Liquid-to-Gas Phase Transition in Quantum Systems at Zero Temperature*

M. D. Miller

Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

and

L. H. Nosanow

Division of Materials Research, National Science Foundation, Washington, D. C. 20550

and

L. J. Parish

Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

The liquid-to-gas transition at zero temperature in quantum systems obeying both Bose and Fermi statistics is studied. In contrast to well-known systems, the nature of this transition in these quantum systems depends on the statistics in a fundamental way. For Bose systems there is no coexistence region. For Fermi systems there is a range of masses for which there is a coexistence region and a critical mass below which this region disappears.

Ever since Van der Waals's famous work,[1] it has been believed that the essential characteristics of the liquid-to-gas phase transition (e.g., the coexistence curve and the critical point) are determined by two features of the physics. One of these is the attraction between the particles of the system; the other is the exclusion in configuration space due to the strong, short-range repulsion between these particles.[2] As both of these features are "classical" in nature, it has been thought that quantum effects are unimportant in understanding the essential characteristics of condensation and this appears to be the case for all systems considered to date.

In the present work we discuss systems in which quantum effects play a vital role in determining the nature of the liquid-to-gas phase transition. We consider systems composed of bosons or spin-$\frac{1}{2}$ fermions of varying mass at zero temperature. For definiteness, we assume that the pair interaction is of the Lennard-Jones form, although any qualitatively similar potential would yield the same results. For such systems, it is intuitively clear that both liquid and gas phases should, in principle, exist. At zero pressure, a liquid corresponds to a bound state of the whole system, whereas, a gas corresponds to an unbound state. Further, as the particle mass decreases at a fixed density, the kinetic energy increases relative to the magnitude of the potential energy. Thus, there will be a mass small enough to cause the quantum system to become unbound. At zero pressure, the ground state of

the system will be either a liquid or a gas depending on the particle mass, and there will be a liquid-to-gas phase transition at some critical mass.

We find that this liquid-to-gas transition does exist in zero-temperature quantum systems. However, there is a striking difference between the behavior of a system of bosons and that of a system of fermions due to the effects of quantum statistics. In the boson case, there is *no* coexistence region; i.e., the system is either a liquid or a gas. Consequently, when compressed, a Bose system, which is a gas at $T = 0$, will not exhibit a gas-to-liquid transition prior to crystallization. In the fermion case, there does exist a coexistence region for a range of masses. Thus, for a fermion system with an appropriate mass, it is possible for the system to undergo a gas-to-liquid transition at zero temperature with an increase in pressure. Such a transition is clearly analogous to the liquid-to-crystal transition which is well known to occur in helium at zero temperature.[3,4] The coexistence of the liquid and gas phases in the fermion system is caused by the "repulsive" pressure introduced by the Fermi statistics rather than by the aforementioned exclusion in phase space due to the strong, short-range repulsion between particles. Since quantum effects are so important in this liquid-to-gas transition, it seems appropriate to call it a *quantum condensation.*

An illuminating way to view these phase transitions is to utilize the quantum theorem of corresponding states.[5] This theorem states that the

Helmholtz free energy may be written

$$F = N\epsilon\, F^*(T^*, V^*, \eta), \qquad (1)$$

where F^*, the reduced free energy, depends only on reduced temperature $T^* \equiv kT/\epsilon$, the reduced volume $V^* \equiv V/N\sigma^3$, and the quantum parameter $\eta \equiv \hbar^2/m\epsilon\sigma^2$; the form of F^* also depends upon whether the system consists of bosons or fermions. Equation (1) can be derived straightforwardly for any system whose pair potential may be written in the form $v(r) = \epsilon v^*(r/\sigma)$, where ϵ and σ have the dimensions of energy and length, respectively. It is convenient to introduce the reduced pressure $P^* \equiv P\sigma^3/\epsilon$, the reduced density $\rho^* \equiv 1/V^*$, and the reduced energy $E^* \equiv E/N\epsilon$. A more complete discussion of this theorem is given in Ref. 4, where it is pointed out that it is conceptually useful to extend the usual thermodynamic variable space to include η when one studies phase transitions in quantum systems.

We may now consider the ground state of a boson system and, in particular, its dependence on η. The numerical results we will present were obtained from variational calculations using trial wave functions of the Bijl-Jastrow form and the Bogoliubov-Born-Green-Kirkwood-Yvon equation with the Kirkwood superposition approximation.[6] However, the qualitative features of these results are model independent and can be understood in simple terms. It is clear that the equilibrium density will decrease as η increases. Thus, for sufficiently large values of η, it is to be expected that E^* can be expanded in powers of the density ρ^*; i.e.,

$$E_B{}^* = \rho^* B_B(\eta) + \rho^{*2} C_B(\eta) + \dots . \qquad (2)$$

Our calculations show that $B_B(\eta)$ changes sign from negative to positive at a particular value of η, which we call η_{CB}, and $C_B(\eta)$ is positive near η_{CB}. It is a straightforward Landau-theory calculation[7,8] to show that there is a critical density $\rho_{CB}{}^* = 0$ and a critical pressure $P_{CB}{}^* = 0$. Thus, there is a second-order phase transition in η and there are never coexisting liquid and gas phases for the boson system. The detailed numerical calculations yield $\eta_{CB} = 0.45$ and the results are presented in Fig. 1.

The situation for the fermion system is very different from that of the boson system. For fermions the lowest-order term in a density expansion of the energy is clearly the Fermi energy,
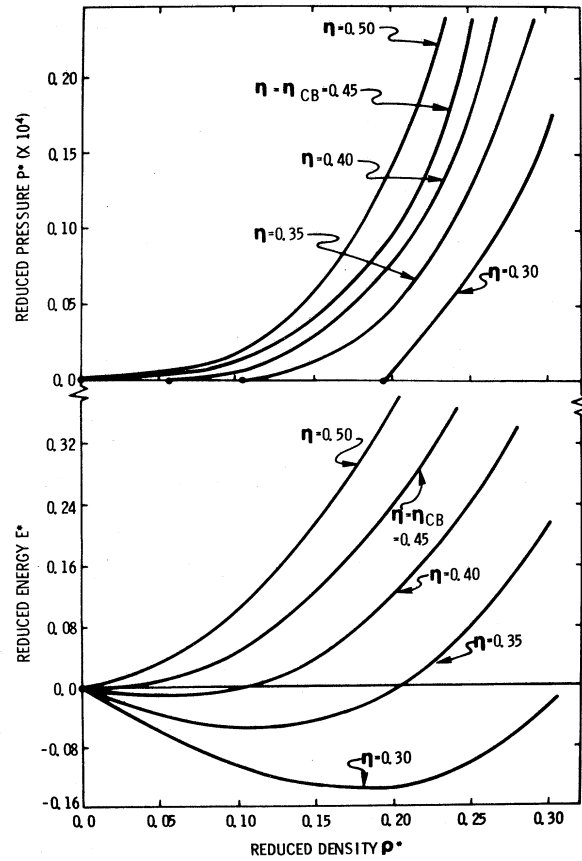

FIG. 1. E^* and P^* as functions of ρ^* for various values of η for boson systems.

so that one may write[9]

$$E_F{}^* = (\rho^*)^{2/3} a\eta + \rho^* B_F(\eta) + \rho^{*2} C_F(\eta)$$
$$+ \rho^{*3} D_F(\eta) + \dots , \qquad (3)$$

where $a = 2.7(\pi/3)^{4/3}$. It is evident that as ρ^* decreases, $E_F{}^*$ always approaches zero through positive values of $E_F{}^*$; this behavior is in marked contrast to that of a boson system. An exact density expansion of $E_F{}^*$ will involve additional powers of the density, but the Fermi energy will still be the lowest-order term and the phase diagram will be essentially the same as for this simple model. Thus, for fermions there will be a value of $\eta = \eta_{LF}$, which is the lowest value of η for which the liquid and gas can coexist. For $\eta_{LF} < \eta < \eta_{CF}$, there will be a Van der Waals–like loop[10] in the P^*-V^* curve and the liquid and gas can coexist. For $\eta > \eta_{CF}$ there is no transition as in the usual case. We have also carried out detailed calculations for the Fermi system. We find $\eta_{LF} = 0.269$,
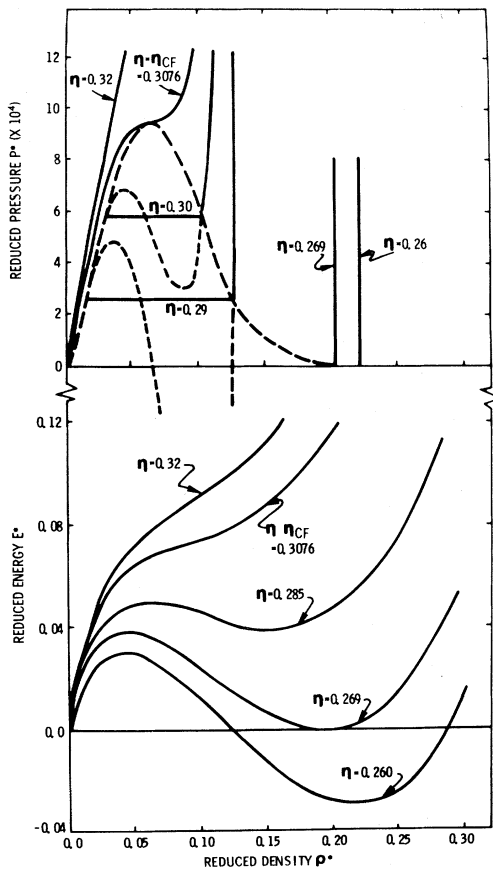
FIG. 2. E^* and P^* as functions of ρ^* for various values of η for fermion systems. The values of P^* in the coexistence region were determined by a Maxwell construction.

$\eta_{CF} = 0.3076$, and the reduced critical pressure $P_c^* = 9.43 \times 10^{-4}$; the results are presented in Fig. 2. In the critical region, Eq. (3) gives an accurate representation of our numerical results.

We wish to conclude this Letter with several comments. (1) In Fig. 3, we give the phase diagram for boson and fermion systems in the P^*-η plane, which clearly shows the qualitative difference between thse two systems. This figure should be compared to Fig. 10 of Ref. 4 and with the usual phase diagram in the P^*-T^* plane.[3] (2) From these results, it is clear that there is a line of critical points in P^*-T^*-η space. We believe that it would be worthwhile to investigate the behavior of the system along this line of critical points, particularly for T^* near zero. (3) We have also considered Fermi systems of reduced dimensionality. It is clear from dimensional arguments that the results we have found require a system of more than two dimensions. (4) In
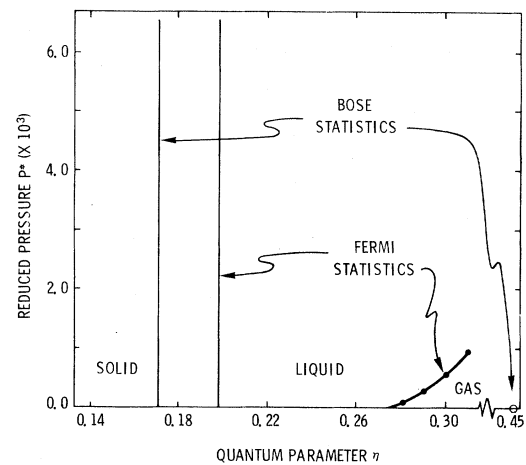

FIG. 3. P^*-η phase diagram at $T = 0$. The coexistence curves for the liquid-to-crystal transition are taken from Ref. 4.

our work, we have neglected the superfluidity of both boson and fermion systems. We believe that this can have only a small effect on our results because the energy differences caused by the superfluidity are small. (5) We also considered the possible effect of including long-range correlations due to zero-point phonons in the boson system. Again we believe that these effects would be quantitatively small and would not change our results qualitatively. (6) It may be that the system of neutrons and protons that is thought to exist in the interior of neutron stars will also have a critical point such as we have found. We believe that it is important to investigate the possible astrophysical consequences of this result.

The authors wish to thank the Department of Physics and Astronomy of the University of Maryland for its kind hospitality during the course of this work. They wish to thank the University of Maryland Computer Science Center for financial assistance. They also wish to acknowledge financial assistance from the University of Florida.

[1]J. D. van der Waals, Ph. D. thesis, University of Leiden, 1873 (unpublished).

[2]For an illuminating discussion of these points, see N. G. van Kampen, Phys. Rev. 135, A362 (1964).

[3]See, e.g., J. Wilks, Liquid and Solid Helium (Clarendon Press, Oxford, England, 1967).

[4]L. H. Nosanow, L. J. Parish, and F. J. Pinski, Phys. Rev. B 11, 191 (1975). The liquid-to-crystal phase transition is extensively discussed in this work.

[5]J. de Boer, Physica (Utrecht) 14, 139 (1948); J. de Boer and B. S. Blaisse, Physica (Utrecht) 14, 149 (1948); J. de Boer and R. J. Lunbeck, Physica (Utrecht) 14, 520 (1948).

[6]For discussions of these calculations and techniques, see, e.g., E. Feenberg, *Theory of Quantum Fluids* (Academic, New York, 1969), and Ref. 4 and references therein.

[7]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1958).

[8]H. E. Stanley, *Introduction to Phase Transitions and* *Critical Phenomena* (Oxford Univ. Press, Oxford, 1971).

[9]Here we are assuming that a cluster expansion has been made to treat the antisymmetrized part of the trial wave function (see Ref. 4); the density dependence would be qualitatively the same if the renormalized Fermi energy were used.

[10]This loop occurs because the trial wave function is assumed to be translationally invariant and would not appear if a more general trial function were used. See Ref. 2.

New Method to Measure Structural Disorder: Application to GeO₂ Glass*

D. E. Sayers and E. A. Stern
Physics Department, University of Washington, Seattle, Washington 98195

and

F. W. Lytle
Boeing Company, Seattle, Washington 98124
(Received 24 March 1975)

A new method is presented for measuring thermal or structural disorder. The additional disorder in the first Ge–O and Ge–Ge distances in amorphous GeO₂ was measured by comparison with crystalline (α-quartz) GeO₂, and showed no additional disorder in the Ge–O distances but deviations in the Ge–Ge distance consistent with a ±6.5° variation about a Ge–O–Ge bond angle of 130°. These results rule out the proposed microcrystalline models.

This Letter introduces a new method to determine the disorder in noncrystalline or crystalline matter. The method follows from an advance in interpreting the extended x-ray-absorption fine-structure (EXAFS) data. The technique is able to measure accurately substantially smaller amounts of disorder than more conventional techniques such as x-ray or neutron scattering. To illustrate the possibilities, GeO₂ glass is studied and the disorder in the first two shells around Ge atoms is determined for the first time as are their average position and the coordination of the first shell. By comparing the disorder in the glass to corresponding values in the crystalline homomorph, it is proved that the microcrystalline model cannot describe the glassy structure.

Previously we have shown[1-3] that Fourier transforms of EXAFS can be interpreted in terms of the local atomic structure about the kind of atom whose edge is being studied. This paper extends the analysis to the measurement of amorphous systems.

Consider the real part of the Fourier transform of EXAFS of both crystalline GeO₂ (α-quartz structure) and amorphous GeO₂ as shown in Fig.

1. The data were taken from the Ge K-edge EXAFS at $T = 77°K$ so that the curves represent the location of atoms about an average Ge atom in the material. The data were normalized so that both curves are on the same (per atom) scale and
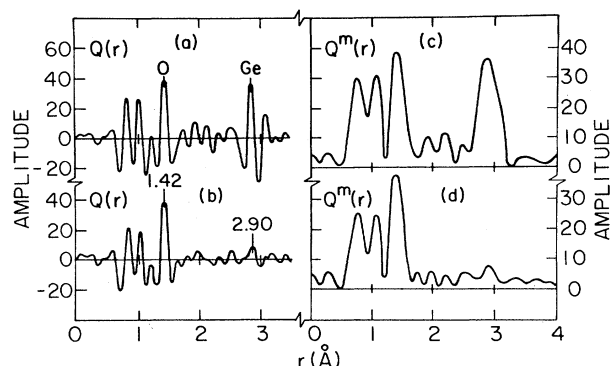
FIG. 1. (a),(b) The real part Q and (c),(d) the magnitude Q^m of the Fourier transform of the Ge edge EXAFS in (a),(c) crystalline (α-quartz) and (b),(d) amorphous GeO₂. The data are normalized to the same scale and transformed over the same interval in k space (2.2–17.5 Å⁻¹).