's theory of the liquid-vapor interface<sup>1-4</sup> is summarized graphically in Fig. 1.

In Fig. 1(a) is shown the analytic chemical-potential-density isotherm,  $\mu(\rho)$ , and the equal-areas

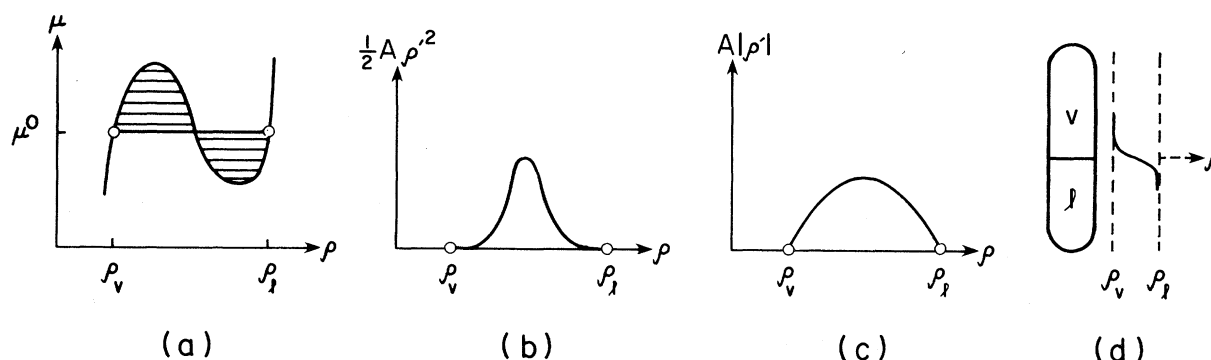


FIG. 1. (a) Analytic  $\mu(\rho)$  isotherm and equal-areas construction. (b), (c) Square and magnitude of the density gradient as functions of the local density. (d) Density profile of the interface.

construction that yields the densities  $\rho_v$  and  $\rho_l$  of the bulk vapor and liquid phases at the equilibrium chemical potential  $\mu^0$ . The square of the density gradient,  $\rho'^2$ , through the interface, is determined as an integral over the analytic  $\mu(\rho)$  of Fig. 1(a) by

$$\frac{1}{2}A\rho'^2 = \int_{\rho_v}^{\rho} [\mu(\rho) - \mu^0] d\rho, \quad (1)$$

where  $A$  is some proportionality constant. The resulting  $\frac{1}{2}A\rho'^2$  and  $A|\rho'|$  are shown as functions of  $\rho$  in Figs. 1(b) and 1(c). The area under the latter curve, between  $\rho = \rho_v$  and  $\rho = \rho_l$ , is the interfacial tension  $\sigma$ ,

$$\sigma = A \int_{\rho_v}^{\rho_l} |\rho'| d\rho. \quad (2)$$

The density profile through the interface, as inferred from Fig. 1(b) or 1(c), is shown in Fig. 1(d). The variation from  $\rho_v$  to  $\rho_l$  occurs over a microscopic distance equal to the range of correlation of density fluctuations in the bulk fluids. This interface thickness diverges on approach to the liquid-vapor critical point.

We may now sketch the analogous theory for the

equilibrium of three phases,  $\alpha, \beta, \gamma$ . Let  $\psi$  be any density or composition variable and  $b$  its thermodynamic conjugate,<sup>5</sup> and plot the analytic  $b(\psi)$  as a function of  $\psi$  for fixed values of the remaining thermodynamic fields,<sup>5-7</sup> as in Fig. 2(a). The equal-areas construction shown in that figure yields the value of  $\psi$  in each of the three phases, and also gives the equilibrium value,  $b^0$ , of  $b$ . The square of the composition gradient,  $\psi'^2$ , is then determined by

$$\frac{1}{2}A\psi'^2 = \int_{\psi_\alpha}^{\psi} [b(\psi) - b^0] d\psi, \quad (3)$$

where  $A$  is again some proportionality constant. The resulting  $\frac{1}{2}A\psi'^2$  and  $A|\psi'|$  are shown as functions of  $\psi$  in Figs. 2(b) and 2(c). The area under the latter curve between  $\psi = \psi_\alpha$  and  $\psi = \psi_\beta$  is the tension of the  $\alpha\beta$  interface, the area under the curve between  $\psi_\beta$  and  $\psi_\gamma$  is the tension of the  $\beta\gamma$  interface, and the area under the curve between  $\psi_\alpha$  and  $\psi_\gamma$  is the tension of the  $\alpha\gamma$  interface:

$$\begin{aligned} \sigma_{\alpha\beta} &= A \int_{\psi_\alpha}^{\psi_\beta} |\psi'| d\psi, & \sigma_{\beta\gamma} &= A \int_{\psi_\beta}^{\psi_\gamma} |\psi'| d\psi, \\ \sigma_{\alpha\gamma} &= A \int_{\psi_\alpha}^{\psi_\gamma} |\psi'| d\psi. \end{aligned} \quad (4)$$

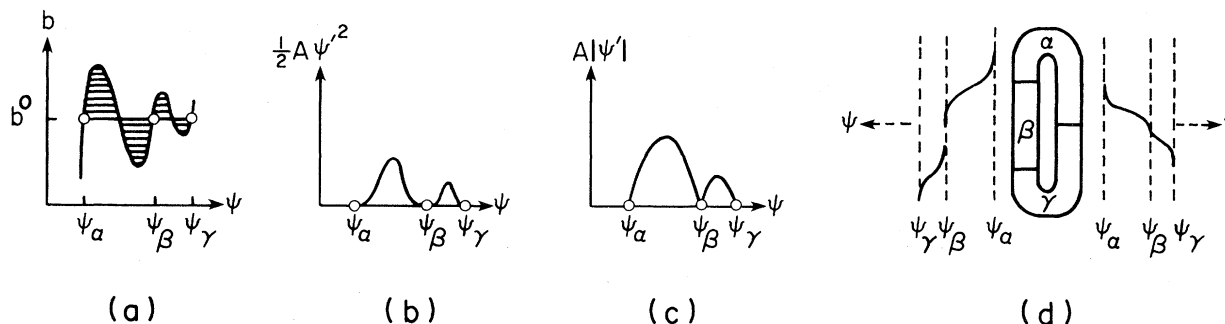


FIG. 2. (a) Analytic  $b(\psi)$  and equal-areas construction. (b), (c) Square and magnitude of the gradient in the order parameter as functions of the local value of the order parameter. (d) Composition profiles of the three interfaces.

The profile of  $\psi$  through each of the three interfaces, as inferred from Figs. 2(b) or 2(c), is shown in Fig. 2(d).

From (4) it follows that

$$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma}, \quad (5)$$

a general form<sup>8</sup> of "Antonoff's rule." That rule cannot always hold; in general one can expect only the inequality  $\sigma_{\max} < \sigma_{\text{med}} + \sigma_{\min}$ , where  $\sigma_{\max}$  is the largest,  $\sigma_{\text{med}}$  the median, and  $\sigma_{\min}$  the smallest of the three interfacial tensions.<sup>8</sup> Deviations from (5) mean either that the three-phase equilibrium cannot be adequately characterized by a single order parameter  $\psi$ , or else that the interfacial tensions are not expressible as integrals of the form

$$\sigma_{\alpha\beta} = \int_{\psi_{\alpha}}^{\psi_{\beta}} f(\psi) d\psi, \text{ etc.}, \quad (6)$$

where  $f$  is a function of the local  $\psi$ . (In the Van der Waals theory the function  $f$  is  $A|\psi'|$ , but Antonoff's rule would be implied by any  $f$ .) With respect to the former possibility, note that in the unsymmetrical three-phase equilibrium envisioned by Griffiths,<sup>5</sup> of which Fig. 2(a) is an expression,<sup>7</sup> the  $\beta$  phase plays a distinguished role<sup>5,8,9</sup> ( $\psi_{\alpha} < \psi_{\beta} < \psi_{\gamma}$ ). As Griffiths observes,<sup>5</sup> this is unlike the symmetrical three-phase equilibrium found by Straley and Fisher<sup>10</sup> in a model system. In such a fully symmetrical case,  $\sigma_{\alpha\beta} = \sigma_{\beta\gamma} = \sigma_{\alpha\gamma}$ , which satisfies the inequality  $\sigma_{\max} < \sigma_{\text{med}} + \sigma_{\min}$  but violates Antonoff's rule, Eq. (5). The evidence so far in multicomponent fluids is that those three-phase equilibria that can be followed to their tricritical points are of the unsymmetrical, Griffiths type.<sup>5</sup>

Just as the Van der Waals theory of the liquid-vapor interface, as summarized in Fig. 1 and in Eqs. (1) and (2), is expected to be correct only asymptotically on approach to the critical point,<sup>4</sup> where the interface thickness becomes much greater than the range of the intermolecular forces and the distance between neighboring molecules, so the analogous theory of three-phase equilibrium, as summarized in Fig. 2 and in Eqs. (3) and (4), would be expected to be correct only asymptotically on approach to the tricritical point of that phase equilibrium. We therefore expect that Antonoff's rule, Eq. (5), will hold as an asymptotic law:

$$\sigma_{\alpha\gamma}/(\sigma_{\alpha\beta} + \sigma_{\beta\gamma}) \rightarrow 1 \quad (7)$$

as the tricritical point is approached on any path along which three phases are always present. The same measurements previously proposed<sup>8</sup> to

test the inequality  $\sigma_{\max} < \sigma_{\text{med}} + \sigma_{\min}$  and to test the predicted value of the tricritical-point surface-tension exponent, would serve to test (7) as well.

Figure 2(d) shows a plateau in the composition profile of the  $\alpha\gamma$  interface, where  $\psi$ , as it varies between the values  $\psi_{\alpha}$  and  $\psi_{\gamma}$  characteristic of the bulk  $\alpha$  and  $\gamma$  phases, passes through the intermediate value  $\psi_{\beta}$  characteristic of bulk  $\beta$ . Indeed, Fig. 2(c) shows  $|\psi'|$  linear in  $|\psi - \psi_{\beta}|$  near  $\psi = \psi_{\beta}$ , which implies that the plateau extends over a logarithmically divergent distance. This is the natural accompaniment of Antonoff's rule, Eq. (5); for when the inequality  $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$  reduces to an equality, the system is at the threshold of having the  $\alpha\gamma$  interface be simply a macroscopic sheath of bulk  $\beta$  phase.<sup>8</sup> If, then, this theory does become correct asymptotically on approach to the tricritical point, there should be seen a plateau in the composition profile of the  $\alpha\gamma$  interface, and the spatial distance over which the plateau extends should be seen to increase as the tricritical point is approached. The structure of the  $\alpha\gamma$  interface is thus predicted to be qualitatively different from that of the  $\alpha\beta$  and  $\beta\gamma$  interfaces. This may be tested experimentally by reflectance measurements like those with which Webb and co-workers have determined other interface profiles.<sup>11-13</sup> The order parameter  $\psi$  may then be thought of as the index of refraction.

Experimental tests of the asymptotic law (7), and of the composition profiles of the three interfaces predicted in Fig. 2(d), would thus confirm or refute some of the ideas on which our present understanding of phase equilibrium rests.

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## Direction of Paired Spins in the $A_1$ Phase of $^3\text{He}$ : A Test of the Paramagnon-Induced-Pairing Hypothesis\*

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It is shown within the context of simple paramagnon theory that if spin fluctuations are responsible for the pairing in superfluid  $^3\text{He}$ , then the direction of paired spins in the  $A_1$  phase should be opposite to that of the field-induced magnetization in the normal state, in contradiction to predictions made using weak-coupling theory. Measurements of the direction of paired spins in the  $A_1$  phase can thus help to test the paramagnon-pairing hypothesis.

The interaction via spin fluctuations of two  $^3\text{He}$  atoms has been shown to be attractive when the pair is in a state having odd angular momentum.<sup>1</sup> It has been suggested that this attractive interaction is responsible for the two superfluid transitions which have been observed in  $^3\text{He}$ . Experimental evidence in support of this hypothesis is indirect. Anderson and Brinkman,<sup>2</sup> as well as other groups,<sup>3</sup> have pointed out that spin-fluctuation-induced pairing must be treated within the framework of a new kind of a "strong-coupling" theory: The paramagnons which mediate the pairing must also be modified as a result of the pairing. This "feedback effect" gives rise to a difference in the free energies of the Anderson-Morel and Balian-Werthamer states.<sup>4</sup>

We believe that this recently proposed mechanism for superfluidity is sufficiently novel that it deserves further study and experimental confirmation. It is the purpose of the present note to demonstrate that there exists a concrete experiment which can provide a strong test of the paramagnon-induced-pairing hypothesis. We confine ourselves here entirely to spin-fluctuation theories of the "paramagnon," as distinguished from "Fermi liquid," type in which the enhancement factor is roughly 20 at a pressure of 27 atm. The paramagnon theory of normal  $^3\text{He}$  is strongly supported by experiments of Meyer and co-workers on the normal-state  $^3\text{He}$  susceptibility which give an excellent fit to the calculations of Béal-Monod, Ma, and Fredkin<sup>5</sup> with no adjustable parameters.

In order to find an experimental test of the paramagnon-induced-pairing hypothesis we derive the gap equations for superfluid  $^3\text{He}$  in the presence of a uniform, static magnetic field,  $H$ , using the spin-fluctuation theory, previously discussed by Anderson and Brinkman,<sup>2</sup> extended to the case  $H \neq 0$ . From the gap equations the transition temperatures are calculated and the nature of the paired states in the presence of a field is discussed. The paramagnon-induced attractive interaction is field dependent. This field dependence is analogous to the feedback effect mentioned above and results from the fact that the paramagnons, which mediate the pairing, are modified in the presence of a magnetic field. This behavior is in contrast to that which one obtains for ordinary (phonon-induced) superconductivity. Because of these effects, studies of the behavior of the system when  $H \neq 0$  should help to provide insight into the pairing mechanism in  $^3\text{He}$ . In particular, it will be shown below that the predicted direction of alignment of the paired spins in the  $A_1$  phase<sup>6</sup> is different in spin-fluctuation and weak-coupling theories.<sup>7</sup> Thus a measurement of this spin direction should provide a strong test of the spin-fluctuation hypothesis.

The gap equations for paramagnon-induced pairing are obtained by analogy with ordinary phonon-induced superconductivity. The generalized Green's function is related to a generalized self-energy using the equations of motion for the  $^3\text{He}$  atoms. The self-energy is then written approxi-