Zero-temperature properties of matter and the quantum theorem of corresponding states. II. The liquid-to-gas phase transition for Fermi and Bose systems*

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The zero-temperature properties of matter with an interaction pair potential of the Lennard-Jones form are studied further within the context of the quantum theorem of corresponding states. In particular, the phase transition between the liquid and gaseous phases is studied for systems obeying either Bose-Einstein or Fermi-Dirac statistics. In contrast to well-known systems, the nature of this transition in these quantum systems depends on the statistics in a fundamental way. We find that it is illuminating to extend the usual thermodynamic variable space to include the corresponding-states quantum parameter $\eta = \hbar^2/m\epsilon\sigma^2$. It is shown that the phase transition occurs at a value of $\eta = 0.456$. Thus, for Bose systems there is no coexistence region. In sharp contrast, for Fermi systems, there is a range of values of η for which the liquid and gaseous phases can coexist. This coexistence region exists in the range $0.29 \le \eta \le 0.33$. The essential features of the behavior of both Bose and Fermi systems can be understood in terms of simple models. Detailed numerical results are presented for both cases.

I. INTRODUCTION

In a recent paper, Nosanow, Parish, and Pinski¹ (hereafter referred to as NPP) studied the liquid-to-crystal phase transition for zerotemperature quantum systems obeying both Fermi-Dirac and Bose-Einstein statistics. One of the main results of their work was that the solidification pressure P_s depended significantly upon whether the system obeyed Bose-Einstein or Fermi-Dirac statistics. In addition, they found that it was illuminating to view these phase transitions within the context of the quantum theorem of corresponding states (QTCS), originally proposed and discussed by de Boer and $co-workers^{2-4}$ and recently extended⁵ to study ⁶He and possible "new" quantum systems.⁶ NPP found it convenient to conceptually extend the usual thermodynamic variable space to include the quantum parameter η . where

$$\eta \equiv \hbar^2 / m \epsilon \sigma^2 = (\Lambda^* / 2\pi)^2, \qquad (1.1)$$

and Λ^* is the de Boer parameter. They calculated the phase diagram for the liquid-to-crystal phase transition and found it most convenient to plot it in *P*- η space. This result is given in Fig. 10 of NPP, which clearly shows the effect of the "statistics" on the liquid-to-crystal phase transition.

The present work is devoted to a study of the liquid-to-gas phase transition at zero temperature,

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again within the context of the QTCS. A preliminary report of this work has already been published.⁷ As with the liquid-to-crystal transition. we find that the behavior of the system is profoundly affected by the "statistics." That there should be a liquid-to-gas phase transition at zero temperature is not surprising. After all, from an intuitive point of view the quantum parameter η is approximately proportional to the ratio of the average kinetic energy to the magnitude of the average potential energy. Thus, it is intuitively clear that there will be a value of η sufficiently large to cause the ground state of the system to be unbound; i.e., to be a gas at zero temperature and pressure. This state should be contrasted to that of a liquid, which is a bound state of the manybody system at zero temperature and pressure. It is then to be expected that the system will be either a liquid or a gas, depending on the value of η and that there will be a liquid-to-gas phase transition for a special value of η .

We find that this liquid-to-gas transition does, in fact, exist for both Bose and Fermi quantum systems at zero temperature. 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 Sec. IV, we discuss the *Bose* system. In this case, it turns out that there is *no* coexistence region at zero temperature; i.e., the system is *either* a liquid or a gas. Consequently, when compressed, a *Bose* system, which is gaseous at T = 0 will not exhibit a gas-to-liquid transition prior to crystallization. The essential features of the behavior of this system are shown to follow from a simple Landau-like model.

In Sec. V, we discuss the *fermion* system. In this case, we demonstrate that there does exist a liquid-gas coexistence region for a finite range of values of η . Thus, a system of fermions with an appropriate value of η can undergo a gas-to-liquid transition at T = 0 with an increase in pressure. The essential features of the behavior of this system are again shown to follow from a simple Landau-like model. We wish to contrast the condensation that occurs in this Fermi system at T = 0 with the wellknown condensation observed in all other systems. In the latter case, the essential characteristics of the phase transition are determined by two features of the physics.⁸ 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. In the fermion system, we shall show that this second feature is replaced by the "repulsive" pressure caused by the Fermi statistics. Since quantum effects are so important in this liquid-togas transition, it seems appropriate to call it a quantum condensation.

The ground work for discussing the Bose and Fermi systems is laid in Secs. II and III. In the former, we define the QTCS and introduce the system of reduced units for the thermodynamic variables. In the latter, we give the details of the calculation of the energy expectation values. In Sec. VI, we discuss a number of aspects of our results, in particular, their connection with those of perturbation theory for the fermion liquid. In Appendix A, the details of the calculation for the Fermi system are given. In Appendix B, the validity of the approximations used in the calculation of the Bose system are discussed.

II. QUANTUM THEOREM OF CORRESPONDING STATES

The $QTCS^{2-4}$ applies to a class of systems with a pair potential of the form

$$v(r) = \epsilon v^*(r/\sigma) , \qquad (2.1)$$

where ϵ is the coupling constant (with dimensions of energy), σ is a range parameter (with dimensions of length), and $v^*(x)$ is the same dimensionless function of its argument for each member of this class of systems. In this paper, numerical results will be given for systems where $v^*(x)$ may be well approximated by the Lennard-Jones form; i.e.,

$$v^*(x) = 4(x^{-12} - x^{-6}). \tag{2.2}$$

To state the QTCS, it is convenient first to introduce the quantum parameter η defined by Eq. (1.1). We have found it notationally more convenient to use η than the de Boer parameter Λ^* ; they are related by $\eta = (\Lambda^*/2\pi)^2$. Values of η along with values of ϵ , σ , and other useful quantities are given for various substances in Table I. It is further convenient to introduce several dimensionless or "reduced" variables as follows:

$$T^* \equiv k_B T / \epsilon , \qquad (2.3a)$$

$$V^* \equiv V/N\sigma^3 = 1/\rho^*$$
, (2.3b)

$$P^* \equiv P\sigma^3/\epsilon , \qquad (2.3c)$$

$$F^* \equiv F/N\epsilon , \qquad (2.3d)$$

where *T* is the temperature, *V* is the volume, *N* is the number of particles, ρ is the number density, *P* is the pressure, and *F* is the Helmholtz free energy. The QTCS states that, for a onecomponent system.

$$F^* = F^*(T^*, V^*, \eta) , \qquad (2.4)$$

where F^* depends *only* on the form $v^*(x)$ and on whether the particles obey *Bose-Einstein* or *Fermi-Dirac* statistics. A more complete discussion of the QTCS as it relates to the present work can be found in NPP.

III. METHOD OF CALCULATION AND NUMERICAL RESULTS

We consider systems with a Hamiltonian of the form

$$H = \epsilon(\eta t + \omega) , \qquad (3.1)$$

which is defined in Eq. (2.5)-(2.7) of NPP. Using parametrized trial wave functions, we minimize the expectation value of *H* utilizing well-known techniques of McMillan,⁹ Feenberg and co-workers,¹⁰ and Schiff and Verlet.¹¹ We choose our trial wave functions in the usual product form constructed with the necessary symmetry requirements for a Bose (*B*) or Fermi (*F*) system; viz.,

$$\psi_B = \prod_{i < j} e^{-u(r_{ij})/2} , \qquad (3.2)$$

$$\psi_F = \prod_{i < j} e^{-u(r_{ij})/2} A\left(\prod_i e^{i\mathfrak{k}_i \circ \mathfrak{k}_i} \xi_i\right), \qquad (3.3)$$

where $u(r_{ij})$ will be chosen to be a simple, parametrized function necessary to take proper account of the short-range correlations induced by the strong short-range repulsion in v^* , A is the antisymmetrizer and ξ_j are spin functions.

We choose the pair function to have the form

$$u(r) = (b\sigma/r)^5 = (b/x)^5, \qquad (3.4)$$

for both the Bose and Fermi systems. For a pair function with this simple power-law form and a pair potential which is just a sum of simple powers a scaling procedure is available which greatly simplifies the calculation of the minimized energy expectation values. This property was first used by McMillan⁹ in his study of ⁴He and can be simply presented by introducing lengths scaled in units of $b\sigma$; i.e.,

$$R \equiv r/b\sigma = x/b , \qquad (3.5)$$

$$D = \rho \sigma^3 b^3 = \rho^* b^3 \,. \tag{3.6}$$

It is straightforward to show that the averages which one needs in order to calculate the reduced energy E^* are functions of D (and the particular statistics) only. Thus the energy can be written in the simple form¹²

$$E_{X}^{*}(\rho^{*},\eta;b) = \eta b^{-2} \langle t/N \rangle_{D,X} + 4b^{-12} \langle R^{-12} \rangle_{D,X} - 4b^{-6} \langle R^{-6} \rangle_{D,X}, \qquad (3.7)$$

and X stands for Bose or Fermi. The brackets represent averages defined by

$$\langle R^{-n} \rangle_{D,X} = \frac{1}{2} D \int g_x(R;D) R^{-n} d\vec{\mathbf{R}}$$
 (3.8)

and

$$\left\langle \frac{t}{N} \right\rangle_{D,X} = -\frac{1}{2N} \sum_{i=1}^{N} \left(\int \psi_x^* \nabla_i^2 \psi_x \, d\vec{\mathbf{R}}^N \right) \left(\int |\psi_x|^2 \, d\vec{\mathbf{R}}^N \right)^{-1}$$
(3.9)

The $g_x(R; D)$ are Bose or Fermi radial distribution functions defined by

$$g_{x}(R_{12};D) = \frac{N(N-1)}{D^{2}} \left(\int |\psi_{x}|^{2} dR_{3}, \dots, d\vec{\mathbf{R}}_{N} \right) \left(\int |\psi_{x}|^{2} d\vec{\mathbf{R}}^{N} \right)^{-1}.$$
(3.10)

For the case of Bose statistics Eq. (3.9) reduces to $5\langle R^{-7}\rangle_{D,B}$. The spin-averaged fermion radial distribution function and the fermion kinetic energy are calculated approximately using the statistical cluster expansion of Wu and Feenberg.¹³ Thus, for $g_F(R;D)$ we have

$$g_F(R_{12};D) = g_B(R_{12};D) \left[1 + F^{(2)}(R_{12}) + F^{(3)}(R_{12};D) + \cdots \right], \qquad (3.11)$$

where

$$F^{(2)}(R_{12}) = -\frac{1}{2}l^2(Y_{12}), \qquad (3.12)$$

$$F^{(3)}(R_{12};D) = -D \int g_B(R_{23};D)h(R_{13};D)l^2(Y_{23}) d\vec{\mathbf{R}}_3 + \frac{1}{2}Dl(Y_{12}) \int g_B(R_{23};D)h(R_{13};D)l(Y_{13})l(Y_{23}) d\vec{\mathbf{R}}_3, \qquad (3.13)$$

and we have defined the following quantities:

$$h(r) \equiv g_{\mathcal{B}}(R) - 1 , \qquad (3.14)$$

$$l(Y) = 3[\sin(Y) - Y\cos(Y)]/Y^3, \qquad (3.15)$$

$$Y \equiv k_D R , \qquad (3.16)$$

and

$$k_{p} \equiv (3\pi^{2}D)^{1/3} \,. \tag{3.17}$$

The *n*th term in (3.11) represents the contribution to $g_F(R)$ coming from *n*-particle exchange in the Slater determinant of ψ_F . We truncate the series after the *n*=3 term in g_F . In order to evaluate $F^{(3)}$, the Kirkwood superposition approximation (KSA) has been used for the three-particle distribution function; i.e.,

$$P_{\text{KSA}}^{(3)}(1,2,3;D) = D^3 g_B(R_{12}) g_B(R_{23}) g_B(R_{31})$$
. (3.18)

The power form for u(R) thus allows all of the energy expectation values to be obtained from the calculation of a *single* set of $g_B(R)$'s as functions of *D* only. These can then be used at any density with a variational parameter *b* given by Eq. (3.6).

The fermion kinetic energy can be written

$$\langle t/N \rangle_{D,F} = 5 \langle R^{-7} \rangle_{D,F} + E_{1F} + E_{2F} + E_{3F} + \cdots ,$$
(3.19)

where

$$E_{1F} = \frac{3}{10} k_D^2 , \qquad (3.20)$$

$$E_{2F} = 20E_{1F} \int_0^1 u(2k_D x)(1 - \frac{3}{2}x + \frac{1}{2}x^3)x^4 dx , \quad (3.21)$$

$$\begin{split} E_{3F} &= -\frac{5}{6} E_{1F} \left(\frac{3}{8\pi}\right)^3 \int x_{12}^2 S(x_{12}k_D) u(x_{23}k_D) \\ & \times u(x_{13}k_D) \, d\vec{\mathbf{x}}_1 \, d\vec{\mathbf{x}}_2 \, d\vec{\mathbf{x}}_3 \, , \end{split}$$

and

$$u(k) = S(k) - 1 = D \int e^{i\vec{k}\cdot\vec{R}}h(R) dR . \qquad (3.23)$$

(3.22)

To evaluate the E_{3F} term, we used the convolution approximation for the three-particle distribution function; i.e.,

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TABLE I. Quantum parameter η for various substances. Also included are the masses (in amu, i.e., $1.660\ 24 \times 10^{-24}$ g), the coupling constants ϵ (in K, $k_B = 1.380\ 54 \times 10^{-16}$ erg/particle K), the "core diameters" σ (in Å), and the quantities ϵ/σ^3 (in atm) and $N_0\sigma^3$ (in cm³/mole). We use $\hbar = 1.054\ 50 \times 10^{-27}$ erg sec and $N_0 = 6.022\ 52 \times 10^{23}$ particle/mole.

Substance	m	E	σ	ϵ/σ^3	$N_0\sigma^3$	η
³ He	3.016	10.22	2,556	83.39	10.06	0.2409
⁴ He	4.003	10.22	2.556	83.39	10.06	0.1815
⁶ He	6.019	10.22	2.556	83.39	10.06	0.1207
H_2	2.016	37.0	2.92	202.48	14.99	0.0763
\mathbf{D}_2	4.028	37.0	2.92	202.48	14.99	0.0382
Ne	20.18	35.6	2.74	235.79	12.39	0.0085
Ar	39.95	120	3.41	412.33	23.88	0.00088

$$P^{(3)}(1,2,2;D) = D^{3} \left(1 + h(R_{12}) + h(R_{23}) + h(R_{31}) + h(R_{12})h(R_{23}) + h(R_{23})h(R_{31}) + h(R_{31})h(R_{12}) + D \int h(R_{14})h(R_{24})h(R_{34}) d\vec{\mathbf{R}}_{4} \right).$$
(3.24)

A quadratic approximation for S(k) was employed in order to evaluate the E_{3F} term.^{13,14} The boson g(R)'s were obtained by solution of the Bogoliubov-Born-Green-Kirkwood-Yvon equation¹⁵

$$\vec{\nabla}_{1}g(R_{12}) = \vec{\nabla}_{1}u(R_{12})g(R_{12}) + D \int \left(\frac{P^{(3)}(1,2,3)}{D^{3}}\right)\vec{\nabla}_{1}u(R_{13}) d\vec{R}_{3}, \qquad (3.25)$$

with the KSA approximation for the three-particle distribution function. The details of the solution of this equation and the convergence of the statistical cluster expansion will be reported else-where.¹⁶

In Table II we show the Bose and Fermi averages as defined in Eqs. (3.8) and (3.9) as functions of *D*. We note that they are smooth and monotonic and relatively slowly varying over a large range in *D*. We can thus fit these averages with cubic polynomials in *D* rather accurately and obtain relatively simple expressions for the Bose and Fermi energies as explicit functions of ρ^* , η , and *b*. In subsequent sections, we will obtain the equations of state and the critical parameters by analyzing the polynomials which have been obtained in this way.

The polynomial coefficients are defined as follows:

$$\left\langle \frac{t}{N} \right\rangle_{D,X} \equiv \alpha_{0,X} D^{2/3} + \sum_{i=1}^{3} \alpha_{i,X} D^{i}, \qquad (3.26a)$$

$$\langle R^{-6} \rangle_{D,X} \equiv \sum_{i=1}^{3} \beta_{i,X} D^{i}, \qquad (3.26b)$$

$$\langle R^{-12} \rangle_{D,X} \equiv \sum_{i=1}^{3} \gamma_{i,X} D^{i} , \qquad (3.26c)$$

with

$$\alpha_{0,X} = \begin{cases} 2.7(\frac{1}{3}\pi)^{4/3}, & X = F \\ 0, & X = B. \end{cases}$$
(3.27)

We have separated off the fermion independentparticle average kinetic energy in Eq. (3.26a) because that term is independent of b. The α , β , and γ coefficients are displayed in Table III and were obtained by means of a Chebyshev curve fit.¹⁷ In Table IV we show a comparison of the calculated and curve-fit energies at the arbitrary density $\rho^* = 1.0$. The root-mean-square fractional difference is 0.001 19 for the bosons and 0.008 29 for the fermions. The maximum percentage error is 0.24% for the bosons at D = 0.02 and 2.15% for the fermions at D = 0.02. These curve fits thus yield a good representation of the data and are quite adequate for our purposes.

IV. BOSE SYSTEM

In this section we shall analyze the liquid-to-gas transition in a Bose system at zero temperature.

				10 2		
D	$\langle t/N \rangle_F^+$	$\langle R^{-6} \rangle_F$	$\langle R^{-12} \rangle_F$	$\left< t/N \right>_B$	$\langle R^{-6} \rangle_B$	$\langle R^{-12} \rangle_B$
0.020	0.09106	0.02584	0.01472	0.15243	0.03878	0.02472
0.040	0.205 03	0.058 57	0.03353	0.31715	0.08024	0.05217
0.060	0.33680	0.09581	0.05572	0.49423	0.12434	0.08247
0.080	0.48442	0.13678	0.08112	0.68372	0.17107	0.11578
0.100	0.64633	0.180 89	0.109 65	0.88428	0.22003	0.15197
0.120	0.82290	0.22823	0.14145	1.09837	0.27183	0.19160
0.140	1.01330	0.27850	0.17654	1.32502	0.32619	0.23463
0.160	1.21727	0.331 58	0.21503	1.56426	0.38306	0.28118
0.180	1.43463	0.387 39	0.25700	1.81614	0.44245	0.33140
0.200	1.66529	0.44586	0.30258	2.08068	0.50432	0.38541
0.225	1.97216	0.52263	0.36478	2.42917	0.58512	0.45844
0.250	2.29957	0.60339	0.43302	2.79748	0.66972	0.53783
0.275	2.64741	0.688 09	0.507 50	3.18562	0.75808	0.62380
0.300	3.015 61	0.77666	0.58846	3.59356	0.85017	0.71658
0.325	3.40412	0.869 05	0.67611	4.02128	0.94593	0.816 39
0.350	3.81284	0.96520	0.77067	4.46872	1.04533	0.92341
0.375	4.24172	1.06507	0.87234	4.93583	1.14831	1.03785
0.400	4.69066	1.16862	0.981 31	5.42253	1.25484	1.15989
0.425	5.159 58	1.27578	1.097 78	5.92871	1.36487	1.28970
0.450	5.64839	1.38653	1.22191	6.45426	1.47834	1.42741
0.475	6.15699	1.500 81	1.35389	6.99907	1.59523	1.57319
0.500	6.68525	1.61858	1.49385	7.56297	1.71546	1.72713

TABLE II. Components of E^* as functions of D for both Bose and Fermi systems. The averages are defined in Eqs. (3.8) and (3.9); $\langle t/N \rangle_F^F = \langle t/N \rangle_F + \frac{3}{10} k_D^2$.

We shall begin by using the expression for the energy in terms of the cubic polynomial fits given in Sec. III. It is particularly illuminating to view the properties of this system as a function of η ; thus, we shall adopt the point of view of NPP and regard η as a conceptual thermodynamic variable and extend the space of thermodynamic variables to include η . We shall then show that the Bose system, viewed as a function of η , undergoes a second-order phase transition from liquid to gas at a critical value of $\eta = \eta_{CB} = 0.45576$; whereas, there is no liquid-to-gas transition as a function of P^* . We analyze the system further and show that these results are general and do not depend on the details of our calculation. We wish to mention the recent work of Bruch,¹⁸ who has viewed the transition in terms of the self-binding of the many-body Bose system and has developed a differential equation to obtain η_{CB} . His results confirm those we have obtained.

Using the results from Sec. III and, in particular, Eqs. (3.7) and (3.26), we may write the reduced ground-state energy for a Bose system as

$$E_{B}^{*}(\rho^{*},\eta;b) = \sum_{n=1}^{3} D^{n}(\eta b^{-2}\alpha_{n} - 4b^{-6}\beta_{n} + 4b^{-12}\gamma_{n}) ,$$
(4.1)

where in this section α_n , β_n , and γ_n will only be

those for Bose systems. We note that (4.1) is *not* a cubic polynomial in ρ^* since *b* also depends on ρ^* (and η as well). It follows straightforwardly that the pressure is given by

$$P^* = \rho^* \sum_{n=1}^{3} n D^n (\eta b^{-2} \alpha_n - 4b^{-6} \beta_n + 4b^{-12} \gamma_n) .$$
 (4.2)

Further, the variational parameter b is determined by

$$\left(\frac{\partial E^*}{\partial b}\right)_{\rho^*,\eta} = 0 = \rho^* \sum_{n=1}^3 D^{n-1} \left[(3n-2)\eta \alpha_n - 12(n-2)b^{-4}\beta_n + 12(n-4)b^{-10}\gamma_n \right].$$
(4.3)

TABLE III. Coefficients for the polynomial fits to the averages given in Table II. They are defined by Eqs. (3.26a)-(3.26c).

Coefficient	Bosons	Fermions
α_1	7.30454	4.21592
α_2	15.41506	22.34303
$lpha_3^-$	0.48871	-8.49248
β_1	1.87417	1.22160
$\hat{\beta_2}$	3.31725	5.84436
β_3	-0.40845	-3.806 37
γ_1	1.16610	0.67201
γ_2	3.30476	3.977 93
γ_3^-	2.55491	1.24357

Ь	E_B (cale)	E_{B} (fit)	Δ_B	E_F (calc)	E_{F} (fit)	Δ_{F}
0.2714	617695	616 223	0.238	367 861	375768	2.149
0.3420	81315.8	81 200.8	0.141	52244.7	51 929.3	-0.603
0.3915	25320.2	25301.8	0.072	17095.1	16848.5	-1.442
0.4309	11203.3	11200.2	0.027	7842.12	7720.63	-1.549
0.4642	5994.95	6004.54	-0.159	4319.43	4264.05	-1.282
0.4932	3624.98	3631.43	-0.177	2671.39	2645.95	-0.952
0.5192	2381.35	2385.62	-0.179	1788.03	1777.40	-0.594
0.5429	1661.66	1664.46	-0.168	1267.62	1264.40	-0.254
0.5646	1213.85	1215.64	-0.147	938.834	939.230	0.042
0.5848	919.182	920.285	-0.120	719.604	721.654	0.284
0.6082	675.844	676.380	-0.079	536.242	538.962	0.507
0.6300	514.925	515.106	-0.035	413.458	416.113	0.642
0.6503	403.727	403.694	0.008	327.686	329,974	0.698
0.6694	324.102	323.947	0.047	265.681	267.505	0.686
0.6875	265.384	265.170	0.080	219.570	220.934	0.621
0.7047	221.005	220.776	0.103	184.458	185.409	0.515
0.7211	186.757	186.543	0.114	157.182	157.782	0.381
0.7368	159.851	159.675	0.109	135.626	135.942	0.233
0.7518	138.384	138.263	0.087	118.338	118.436	0.082
0.7663	121.028	120.972	0.045	104.295	104.233	-0.059
0.7802	106.829	106.849	-0.018	92,7597	92.5902	-0.182
0.7937	95.0945	95.1973	-0.108	83.1923	82,9612	-0.277

TABLE IV. Comparison of the fitted and calculated energies at $\rho *=1.0$. At this density, $D = b^3$. Further $\Delta_{B(F)} \equiv 100[E_{B(F)}(\text{calc}) - E_{B(F)}(\text{fit})]/E_{B(F)}(\text{calc})$.

Substitution of the solution of (4.3) and (4.1) and (4.2) yields the plots of E^* vs ρ^* , P^* vs ρ^* , and ρ^* vs η shown, respectively, on Figs. 1-3.

We note that for $\eta < \eta_{CB}$, there will exist a density ρ_L^* at which the system is self-bound (negative energy at zero pressure). As η is increased ρ_L^* decreases until η_{CB} is reached at which point ρ_L^* $= \rho_{CB}^* = 0.0$. This behavior is clearly shown in Fig. 3 by following the $P^* = 0.0$ isobar. For those $\eta > \eta_{CB}$ there are no zero-pressure solutions (with nonzero density); thus, the system is a gas since it is unbound at every density. Thus, when viewed as a function of η , a liquid-to-gas transition occurs at $\eta_{CB}.$ On Fig. 4, the reduced ground-state energy is given as a function of η (this graph should be compared with Fig. 5 of NPP) and clearly shows the liqud-to-crystal and liquid-to-gas transitions for both Bose and Fermi systems. This behavior is further illuminated on the $P^*-\eta$ phase diagram given in Fig. 5 (this figure should be compared with Fig. 10 of NPP).

The equations for the pressure (4.2) and the optimal variational parameter (4.3) can be used to determine η_{CB} . Below η_{CB} there are three solutions for $P^* = 0.0$; there is a trivial double root at $\rho^* = 0.0$ and a simple root at ρ_L^* . The confluence of these three roots determines η_{CB} . Then, since $\rho_{CB}^* = 0.0$, Eqs. (4.2) and (4.3) yield

$$\eta_{CB}\alpha_1 b_c - 4\beta_1 b_c^{-3} + 4\gamma_1 b_c^{-9} = 0 , \qquad (4.4)$$



FIG. 1. Reduced energy E^* as a function of the reduced density ρ^* for systems obeying Bose-Einstein statistics. The arrows locate the positions of the energy minima.



FIG. 2. Reduced pressure P^* as a function of the reduced density ρ^* for systems obeying Bose-Einstein statistics.

$$\eta_{CB}\alpha_1 b_c + 12\beta_1 b_c^{-3} - 36\gamma_1 b_c^{-9} = 0.$$
(4.5)

Solving Eqs. (4.4) and (4.5) simultaneously, we obtain the critical quantities

$$b_c^6 = \frac{5}{2}(\gamma_1/\beta_1) , \qquad (4.6)$$

$$\eta_{CB} = \frac{24}{25} (\beta_1^2 / \alpha_1 \gamma_1) b_c^2 \,. \tag{4.7}$$

Instead of immediately substituting the curve-fit coefficients from Table III into Eqs. (4.6) and (4.7), we note that in the zero-density limit, we can calculate α_1 , β_1 , and γ_1 exactly using the pair function of Eq. (3.4). We find

$$\alpha_1 = \frac{5}{2} \int e^{-R^{-5}} R^{-7} \, d\vec{\mathbf{R}} = \frac{5}{2} \pi \Gamma(\frac{9}{5}) = 7.315\,07 \,, \qquad (4.8)$$

$$\beta_1 = \frac{1}{2} \int e^{-R^{-5}} R^{-6} \, d\vec{\mathbf{R}} = \frac{2}{3} \pi \Gamma(\frac{8}{5}) = 1.871\,37 \,, \qquad (4.9)$$

$$\gamma_1 = \frac{1}{2} \int e^{-R^{-5}} R^{-12} \, d\vec{\mathbf{R}} = \frac{2}{5} \, \pi \Gamma(\frac{9}{5}) = 1.17041 \,, \tag{4.10}$$

where these follow from Eqs. (3.8) and (3.9) in the low-density limit, in which case $g(r) \rightarrow e^{-u(R)}$. The coefficients of Eqs. (4.8)–(4.10) yield

$$b_c = 1.07734$$
 (4.11)

and

$$\eta_{CB} = 0.455\,76\,. \tag{4.12}$$

The coefficients α_1 , β_1 , and γ_1 given above are in extremely good agreement with the curve-fit results of Table III. Equations (4.6) and (4.7) are special cases of a pair of equations valid for the exact eigenfunction.

At η_{CB} the energy is zero; thus, we may write



FIG. 3. Reduced density ρ^* as a function of the quantum parameter η for Bose-Einstein systems. The arrows locate the points at which $E^*=0.0$. Only the zero-pressure curve has a zero density intercept at η_{CB} .

$$\eta_{CB}\phi + \epsilon_{12} - \epsilon_6 = 0, \qquad (4.13)$$

where $\epsilon_{12}(\epsilon_6)$ is the repulsive (attractive) part of the potential energy. Following NPP, we write

$$\phi \equiv \left(\frac{\partial E^*}{\partial \eta}\right)_{V^*, N} = \frac{\langle K \rangle}{\eta} , \qquad (4.14)$$

where ϕ is the "thermodynamic" variable conjugate to η , and K is the kinetic-energy part of the Hamiltonian. Using (4.14), we obtain a second relationship from the virial theorem¹⁰ at zero pressure; i.e.,

$$\eta_{CB}\phi + 6\epsilon_{12} - 3\epsilon_6 = 0. \tag{4.15}$$

Combining Eqs. (4.13) and (4.15), we find the equations corresponding to (4.6) and (4.7); i.e.,

$$\epsilon_6/\epsilon_{12} = \frac{5}{2}, \qquad (4.16)$$

$$\eta_{CB} = \frac{3}{5} (\epsilon_6 / \phi) . \tag{4.17}$$

It is convenient to discuss the nature of the phase transition in terms of ϕ . In particular, we shall show that ϕ is continuous at η_{CB} ; whereas $\partial \phi / \partial \eta$ is not. This behavior is the signature of a second-order phase transition in the traditional Ehrenfest sense.¹⁹ The transition is most simply analyzed by writing the energy in the usual Landau form for a second-order phase transition with the square root of the density as the order parameter. Thus, from Eq. (4.1),

$$E_B^* = A_1(\eta)\rho^* + A_2(\eta)\rho^{*2}, \qquad (4.18)$$



FIG. 4. Reduced energy E^* at zero pressure as a function of the quantum parameter η . The zero-energy intercepts η_{LF} for the Fermi fluid and η_{CB} for the Bose fluid, are shown. These fluid branches meet the crystal-line curve (from NPP) with a definite change in slope indicating a first-order phase transition at a critical value of η which depends upon statistics.

where

$$A_{i}(\eta) = \eta b \alpha_{i} - 4b^{-3}\beta_{i} + 4b^{-9}\gamma_{i}. \qquad (4.19)$$

i=1,2 and b is calculated by minimizing the energy at a given η and ρ^* . Since $\rho^*_{CB} = 0.0$, we can neglect the cubic term in Eq. (4.1). At zero pressure we find

$$\rho_L^* = -A_1 / 2A_2, \qquad (4.20)$$

$$E_{B}^{*} = -(A_{1}^{2}/4A_{2}), \qquad (4.21)$$

For $\eta < \eta_{CB}, A_2(\eta) > 0$ since we have a bound state at ρ_L^* and $A_1(\eta) < 0$ for a positive density. For $\eta > \eta_{CB}$ the only solution to $P^* = 0.0$ is ρ_{CB}^* .

From the definition of ϕ given by (4.14) and (4.18), we have (the primes denote derivitives with respect to η) for $\eta < \eta_{CB}$

$$\phi^{\prime} = A_1 \left[-(A_1^{\prime}/2A_2) + (A_1A_2^{\prime}/4A_2^2) \right].$$
 (4.22a)

Now for $\eta > \eta_{CB}$, $\rho_L^* = 0$ and

$$\phi^{>} = 0.0$$
. (4.22b)

Since A_1 vanishes at the critical point, it follows that ϕ is continuous at η_{CB} . By further differentiation

$$\lim_{\eta \to \eta_{CB}} \frac{\partial \phi^{<}}{\partial \eta} = -\frac{1}{2} \frac{A_1^{\prime 2}}{A_2} , \qquad (4.23a)$$



FIG. 5. $P^*-\eta$ phase diagram at $T^*=0$. The coexistence curves for the liquid-to-crystal transition are taken from NPP.

$$\frac{\partial \phi^{>}}{\partial \eta} = 0. \qquad (4.23b)$$

Therefore the second derivative of the energy with respect to η has a discontinuity of magnitude Δ , given by

$$\Delta = \left| (A_1')^2 / 2A_2 \right| = 6.547 , \qquad (4.24)$$

where the coefficients from Table III have been used. In Fig. 6 we show E, $\partial E/\partial \eta$, and $\partial^2 E/\partial \eta^2$ as functions of η . In Fig. 7 we show the average kinetic energy, the magnitude of the average potential energy and their ratio at $P^* = 0.0$. We see that the *slopes* of the kinetic and potential energies change discontinuously at η_{CB} but in an equal and opposite manner to insure that the slope of the total energy ϕ is continuous. This is immediately evident by noting that, since $\phi(\eta_{CB}) = 0$

$$\phi(\eta_{CB}) \equiv \left(\frac{\partial E^*}{\partial \eta}\right)_{\eta_{CB}} = 0 ,$$

which implies

$$\frac{\partial \langle K \rangle}{\partial \eta_{CB}} = -\frac{\partial \langle V \rangle}{\partial \eta_{CB}} . \tag{4.25}$$

The ratio of the kinetic and potential energies, of course, goes to unity as $\eta \rightarrow \eta_{CB}$, and it is interesting to note that the curve is linear near η_{CB} . This is due to the fact that, in the range of η shown in Fig. 6, the equilibrium density ρ_L^* is relatively small (as seen in Fig. 3). Thus, *b* is only weakly dependent on η and the only important dependence is the explicit η dependence in $\langle K \rangle$. This behavior changes somewhat as η gets smaller (disregarding for the moment the solid phase) since the kinetic energy vanishes as $\eta \rightarrow 0$.



FIG. 6. Reduced energy E^* at zero pressure as a function of η together with its first and second derivatives. At η_{CB} the second derivative is discontinuous, signalling a second-order phase transition.

V. FERMI SYSTEM

In this section, we analyze the results for systems which obey *Fermi statistics* in a manner analogous to the analysis of the *Bose* systems in Sec. IV. Once more we treat η as a conceptual thermodynamic parameter and find a liquid-gas transition as η is varied. For Fermi particles, however, we find a first-order transition with coexisting liquid and gas phases and a critical point at a value of $\eta = \eta_{CF}$! This is illustrated on the E^* -vs- η and P^* -vs- η diagrams plotted on Figs. 4 and 5, respectively.

In terms of the cubic polynomials of Eq. (3.2), the reduced energy and pressure can be written

$$E_F^*(\rho^*,\eta;b) = E_{1F}^* + \sum_{n=1}^3 D^n (\eta b^{-2} \alpha_n - 4b^{-6} \beta_n + 4b^{-12} \gamma_n) ,$$
(5.1)

$$P_{F}^{*} = P_{1F}^{*} + \rho^{*} \sum_{n=1}^{3} D^{n} (\eta b^{-2} \alpha_{n} - 4b^{-6} \beta_{n} + 4b^{-12} \alpha_{n}) ,$$
(5.2)

where



FIG. 7. Reduced kinetic and potential energies at zero pressure as a function of η . At η_{CB} , although differing in sign, each has an equal magnitude and the same discontinuity in its slope; thus, ϕ is continuous at η_{CB} (cf., Fig. 6).

$$E_{1F}^{*} \equiv \eta E_{1F} / b^{2} , \qquad (5.3)$$

$$P_{1F}^{*} = \frac{2}{3} \rho^{*} E_{1F}^{*} , \qquad (5.4)$$

and E_{1F} is defined in Eq. (3.20). The coefficients used in this section will refer to the Fermi system. The minimization of E_F^* with respect to *b* once more yields Eq. (4.3) since E_{1F}^* is independent of *b*. For each choice of ρ^* and η there are two real positive roots to Eq. (4.3). That is, in addition to a local minimum, there is a maximum associated with the minus sign of α_3 . The energy and pressure as functions of density and volume obtained from solving Eqs. (5.1)–(5.4) are shown in Figs. 8–11.

If we examine the fermion energy curves, Figs. 8 and 10, we see that for small enough η there exists a density ρ_L^* for which the system is selfbound. If we increase η , we find that ρ_L^* increases, as shown in Fig. 12. At $\eta = \eta_{LF}$ there are two zeroenergy, zero-pressure solutions. One at $\rho^* = 0.0$ may be interpreted as a gas phase, as in the Boson case, the other at $\rho_{LF}^* \neq 0$ is novel to the fermion system and represents the liquid phase. Thus η_{LF} is the lowest value of η for which there are coexisting liquid and gas phases. We note that Eqs. (4.16) and (4.17) are also valid at this point. If we denote the fermion critical η by η_{CF} , then we find typical van der Waals loops in the pressure



FIG. 8. Reduced energy as a function of the reduced volume for a system obeying Fermi-Dirac statistics.

curves (cf. Figs. 9 and 11) for those η in the range $[\eta_{LF}, \eta_{CF}]$. The coexistence region and the condensation pressures may be determined by the Maxwell construction.

The "looping" in E^* as a function of ρ^* (or V^*) is due entirely to the $\rho^{2/3}$ density dependence of the E_{1F}^* term. If this term were omitted, the resultant energy $E_F^* - E_{1F}^*$ would have the same general shape and behavior as the boson energy. This behavior is shown clearly in Fig. 13, where we plot E_F^* , E_B^* , and $E_F^* - E_{1F}^*$ as functions of ρ^* for an arbitrary η in the coexistence region. Indeed, the lowdensity behavior of the fermion system is dominated by E_{1F}^* . There are, of course, two- and three-body exchange contributions to E_F^* and it is worthwhile to note their effect. These higher-pow-



FIG. 9. Reduced pressure P^* as a function of the reduced volume for a system obeying Fermi-Dirac statis- \cdot tics. The coexistence pressures are calculated by a Maxwell construction.



FIG. 10. Reduced energy as a function of the reduced density for a system obeying Fermi-Dirac statistics. It is evident that at low densities the E_{1F}^* term dominates the total energy.

er terms have been absorbed into the coefficients by the Chebyshev curve fit. Their presence is signaled by the fact that the mean-square fractional deviation between the fitted and calculated energies at $\rho^* = 1.0$, as shown in Table IV, is a factor of 7 larger for the Fermi system than the Bose system. We also wish to point out the difference in sign for the α_3 coefficient in the Bose and Fermi cases.

The details of the calculation of the properties of the Fermi system using Eqs. (5.1)-(5.4) are



FIG. 11. Reduced pressure as a function of the reduced density for a system obeying Fermi-Dirac statistics.



FIG. 12. Reduced density as a function of the quantum parameter η for a Fermi-Dirac system. The arrows locate the points where $E^* = 0.0$.

fairly complicated and are, therefore, given in Appendix A. The essential features of the "physics" can be obtained from a simple model as in the Bose case. In this simple model the reduced energy is taken to be

$$E_F^* = \alpha_{0F} \eta \rho^{*2/3} + A_1(\eta) \rho^* + A_2(\eta) \rho^{*2} , \qquad (5.5)$$

where

$$A_{i}(\eta) = \eta A_{i1} - A_{i2}, \qquad (5.6)$$

where i, j=1, 2 and $A_{ij} > 0$. Since the critical density turns out to be finite in this case, unlike the Bose case, this model can not lead to quantitative results. Nevertheless, it does exhibit all of the essential physical features of the system.

By definition along η_{LF} we have

$$E_F^* = 0 = P_F^*, (5.7)$$

which with (5.5) yields

$$\alpha_0 \eta_{LF} \rho_{LF}^{*2/3} + A_1(\eta_{LF}) \rho_{LF}^* + A_2(\eta_{LF}) \rho_{CF}^{*2} = 0 , \quad (5.8)$$

$$\frac{2}{3}\alpha_0\eta_{LF}\rho_{LF}^{*5/3} + A_1(\eta_{LF})\rho_{LF}^{*2} + 2A_2(\eta_{LF})\rho_{LF}^{*3} = 0.$$
(5.9)

Solving these equations, we find

$$\rho_{LE}^* = -A_1(\eta_{LE})/4A_2(\eta_{LE}), \qquad (5.10)$$

$$3 |A_1|^{4/3} = 4^{4/3} \alpha_0 \eta_{LF} A_2^{1/3}(\eta_{LF}) , \qquad (5.11)$$

where (5.11) determines η_{LF} , which with (5.10) determines ρ_{LF}^{*} . We note that $A_1 < 0$.

To calculate the properties at the critical point,



FIG. 13. Reduced Fermion energy, the reduced boson energy, and the fermion energy minus the E_{T}^* part as a function of the reduced density at an arbitrary η (=0.30) in the coexistence region. This illustrates that the looping is due entirely to the E_{LF}^* contribution to the energy.

we note that this point is determined by the conditions

$$\left(\frac{\partial P^*}{\partial V^*}\right)_{\eta} = 0 = \left(\frac{\partial^2 P^*}{\partial V^{*2}}\right)_{\eta}, \qquad (5.12)$$

which with (5.5) yield

$$-\frac{10}{9}\alpha_0\eta_{CF}\rho_{CF}^{*8/3} - 2A_1(\eta_{CF})\rho_{CF}^{*3} - 6A_2(\eta_{CF})\rho_{CF}^{*4} = 0,$$
(5.13)

$$\frac{80}{27}\alpha_{0}\eta_{CF}\rho_{CF}^{*11/3} + 6A_{1}(\eta_{CF})\rho_{CF}^{*4} + 24A_{2}(\eta_{CF})\rho_{CF}^{*5} = 0.$$
(5.14)

Solving these equations we find

$$\rho_{CF}^{*} = -A_{1}(\eta_{CF})/12A_{2}(\eta_{CF}), \qquad (5.15)$$

$$\left| 18A_{1}(\eta_{CF}) \right|^{4/3} = 80\alpha_{0}\eta_{CF}A_{2}^{1/3}(\eta_{CF}) .$$
 (5.16)

where (5.16) determines η_{CF} , whence (5.15) determines ρ_{CF}^* . Again $A_1(\eta_{CF}) < 0$. Furthermore

$$E_{CF}^{*} = 13A_{1}^{2}(\eta_{CF})/360A_{2}(\eta_{CF}), \qquad (5.17)$$

$$P_{CF}^{*} = -A_{1}^{3}(\eta_{CF})/2160A_{2}^{2}(\eta_{CF}) > 0, \qquad (5.18)$$

and

$$P_{CF}^{*}/E_{CF}^{*}\rho_{CF}^{*} = \frac{2}{13}.$$
 (5.19)

The detailed numerical results yield approximately 0.2 for the ratio $P_{CF}^*/E_{CF}^*\rho_{CF}^*$, which is in semiquantitative agreement with (5.19). The analysis about the critical point proceeds exactly as in classical mean-field theories. The transition along the critical isochore is of second order, the coexistence curve is characterized by a critical exponent $\beta = \frac{1}{2}$, and there is a jump discontinuity in $\partial E^*/\partial \eta$ (analogous to that in C_{ν}) as one passes through the critical point. In Figs. 14 and 15, we plot the reduced energy E^* and $\partial E^*/\partial \eta$ at fixed pressure as functions of η , respectively. The discontinuity in $\partial E^*/\partial \eta$ in the coexistence region is analogous to the latent heat in ordinary liquid-gas transitions at finite temperature.

The numerical procedures described in Appendix A yield the following values;

$$\eta_{LF} = 0.290 \pm 0.005$$

$$\rho_{LF}^{*} = 0.19 \pm 0.02$$
,

$$b_{LF} = 1.100 \pm 0.005;$$

and the following values at the critical point:

$$\begin{split} E_{CF}^{*} &= 0.075 \pm 0.007 \;, \\ \eta_{CF} &= 0.33 \pm 0.01 \;, \\ \rho_{CF}^{*} &= 0.074 \pm 0.004 \;, \\ P_{CF}^{*} &= (1.3 \pm 0.3) \times 10^{-3} \;, \\ b_{CF} &= 1.085 \pm 0.001 \;. \end{split}$$

The uncertainties shown in the above numbers



FIG. 14. Reduced energy as a function of the quantum parameter η . The curves are isobars and in particular they show the typical change in energy associated with a first-order phase transition.



FIG. 15. Slope of the energy as a function of η . This figure illustrates the discontinuity in the slope as the energy passes into the coexistence region.

have no physical significance. They are purely numerical and only reflect the extent to which these quantities are susceptible to small adjustments in the input data fed to the Chebyshev curve fit.

VI. DISCUSSION

The main result of this paper has been to show that, at zero temperature, quantum systems can exhibit liquid-to-gas phase transitions and that the nature of these transitions depends in a striking way on whether the systems obey Bose-Einstein or Fermi-Dirac statistics. In this discussion, we wish to emphasize that this behavior is a general qualitative property of these systems and will be true for all such systems that interact via a pair potential with a strong short-range repulsion and a finite-range attraction bounded from below. In addition, we shall briefly discuss an important theoretical consequence of these results; namely, that it is possible to construct zero-temperature perturbation theory for a Fermi liquid starting with the gas as the unperturbed state even though this is certainly not possible at any finite temperature.

The discussion of the boson case is really a discussion of two questions: (i) Has the second-order nature of the transition been imposed by our particular analysis? (ii) How accurate a calculation have we performed? If the bosons were to undergo a first-order transition like the fermions do, then there should be some density-dependent, manifest-

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ly positive contribution to the energy which at low densities is proportional to the density raised to a power less than one. We were able to find only one possible candidate, namely the zero-point phonons. In Appendix B, we argue that their presence should not affect the low-density equation of state. Thus the transition for bosons is second order. We could improve on our choice of a variational wave function in two ways: (i) by generalizing the wave function to include three-body forms; and (ii) by using a multiphonon basis for a perturbation-theoretic improvement of the ground-state energy. In Appendix B, we show further that in a density (cluster) expansion of the energy neither improvement will affect the leading $O(\rho)$ term. Thus, it appears that an optimized product of pair functions should yield the critical η *exactly*. The form we have used, Eq. (3.4), has the basic exponential form of the WKB two-body solution at small distances; therefore, we expect that it should yield very good results. In fact $\eta_{CB} = 0.456$ differs by only 1% from the critical η calculated by Bruch¹⁸ using a different criterion.

We have argued that the transition for Bose system is second-order. But are there Bose systems which do not undergo a phase transition at all? Clearly a system with a purely repulsive interaction will not. Also, if the boson system has only a weak short-range repulsion relative to the long-er-range attraction it will probably not undergo a transition since it is unlikely that there will be a point of zero pressure. That is, the question of the existence of η_{CB} and whether the potential-energy function is capable of saturation at some density are closely related.

Since the fermion critical density is finite, the associated critical η is far more complicated to obtain. The main reason for this is that the calculation of the (normal) ground state of the fermion system is not as refined as is the boson system. For example, there is no systematic way to obtain the optimum distribution function at a given density for a given potential. Nevertheless, it is clear that the critical behavior we have found is quite general. It depends really on two features of the Fermi system. The first is E_{1F}^* , the contribution to E_F^* due to the "effective repulsion" between fermions. This term is proportional to $\eta \rho^{*2/3}$ and will clearly be present no matter how one chooses to write the leading term in a density expansion and renormalize it. Thus, E_{1F}^* will dominate the energy at sufficiently low density! The second feature is that the next term in E_{E}^{*} must be proportional to ρ^* . The reasons for this behavior are the same as those for a Bose gas and are clearly quite general. Thus, we can conclude that the behavior we have found is general for a

fermion system of sufficiently low mass with an interaction characterized by a strong short-range repulsion and a finite-range attraction bounded from below.

We also wish to discuss a theoretical point which we believe is a direct consequence of our results. Ever since the early work of Brueckner and co-workers²⁰ treating the ground state of a Fermi system by means of systematic perturbation theory, there has been a question of whether it is possible to calculate the properties of a liquid using perturbation theory with a gas as the unperturbed state. This question has been considered by Ramirez and de Llano.²¹ After all, it has been known for many years, that such an approach is impossible in classical statistical mechanics.²² However, there is an enormous difference between the liquid-to-gas transition that takes place at finite temperatures and the one discussed in the present work. In the former case, the critical region exists because of the exclusion in phase space owing to the strong short-range repulsion.⁸ In our case, it exists because of the long-range nature of the "effective repulsion" due to the Fermi statistics. Thus, at zero temperature, it is possible to get *both* the liquid and gas phases from a systematic density expansion using only a finite number of terms. In the finite temperature case, an infinite number of terms is *always* needed. Thus, we believe that perturbation theoretical treatments of a Fermi liquid at zero temperature rest on a secure theoretical base.

There is one last comment we wish to make. It is clear that we find regions where $\partial P/\partial V > 0$, which is in violation of van Hove's theorem.²³ This problem results only from the fact that we have chosen a translationally invariant trial wave function. If we had chosen a wave function sufficiently general to allow for spatial inhomogeneity, we would undoubtedly have found no region where $\partial P/\partial V > 0$. We believe that this point is, in essence, the same as that discussed elegantly by van Kampen.⁸

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APPENDIX A: CALCULATIONAL DETAILS FOR THE FERMI SYSTEM

We first calculate the quantities η_{LF} and ρ_{LF}^* . These are determined by the simultaneous solution of Eqs. (5.6); i.e.,

$$E_{LF}^* = 0 , \qquad (A1)$$

 $P_{LF}^* = 0$, (A2)

$$\frac{\partial E^*}{\partial b} = 0. \tag{A3}$$

Writing Eqs. (A1)-(A3) explicitly, we have

$$E_{LF}^* = E_{1F}^* + \sum_{n=1}^{3} x_n D^n = 0, \qquad (A4)$$

$$P_{LF}^{*} = P_{1F}^{*} + \rho^{*} \sum_{n=1}^{3} n x_{n} D^{n} = 0, \qquad (A5)$$

$$\frac{\partial E^*}{\partial b} = \sum_{n=1}^{3} y_n D^n = 0 .$$
 (A6)

where

$$x_{i} = \eta b^{-2} \alpha_{i} - 4b^{-6} \beta_{i} + 4b^{-12} \gamma_{i} , \qquad (A7)$$

$$y_{i} = (-2+3i)b^{-7}\eta\alpha_{i} + 12(2-i)b^{-7}\beta_{i} + 12(-4+i)b^{-13}\gamma_{i} , \qquad (A8)$$

and E_{1F}^* and P_{1F}^* are defined in Eqs. (3.60) and (5.3), respectively. We eliminate the Fermi energy terms from Eqs. (A4) and (A5) by multiplying Eqs. (A4) by $\frac{2}{3}$ and subtracting from Eq. (A5); whence

$$x_1 + 4x_2D + 7x_3D^2 = 0. (A9)$$

Then Eqs. (A6) and (A9) give D as a function of η and b; i.e.,

$$D = (y_1/y_3 - x_1/7x_3)/(4x_2/7x_3 - y_2/y_3).$$
 (A10)

Equations (A4), (A6), and (A9) are each linear in η . These yield three equations for η in terms of b and D; i.e.,

$$\eta = -(P_6 + P_4/b^6)/P_5 b^4, \qquad (A11)$$

$$\eta = 3(P_3 + P_1/b^6)/P_2b^4, \qquad (A12)$$

$$\eta = -(P_9 + P_7 / b^6) / P_8 b^4, \qquad (A13)$$

where we have defined the following convenient set of polynomials:

$$P_{1} = 12\gamma_{1} + 8\gamma_{2}D + 4\gamma_{3}D^{2},$$

$$P_{2} = \alpha_{1} + 4\alpha_{2}D + 7\alpha_{3}D^{2},$$

$$P_{3} = -4\beta_{1} + 4\beta_{3}D^{2},$$

$$P_{4} = 4\gamma_{1} + 16\gamma_{2}D + 28\gamma_{3}D^{2},$$
(A14)

$$P_4 = 4\gamma_1 + 16\gamma_2 D + 28\gamma_3 D^2,$$

$$P_5 = \alpha_1 + 4\alpha_2 D + 7\alpha_3 D^2,$$

$$\begin{split} P_6 &= -4\beta_1 - 16\beta_2 D + 4\beta_3 D^3 , \\ P_7 &= 4\gamma_1 D + 4\gamma_2 D^2 + 4\gamma_3 D^3 , \\ P_8 &= \alpha_0 D^{2/3} + \alpha_1 D + \alpha_2 D^2 + \alpha_3 D^3 , \\ P_9 &= -4\beta_1 D - 4\beta_2 D^2 - 4\beta_3 D^3 . \end{split}$$

Now we may eliminate η between, say, Eqs. (A11) and (A12); i.e.,

$$b^{6} = -(3P_{1}/P_{2} + P_{4}/P_{5})/(3P_{3}/P_{2} + P_{6}/P_{5}).$$
 (A15)

Equation (A15) yields b as a function of D and it completes the algorithm. The solution proceeds iteratively as follows: we insert some initial guess for $D_{LF}^{(0)}$ in Eq. (A15) which yields as initial $b_{LF}^{(0)}$. Then Eq. (A13) gives the $\eta_{LF}^{(0)}$ concomitant to $(b_{LF}^{(0)}, D_{LF}^{(0)})$. Finally Eq. (A10) is used to find a new $D_{LF}^{(1)}$ from $b_{LF}^{(0)}$ and $\eta_{LF}^{(0)}$ and the cycle is repeated until the input $D_{LF}^{(4)}$ is the same as the output $D_{LF}^{(4+1)}$. Numerically, we required D_{LF} to converge to one part in 10⁶.

The critical-point parameters are calculated by the same general technique. From Eq. (5.10) η_{CF} and ρ_{CF}^* are determined by

$$\frac{\partial P^*}{\partial V^*} = 0 = \frac{\partial^2 P^*}{\partial V^{*2}} = 0 = \frac{\partial E^*}{\partial b} .$$
 (A16)

We can equivalently (and much more conveniently) solve the set of equations

$$\frac{\partial P^*}{\partial D} = 0 = \frac{\partial^2 P^*}{\partial D^2} = 0 = \frac{\partial E^*}{\partial b} \quad . \tag{A17}$$

From Eqs. (A4)-(A6) we have

$$\frac{10}{9} \alpha_0 \eta \rho^{*2/3} + 2x_1 D + 6x_1 D^2 + 12x_3 D^3 = 0 , \qquad (A18)$$

$$\frac{20}{27} \alpha_0 \eta \rho^{*2/3} + 2x_1 D + 12x_2 D^2 + 36x_3 D^3 = 0, \quad (A19)$$

and as before

$$y_1 D + y_2 D^2 + y_3 D^3 = 0$$
. (A20)

Eliminating the $\rho^{*2/3}$ term between Eqs. (A18) and (A19), we find

$$y_1 + 12x_2D + 42x_3D^2 = 0 . (A21)$$

Equations (A20) and (A21) yield D as a function of b and η

$$D = (y_1/y_3 - x_1/42x_3)/(2x_2/7x_3 - y_2/y_3).$$
 (A22)

We may now write Eqs. (A18), (A20), and (A21) as

$$\eta = -(P_6 + P_4/b^6)/P_5 b^4, \qquad (A23)$$

$$\eta = 3(P_3 + P_1/b^6)/P_2b^4, \qquad (A24)$$

$$\eta = -(P_9 + P_7/b^6)/P_8 b^4, \qquad (A25)$$

where we have defined the following polynomials, which are functions of b and D:

$$\begin{split} P_{1} &= 12\gamma_{1} + 8\gamma_{2}D + 4\gamma_{3}D^{2} ,\\ P_{2} &= \alpha_{1} + 4\alpha_{2}D + 7\alpha_{3}D^{2} ,\\ P_{3} &= -4\beta_{1} + 4\beta_{3}D^{2} ,\\ P_{4} &= 4\gamma_{1} + 48\gamma_{2}D + 168\gamma_{3}D^{2} ,\\ P_{5} &= \alpha_{1} + 12\alpha_{2}D + 42\alpha_{3}D^{2} ,\\ P_{6} &= -4\beta_{1} - 48\beta_{2}D - 168\beta_{3}D^{2} ,\\ P_{7} &= 4\gamma_{1}D + 12\gamma_{2}D^{2} + 24\gamma_{3}D^{3} ,\\ P_{8} &= \frac{5}{9}\alpha_{0}D^{2/3} + \alpha_{1}D + 3\alpha_{2}D^{2} + 6\alpha_{3}D^{3} ,\\ P_{9} &= -4\beta_{1}D - 12\beta_{2}D^{2} - 24\beta_{3}D^{3} . \end{split}$$

We may eliminate η between Eqs. (A23) and (A24) and solve for *b* as a function of *D*; whence

$$b^{6} = -(3P_{1}/P_{2} + P_{4}/P_{5})/(3P_{3}/P_{2} + P_{6}/P_{5}).$$
 (A27)

The iterative solution for D_{CF} using Eqs. (A27), (A25), and (A22) is identical to that described for D_{LF} . We required D_{CF} to converge to one part in 10⁶; in terms of Eqs. (A16) this meant

$$\frac{\partial P^*}{\partial V^*} \sim 10^{-14},$$

$$\frac{\partial^2 P^*}{\partial V^{*2}} \sim 10^{-9},$$
(A28)
$$\frac{\partial E^*}{\partial h} \sim 10^{-8}.$$

APPENDIX B: VARIOUS APPROXIMATIONS FOR THE BOSE SYSTEM

In this appendix we shall discuss in detail the approximations which have been made in this calculation in order to better ascertain the accuracy of the computed critical numbers. It is clear that in both the Bose and Fermi cases, the most important approximation is the particular choice of wave function given in Eqs. (3.2)-(3.4). We shall first discuss the Bose case and consider the following effects: (i) the inclusion of phonons in the trial wave function; (ii) three-body factors in the trial wave function; and (ii) three-phonon effects. Then we shall discuss the Fermi case and consider the statistical cluster expansion and possible perturbative corrections.

As first noted by Feynman²⁴ the low-lying excitations in a strongly interacting Bose system are phonons. One manifestation of these phonons is to alter the long-wavelength behavior of the liquid structure factor such that

$$\lim_{k \to \infty} S(k^*) - (\eta/2c^*)k^* \,. \tag{B1}$$

We have introduced a dimensionless speed of sound c^*

$$c^* = (\hbar/\epsilon\sigma)c$$
. (B2)

Chester and Reatto²⁵ showed that one could obtain the behavior of Eq. (B1) by inclusion of the zeropoint phonons as part of the pair function. The logarithm of their long-ranged wave function is

$$u_{LR}(R) = -(c^*/\pi^2 \rho^* \eta)(1/x^2 + \lambda^2), \qquad (B3)$$

where λ is a momentum cutoff left arbitrary in the theory. Because c^* is a function of ρ^* and η , it is uncertain exactly what effect u_{LR} has on the energy in the limit as $\eta \rightarrow \eta_{CB}$. Owing to the explicit density dependence in the u_{LR} the simple cluster expansion of Eq. (4.13) is not applicable. However, we believe that, in the light of exact solutions of model boson systems, the character of the equation of state at low density is unchanged by the inclusion of the phonon modes. Specifically, Huang²⁶ has shown that, for an imperfect hardsphere Bose gas with attractive interactions, the leading term in a density expansion is *linear* in the density. Moreover for a "critical" value of the ratio of the total potential scattering length to the hard-sphere scattering length, the energy vanishes in lowest order. We note that Huang specifically excludes the possibility of a two-body bound state!

We shall now discuss possible refinements of the Boson calculation and argue that they will not effect the energy to $O(\rho)$. First there is the inclusion of three-body factors in the wave function. This possibility has been discussed by Campbell²⁷ and Coldwell and Woo.²⁸ It is clear, though, that in a cluster decomposition of the energy they can only first appear in the $O(\rho^2)$ term. For example, this is illustrated by the energy series for the weakly interacting Bose gas where to $O(\rho)$ the optimized pair function yields the exact results.

Using a multiphonon basis constructed of density fluctuation operators ρ_k operating on the ground state, one can obtain the optimum pair function by partially diagonalizing the Hamiltonian matrix with respect to paired-phonon elements: $\langle 0 | H | \vec{k}, -\vec{k} | \rangle$, as was shown by Campbell and Feenberg.²⁹ The effect of the next contribution, the three-phonon element, $|\vec{k}, \vec{l}, -\vec{k} - \vec{l} \rangle$, is then obtained by second-order perturbation theory.³⁰ Sim, Woo, and Buchler³¹ showed that, for the weakly interacting Bose case, this term first contributes at $O(\rho^2)$ indeed the same contribution as the three-body wave function. We conclude that from a variational point of view η_{CB} can be calculated exactly by the optimum pair function.

The path to optimizing the calculation in the Fermi case is not as clear as the boson case, since the (normal) ground state for a finitedensity Fermi system is not understood as well as the low-density Boson system. The statistical cluster expansion used in this paper to calculate the energy expectation value suffers from the drawback that its rate of convergence is not at all a settled issue. In addition, there appear to be important perturbative corrections^{14,32} which are difficult to calculate because of the nonorthogonality of the natural basis set. We believe that a Brueckner-Goldstone approach to the problem might be very useful because of the (relatively) low density at which the phenomena occur.

For a given set of data, extracting the critical

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eta represents a whole new level of problems as this point requires the second and third derivatives of the energy-versus-volume curves. For example, there is some small difference between the Fermion results quoted in Ref. 7 and those given above. This difference is attributed basically to the different algorithms used to calculate the critical quantities. We believe that the results presented in the present work are the more accurate of the two.

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