# Thermal Relaxation near the Critical Point\*

David Dahl<sup>†</sup> and M. R. Moldover

School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455 (Received 10 January 1972; revised manuscript received 19 June 1972)

We have measured thermal-relaxation times  $(\tau)$  near the critical point of He<sup>3</sup>.  $\tau$  remains small in one-phase states throughout the critical region. In two-phase states,  $\tau$  increases as the critical temperature  $(T_c)$  is approached in proportion to  $(T_c - T)^{-1.0}$  at all densities. An extra increase in  $\tau$  occurs in two-phase states very near the phase boundary. These observations suggest to us that the diffusion of matter across the liquid-vapor interface is a bottleneck for equilibration. Our data are of value in interpreting puzzling features of several other experiments near critical points.

#### INTRODUCTION

It has been recognized for many years that extremely long times are needed to attain thermal equilibrium in fluid systems near critical points. These long times have always been considered an experimental nuisance, but they have not been documented in sufficient detail to know if they can be explained with the current understanding of transport properties. To help clarify this situation we report a new more complete set of measurements of thermal relaxation times near the liquid-vapor critical point of He<sup>3</sup>. We have used a carefully controlled calorimetric technique. In contrast with earlier calorimetric work<sup>1,2</sup> the present data show unexpectedly long relaxation times only when both liquid and vapor phases are present. The data lead us to conclude that there is some process slower than diffusion of heat which delays the approach to equilibrium when two phases are present. We recall the previously reported observation that the usually rapid transfer of matter between fluid phases by nucleate boiling does not occur near the critical point. That observation taken with the present data leads us to suggest that diffusive transfer of matter across the liquid-vapor interface (i.e., evaporation or condensation) is a slow process which delays attainment of equilibrium near the critical point. Thus, the question of how to calculate the rate of interphase diffusion near a critical point is raised. The data themselves have important implications for the design of future experiments near critical points.

In this paper we will first describe our experimental technique and the resulting data. We then argue that the data are inconsistent with a model of thermal relaxation based on thermal diffusivity. This leads us to speculate on the existence of a bottleneck at the interface. Finally, we discuss the implications of our data for certain other experiments.

## EXPERIMENTAL TECHNIQUE

Most of our observations of thermal relaxation were made in the course of an extended series of "stepwise" measurements of the constant-volume specific heat of He<sup>3</sup> near its critical point at 3.3 K. The calorimeter used and some of the specificheat data (particularly in metastable states) have already been described briefly in a preliminary account.<sup>3</sup> Our calorimeter is made of oxygen-free high-conductivity copper. It contains a 1.06-cm<sup>3</sup> sample volume. Over 99.9% of this volume is in a simple "pancake" shape, i.e., an accurately horizontal cylinder 3.94 cm in diameter and 0.087 cm high. (The diameter reported in Ref. 3 differs slightly from the value quoted here.<sup>4</sup>) The remaining 0. 06% of the volume is a No. 80 drill hole (0.034-cm diameter, 0.72 cm high) through the calorimeter top. This hole is used to fill the calorimeter with a known quantity of He<sup>3</sup>. Then the hole is sealed at its top by a needle which is part of a valve built into the calorimeter top. (A schematic diagram of this valve arrangement appears in Ref. 3 and further details are in Ref. 5.) The valve is operated by a detachable screwdriver and countertorque. After the valve is closed, the volume above it is evacuated and the screwdriver and countertorque are disengaged. The excellent thermal isolation attained in this manner is such that the characteristic time describing the relaxation of the calorimeter temperature towards the surrounding bath's temperature exceeds  $3 \times 10^6$  sec when the calorimeter is filled with He<sup>3</sup> at the critical density and the calorimeter temperature is 3.3 K.

All the calorimeter walls are several millimeters thick. The thermal conductivity of the walls exceeds that of the He<sup>3</sup> they parallel by a factor greater than  $10^4$ . Because of the calorimeter's high thermal conductivity, the outer surface of the He<sup>3</sup> sample is at a single temperature to a very good approximation except during intervals of rapid heating. This temperature is observed with a germanium resistance thermometer attached to the outside of the calorimeter. The calorimeter's heat capacity is less than 4% of the heat capacity of the He<sup>3</sup> sample within it near the critical temperature. The calorimeter's low heat capacity requires that during the approach to equilibrium, to a good ap-

6

proximation, all the heat flowing out of one portion of the sample surface must flow into another portion of the surface.

We have determined the sample densities relative to the critical density  $(\rho/\rho_o)$  and the critical temperature  $(T_o)$  by a fit of all our specific-heat data to the "linear-model" equation of state.<sup>6</sup> Thus  $T_o$  is determined in a manner independent of the thermal-relaxation-time data.

A typical measurement in the temperature range  $|t| < 10^{-3} [t = (T - T_c)/T_c]$  consists of a three-step process. First, the residual drift of the calorimeter temperature towards the bath temperature is balanced with a small heat input until the residual drift is less than  $5\mu K/h$ . The heater used for this purpose is located in a place which avoids temperature gradients appearing across the He<sup>3</sup> sample. Next, the heating rate is altered so the mean sample temperature rises (or falls) 500  $\mu$ K in several minutes. The calorimeter temperature will overshoot (or undershoot). Finally, the heating rate is restored to its initial value and the calorimeter temperature is observed to relax back towards the residual drift rate. The last  $0.5-5 \ \mu K$  of the relaxation were fitted graphically to a simple exponential decay to yield the time constants we discuss below. Measurements at larger amplitude  $(5-50 \ \mu \text{K})$  yielded somewhat shorter time constants, implying the relaxation is not strictly exponential; however, the amplitude dependence is much smaller than the striking temperature dependences which are our primary concern. We used the same measurement procedures further from the critical point, in the temperature range  $10^{-3}$  $< |t| < 3 \times 10^{-2}$ ; however, in those cases the typical residual drift rate, the temperature increment, and the temperature relaxation used to deduce time constants were all ten times as large as the values stated above.

## DATA

Figure 1(a) presents time constant ( $\tau$ ) and specific-heat  $(C_{v})$  data taken when the calorimeter was filled nearly to the critical density. (The maximum value of  $C_v$  occurs below  $T_c$  as expected when gravitationally produced density gradients round the  $C_v$  singularity.) From Fig. 1(a) it is evident that  $\tau$  is much larger in two-phase states below  $T_c$ than in one-phase states above  $T_c$ . The data below  $T_c$  are taken with small cooling and warming steps. The data above  $T_c$  are taken with small cooling steps. Also shown in Fig. 1(a) are two "conflicting" points which show that a large  $\tau$  may be observed even when the final calorimeter temperature is above  $T_c$  if carelessly large temperature steps (involving large temperature gradients) are used. The "conflicting" data suggest that, for example, once a liquid drop is formed, it has a long



FIG. 1. (a) Thermal-relaxation time (logarithmic scale) and normalized specific heat as a function of reduced temperature near the critical temperature.  $\Box$ : relaxation time after large heating step;  $\bigtriangleup$ : relaxation time after large cooling step; dotted line:  $(T_c - T)^{-1}$  curve fit to relaxation data at lower temperatures. Arrows denote upper bound on relaxation time. (b) Thermal-relaxation time and normalized specific heat near the coexistence temperature but "far" from the critical temperature.

lifetime even when relaxing toward a temperature slightly above  $T_c$ .

Figure 1(b) is an example of data taken near the coexistence temperature at which the fluid in the calorimeter becomes a single phase (in this case, vapor). Below the coexistence temperature,  $\tau$  is measurably long. Very near the coexistence temperature (when very little liquid is present), an extra irregular increase in  $\tau$  always occurs. Above the coexistence temperature (when no liquid is present),  $\tau$  is too short for us to measure. In a few favorable cases we established that  $\tau$  is less than 3 sec in one-phase states. ( $\tau$  is also very short in wholly liquid states either above the coexistence temperature.

istence temperature or "superheated" below the coexistence temperature.)

The extra increase in  $\tau$  near the coexistence temperature strongly suggests  $\tau$  depends upon the surface between liquid and vapor phases. Well below the coexistence temperature this surface is horizontal and has an area equal to the cross-sectional area of the calorimeter. Near the coexistence temperature the scarce phase will form a few droplets or bubbles with a much smaller surface area.

Figure 2 presents all of the relaxation-time data taken in two-phase states below  $T_c$  as well as a few of the data points in one-phase states below  $T_c$ . There are four regularities in the data: (i) In onephase states  $\tau$  is always smaller than we can observe. At several densities ( $\rho/\rho_c = 0.94$ , 0.99, 1.08, 1.17, and 1.32) our upper bound is 6 sec at  $T_c$ . (ii) In two-phase states more than 1.5 mK below the coexistence temperature  $[(T - T_{coex})/T_c > 5$ imes10<sup>-4</sup>], all the au data may be described by  $au \propto (T_c$  $(-T)^{-s}$  with s approximately equal to 1.0. (iii) In two-phase states more than 1.5 mK below the coexistence temperature,  $\tau$  is either weakly dependent or independent of the sample density. (iv) In two-phase states within 1.5 mK of the coexistence temperature, an extra large irregular increase in  $\tau$  occurs.

For further analysis we selected all the two-

phase data which fell more than 1.5 mK below the coexistence curve and in the temperature range 0 < t < -0.015 [where  $t = (T - T_c)/T_c$ ]. These data were fitted to functions of the form  $\tau = A(-t)^{-s}$  by the method of least squares. A and s were adjusted in the fit and  $T_c$  was taken from a fit to the  $C_v$  data to be described elsewhere. If both A and s are assumed to be independent of density, the optimum values are

$$\tau_{\text{expt}} = (0.153 \pm 0.004) t^{-0.97 \pm 0.02} \text{ sec}$$
 (1)

Here the errors quoted are one standard deviation. Fits to the data at each density separately yield values of s between 0.8 and 1.2. The data at  $\rho = 1.02$   $\rho_c$  indicate lifetimes which are shorter (at the three-standard-deviation level) than the data at other densities. Except for this small effect, the relative insensitivity of  $\tau$  to the density indicates  $\tau$  is insensitive to the height of the liquid-vapor interface above the bottom of the calorimeter.

### THERMAL DIFFUSIVITY AND CONVECTION

To interpret our data we considered in some detail the possibility that thermal diffusivity, perhaps with convection, was the slowest process during the approach to equilibrium. If the He<sup>3</sup> sample was quiescent, we would expect to measure the time constant associated with the exponential damping of the longest-wavelength thermal mode in the



FIG. 2. Thermal-relaxation time as a function of reduced temperature measured from the critical temperature (both on logarithmic scales) at various densities. The arrows denote upper bounds on relaxation times in one-phase states. Dotted line denotes relaxation times expected from background contribution to thermal diffusivity. Solid line denotes relaxation times expected from both background and critical contributions to thermal diffusivity.

calorimeter. (Shear and sound modes should damp much more rapidly.<sup>7</sup>) Our flat calorimeter has walls of high thermal conductivity and low heat capacity, hence this mode is approximately a onedimensional one in the vertical direction with time constant given by

$$\tau_{\rm thermal} \approx h^2 / (4\pi^2 D_T) \quad . \tag{2}$$

Here *h* is the height of the calorimeter and  $D_T$   $(= \lambda / \rho C_p)$  is the thermal diffusivity  $(\lambda, \rho, \text{ and } C_p)$  are the thermal conductivity, density, and specific heat at constant pressure, respectively).

In order to estimate  $\tau_{\text{thermal}}$  near the critical point of He<sup>3</sup>, attention must be paid to the fact that  $C_p$  and  $\lambda$  are expected to diverge as  $t^{-\gamma}$  and  $t^{-\gamma+\nu}$ , respectively.<sup>7</sup> (Here  $\nu$  is the exponent describing the divergence of the correlation length  $\xi$ , where  $\xi = \xi_0 t^{-\nu}$ .) We have calculated  $C_p$  from our own  $C_{\nu}$ data and published<sup>8</sup> equation-of-state data near the critical point of He<sup>3</sup> using the relation

$$C_{p} = C_{v} - T \left(\frac{\partial P}{\partial T}\right)_{v}^{2} \left(\frac{\partial V}{\partial P}\right)_{T}$$

(In fact,  $C_v$  is less than 10% of  $C_p$  for  $|t| < 10^{-2}$ .)  $\lambda$ has been measured near the critical point of He<sup>3</sup>, but not in sufficient detail to distinguish its critical behavior clearly.<sup>9</sup> Accordingly we have used the following procedure, first, to get a firm upper bound on  $\tau_{\rm thermal}$  based solely on the measured properties of He<sup>3</sup>, and second to get a reasonable estimate of  $\tau_{\rm thermal}$  based on current understanding of transport phenomena near the critical point. We decomposed  $\lambda$  into a temperature-independent "background" contribution and a divergent "critical" contribution which has the value  $(k_B T/6\pi\eta\xi)$  $\times (\rho C_p)$  given by the mode-mode coupling theory.<sup>10</sup> (Here  $\eta$  is the viscosity which has been measured<sup>11</sup> for He<sup>3</sup> and is believed to be at most weakly divergent.) This decomposition of  $\lambda$  has been shown to be accurate near the critical points of  $CO_2$  and xenon<sup>12-14</sup> above the critical temperature. We have taken the background contribution of  $\lambda$  to be 1.5  $\times 10^{-4}$  W/cmK from the data of Kerrisk and Keller<sup>8</sup> and used it alone in Eq. (2) to provide an upper bound to  $\tau_{\rm thermal}$  based solely on experimental information taken from He<sup>3</sup>. This upper bound is the dashed line on Fig. 2. We then estimated the critical contribution to  $\lambda$  by assuming the correlation length in He<sup>3</sup> has the same size as the correlation length in xenon at the same reduced temperature. The correlation length in xenon has been measured<sup>15</sup> along the coexistence curve below  $T_c$ . Our estimate of  $\tau_{\text{thermal}}$  below  $T_c$  including both the background and the critical contributions to  $\boldsymbol{\lambda}$  is shown on Fig. 2 as a solid line. Relaxation times similar to the estimates on Fig. 2 result from our estimates at  $\rho = \rho_c$  above  $T_c$  (210 sec at  $t = 10^{-4}$ , 40 sec at  $t = 10^{-3}$ , and 5 sec at  $t = 10^{-2}$ ). Because  $C_{b}$  is

larger above  $T_c$  than at the same value of t below  $T_c$ , the background contribution to  $\lambda$  imposes a less stringent limit to  $\tau_{\text{thermal}}$  above  $T_c$ .

From our estimates of  $\tau_{\text{thermal}}$  sketched in Fig. 2 it is clear that a thermal-diffusivity model fails to describe our thermal-relaxation-time data. (This contrasts with the widespread belief that the thermal diffusivity has dominated relaxation times in other experiments near critical points.) In particular, a thermal-diffusivity model fails to predict either the long relaxation times we observe in two phases or the order-of-magnitudes drop in relaxation time at the phase boundary (see Fig. 2). A thermal-diffusivity model also fails to predict the correct value for the exponent describing the temperature dependence of relaxation times in the two-phase states below  $T_c$ .

In an effort to understand why relaxation times are shorter in one-phase states than those predicted from a thermal-diffusivity model we have estimated the likelihood of convection occurring within the He<sup>3</sup> sample. If a horizontal fluid layer of thickness *d* is heated steadily from below and sustains a temperature difference  $\Delta T$ , convection will occur when the Rayleigh number (*R*) exceeds 1700 where the Rayleigh number is defined as

$$R = g\Delta T \, d^4 \beta_T / (\eta \, D_T) \, . \tag{3}$$

Here g,  $\beta_T$ , and  $\eta$  are the acceleration of gravity, the coefficient of thermal expansion, and the kinematic viscosity, respectively. Although the He<sup>3</sup> in our calorimeter is heated unsteadily and from all sides, a rough estimate of the Rayleigh numbers encountered during relaxation near  $T_c$  may be made by taking d as half the sample height and  $\Delta T = 5 \times 10^{-6}$  K. Using the same He<sup>3</sup> data cited above, we have estimated Rayleigh numbers to be the following:

t	R
10 <sup>-3</sup>	$5\! imes\!10^5$
10-4	$4\! imes\!10^7$
- 10-4	$3\! imes\!10^6$
$-10^{-3}$	$3 imes 10^4$ .

At such large and rapidly changing values of the Rayleigh number, turbulent convection will occur. Heat transfer may easily be enhanced an order of magnitude over that resulting from thermal diffusivity alone.<sup>16</sup>

Because convection occurs, we are not too surprised that measured relaxation times are much shorter than  $\tau_{\rm thermal}$  in one-phase states. Of course convection is of no help in understanding why relaxation times *exceed*  $\tau_{\rm thermal}$  in two-phase states. This puzzle together with the very large drop in relaxation time at the phase boundary leads

us to ask, "What is the bottleneck to equilibration in two-phase states that is absent in one-phase states?" (Of course the bottleneck could be present in one-phase states if equilibration there involves extremely small temperature changes.) We would like to speculate briefly on the direction an answer to this question might take.

## IS THERE A BOTTLENECK AT THE LIQUID-VAPOR INTERFACE?

We suggest the bottleneck to equilibration of our calorimeter may be diffusion across the liquid-vapor interface (i.e., evaporation or condensation) driven by a chemical-potential difference between the phases. Such a chemical-potential difference could persist for times much longer than  $\tau_{\rm thermal}$  if one of the phases were in a metastable state.

It seems reasonable that diffusion across the interface could become a slow process near the critical point since it is known that the thickness of the interface increases about as rapidly as the correlation length increases near the critical point. (A measurement<sup>17</sup> of the interfacial thickness between components of a binary-liquid mixture near the consolute temperature showed an increase proportional to  $t^{-0.67}$ .)

The persistence of a metastable phase (which is a necessary but not sufficient condition for observation of interphase diffusion) has been demonstrated in our earlier experiments<sup>3</sup> near the critical point of He<sup>3</sup>. Then, we were able to attain "supercooling" of wholly liquid states without the occurrence of nucleated boiling at temperature differences from equilibrium much greater than the temperature differences in the present experiments. We were unable to observe metastability in wholly vapor states. Thus we believe nucleated condensation (perhaps on the walls) is unavoidable.

To set quantitative bounds on the effects of interphase diffusion during equilibration one would need a model of the temperature, pressure, and phase distribution within the sample at the time equilibration begins. Because our measurements are made at times long compared with  $\tau_{\rm thermal}$ , it is reasonable to assume the He<sup>3</sup> sample has a nearly uniform temperature and pressure. Unfortunately there is no way to estimate what proportion of the sample is liquid because of the difficulty in describing the very nonuniform conditions during the heating stage of the experiment. It cannot even be assumed that the proportion of liquid changes monotonically from its initial value to its final value. For example, when there is very little liquid in the calorimeter before heating, there will be even less when equilibrium is finally reached. Nevertheless, condensation probably occurs during the initial moments of the heating stage when a small part of the liquid and/or vapor is warmed

from the calorimeter top and bottom. Because the expansion coefficients of the liquid and vapor are both positive, warming tends to increase the pressure causing condensation at any portion of the interface still at the initial temperature.

Some magnitudes appropriate to the experiment are of interest. The relaxation of a  $5-\mu K$  temperature overshooting at  $t = 5 \times 10^{-3}$  could be achieved by evaporation of 0.0057% of the sample. If the calorimeter contained nearly 100% vapor at t=5 $\times 10^{-3}$ , a 500- $\mu$ K heating interval would result in a net evaporation of 4.6% of the sample, or 820 times as much. If the calorimeter had nearly 100% liquid in it, a 500- $\mu$ K heating interval would result in a net condensation of 6.4% of the sample or 1100 times the evaporation required to account for the overshoot. Thus the slow evaporation of a small amount of liquid (compared with total amount of material which crosses the phase boundary) is all that is required to produce the temperature changes we observe.

We emphasize the speculative nature of these remarks. We have included them primarily because they suggest further experimental and theoretical work to be done. We are now planning to measure evaporation rates directly.

## IMPLICATIONS OF THE DATA

Our data have implications for other experiments regardless of the explanation for the long thermal-relaxation times. First, the data justify the practice of using thermal relaxation times to locate  $T_c$  [by Kierstead, <sup>18</sup> for example] if adequate care is taken [see Fig. 1(a)].

Second, the association of long thermal-relaxation times with the presence of two phases in our calorimeter has led us to reconsider the specificheat and relaxation-time measurements made by Edwards, Lipa, and Buckingham near the critical point of xenon.<sup>2</sup> The xenon measurements were made at a single density in a calorimeter 1 cm high. A computer fit to the  $C_v$  data determined a value of  $T_c$  which fell 35 mK below the temperature of slowest equilibration. We suggest the temperature of slowest equilibration is in fact the critical temperature of xenon in much better agreement with two other measurements<sup>12,19</sup> of  $T_c$ . If this is the case, the sample density must have differed from the critical density. Such a density difference may be the reason the specific-heat exponent found for xenon differs from the exponent found for  $CO_2$  by the same group.<sup>20</sup> (In the case of  $CO_2$ ,  $T_c$ was determined to be much closer to the temperature of slowest equilibration.) We note that by considering gravity effects, Hohenberg and Barmatz have shown<sup>21</sup> that if the mean density of the xenon had been within 5.5% of the critical density, two phases would have coexisted inside the

1-cm-high calorimeter at all temperatures below  $T_c$ .

Finally, our data imply gentle stirring is not likely to hasten equilibration, at least in small samples, since stirring will not alter the interfacial area. The experiments of Chaskin et al.<sup>1</sup> near the critical point of argon seem to confirm this. We also expect copper wire or foil "thermal shorts" will fail to hasten equilibration for the same reason.

Since this paper was initially submitted for publication, the authors have learned that Brown and Meyer<sup>22</sup> have made qualitatively similar observations of thermal relaxation near the critical point of He<sup>3</sup>. Their observations are not as detailed as the present ones and are not made in an apparatus which defines the sample volume and thermalboundary conditions as well as the present one, primarily because they use a horizontal capillary filled with He<sup>3</sup> to lead from the sample volume to a valve at a substantially higher temperature.

\*Work supported in part by the National Science Foundation under Grant No. GP 14431.

<sup>†</sup>Present address: Physics Department, Stanford University, Stanford, Calif. 94305.

<sup>1</sup>Yu. R. Chaskin, A. V. Vornel', V. A. Smirnov, and V. G. Gorbunova, Zh. Eksperim. i Teor. Fiz. 52, 112

(1967) [Sov. Phys. JETP 25, 72 (1967)].

<sup>2</sup>C. Edwards, J. A. Lipa, and M. J. Buckingham, Phys. Rev. Letters 20, 496 (1968).

<sup>3</sup>D. Dahl and M. R. Moldover, Phys. Rev. Letters 27, 1421 (1971).

<sup>4</sup>The volume is found by measuring how much liquid He<sup>4</sup> is required to exactly fill the calorimeter at 1.5 K and using the molar-volume data of E. C. Kerr and R. D. Taylor [Ann. Phys. (N. Y.) 26, 292 (1964)]. The diameter is measured directly. In Ref. 3 the diameter was taken from a shop drawing.

<sup>5</sup>F. Gasparini, Ph.D. thesis (University of Minnesota, 1970) (unpublished).

<sup>6</sup>P. Schofield, J. D. Litster, and J. T. Ho, Phys. Rev. Letters 23, 1098 (1969).

<sup>7</sup>H. Eugene Stanley, Introduction to Phase Transitions and Critical Phenomena (Oxford U. P., Oxford, England, 1971).

<sup>8</sup>B. Wallace, Jr. and H. Meyer, Phys. Rev. A <u>2</u>, 1563 (1970).

Brown and Meyer observe relaxation time in twophase states which exceed by a factor of 2 those we have estimated from thermal diffusivity (when adjusted for their geometry). Brown and Meyer also observe an abrupt drop in  $\tau$  upon entering onephase states, thus their data also show the most puzzling features of the data presented in this paper.

To summarize, we have measured thermal-relaxation times near the critical point of He<sup>3</sup>. The regular features of our data suggest a process involving the interface between liquid and vapor phases is responsible for the unexpectedly long times observed. We suggest this process may be interphase diffusion.

#### ACKNOWLEDGMENTS

The authors would like to thank Professor W. Zimmermann, Jr. for his many stimulating comments. Dr. J. M. H. Levelt Senger has made valuable suggestions which led to improvements of this manuscript.

- <sup>9</sup>J. F. Kerrisk and W. E. Keller, Phys. Rev. 177, 341 (1969).
- <sup>10</sup>K. Kawasaki, Ann. Phys. (N. Y.) <u>61</u>, 1 (1970).
- <sup>11</sup>K. N. Zinov'eva, Zh. Eksperim. i Teor. Fiz. <u>34</u>, 609 (1958) [Sov. Phys. JETP 7, 421 (1958)].

<sup>12</sup>I. W. Smith, M. Giglio, and G. B. Benedek, Phys.

Rev. Letters <u>27</u>, 1556 (1971). <sup>13</sup>B. S. Maccabee and John A. White, Phys. Rev. Letters 27, 495 (1971).

<sup>14</sup>J. V. Sengers and P. H. Keyes, Phys. Rev. Letters 26, 70 (1971). <sup>15</sup>M. Giglio and G. B. Benedek, Phys. Rev. Letters

23, 1145 (1969).
<sup>16</sup>G. E. Willis and J. W. Deardorff, Phys. Fluids <u>10</u>,

1861 (1967).

<sup>17</sup>J. Huang and W. W. Webb, J. Chem. Phys. <u>50</u>,

3677 (1969). <sup>18</sup>H. A. Kierstead, Phys. Rev. A <u>3</u>, 329 (1971).

<sup>19</sup>H. W. Habgood and W. G. Schneider, Can. J. Chem.

32, 98 (1954). <sup>20</sup>J. A. Lipa, C. Edwards, and M. J. Buckingham,

Phys. Rev. Letters 25, 1086 (1970).

<sup>21</sup> P. C. Hohenberg and M. Barmatz, Phys. Rev. A 6, 289 (1972).

<sup>22</sup>G. R. Brown and H. Meyer, Phys. Rev. A <u>6</u>, 364 (1972).

1920