Catastrophe in the Random-Phase Approximation: Critique of a Theory of Phase Transitions

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(Received 19 March 1971)

A detailed investigation is presented of the theory of phase transitions afforded by the random phase approximation (RPA) and Gaussian fluctuation theory. Arguments are given which indicate that these two theories are equivalent. A rigorous analysis is carried out on the RPA for a simple binary model that should exhibit a phase transition. It is found that when the RPA free energy is used to calculate the thermodynamics for the model a catastrophe region exists in which the system collapses to negatively infinite free energy and thermodynamic stability breaks down before (at lower densities and higher temperature) the region is reached. The catastrophe surface which surrounds the region has been identified in the previous literature as the limit of stability for the model, and the singularities associated with the catastrophe have been incorrectly identified as true critical singularities. The incorrect identification leads to results which contradict the second law of thermodynamics. It is shown that there is no sensible solution to the equations obtained from a Maxwell construction to bridge the catastrophe. The RPA for the binary model is also discussed within the context of the compressibility theorem. When this route to the thermodynamics is taken, it is found that the behavior predicted by the RPA is purely classical. Arguments are presented which indicate that the results found with the binary model are general features of the RPA; the application of the approximation to more general one- and two-component systems yield the same results. Finally, a tentative explanation for the catastrophe is given. The explanation suggests a modified RPA which does not violate the second law of thermodynamics; however, the patched up theory is classical.

I. INTRODUCTION

The random phase approximation (RPA) and Gaussian fluctuation theory (GFT) have been applied in recent years to systems which exhibit phase transitions as a way of correcting mean-field theories such as the van der Waals equation.1–9 These treatments predict that the constant-volume heat capacity \( c_v \) of a pure fluid (or the zero-field heat capacity \( c_H \) of a ferromagnet) diverges at the critical point as \( (T-T_c)^{-\beta} \). Since it is found experimentally that \( c_v \) and \( c_H \) do appear to diverge at the critical point, this prediction is taken by proponents of RPA and GFT to be an improvement upon mean field theory (which predicts no divergence) even though the exponent \( \frac{1}{\beta} \) is surely incorrect. Deutch and Zwanzig1 have applied GFT to a two-component fluid where one expects a coexistence surface and a line of critical points. They predict that the heat capacity at constant volume and composition \( c_{v\rho} \) diverges as \( [T-T_c(\rho)]^{-\frac{1}{2}} \) at each point on the critical line, where \( T_c(\rho) \) is the critical temperature at any fixed total density. Such behavior, however, has been shown to be inconsistent with thermodynamic stability.10 In order to simplify the mathematical treatment, Deutch and Zwanzig, however, make an auxiliary assumption that fluctuations in total density may be neglected compared to those in concentration provided the intermolecular potential favors separation into two phases of about equal total density and different composition. Accordingly, they ignore fluctuations in total density throughout.11 The Helmholtz free energy obtained in this way, however, has the property that its second derivative with respect to total density at fixed composition becomes negative before the “critical point” is reached. This violation of thermodynamic stability is a clear indication that density fluctuations cannot be ignored. But the problem is more serious than this, for if one includes both density and concentration fluctuations in this treatment, one finds instabilities which cause the system to collapse to negatively infinite free energy.

In order to examine the nature of this catastrophe more carefully, we consider a simple example of a binary fluid in the RPA. The only interactions present in our fluid are repulsions between molecules of different types: Pure component 1 is an ideal gas, as is pure component 2. The results we shall obtain using RPA are essentially identical to those one obtains by extending GFT to include both density and concentration fluctuations (we argue in Appendix B that these two approximations are exactly equivalent provided that GFT satisfies two rather general statistical mechanical conditions). We have chosen to exhibit this behavior in the language of RPA for several reasons.

(a) The approximations embodied in RPA are all contained in a single mathematical statement which appears explicitly at the beginning of the calculation after which the mathematics may be done rigorously, whereas in the GFT one makes a sequence of approximations (division into cells, separation of forces into long- and short-ranged parts, separate treatment of
short-range free energy, expansion of free energy about uniform system, truncation at quadratic order, etc.), each of which it may be thought is subject to criticism.

(b) Related to this is the fact that there are several different “versions” of GFT, all producing essentially the same results, but using different details and language along the way, whereas the RPA is a relatively well defined approximation in equilibrium statistical mechanics.

(c) The RPA has a degree of theoretical reactivity. It is equivalent to linearized self-consistent-field approximations (in both quantum and classical statistical mechanics) and to well-defined many-body diagrammatic summations, and is the first term in a systematic expansion for the free energy. Further, it has enjoyed significant practical success in predicting properties of systems with long-range forces. The fact that it is a popular and much-studied approximation in many areas of theoretical physics makes the curious behavior found below of particular interest.

In Sec. II we define the simple model fluid for which the catastrophe is studied in detail, and we state the definition of RPA for classical statistical mechanics. In Secs. III and IV the RPA free energy is calculated for the model and the thermodynamic consequences—in particular, the catastrophe—are examined. Here we also point out that the catastrophe is symptomatic of RPA and not the simple model which we analyze. The application of RPA to more general systems leads to the same type of results.

Of course, the thermodynamic behavior can also be extracted from the compressibility theorem. This route to the thermodynamics is analyzed in Sec. V. Since RPA is not exact, the results obtained from compressibility theorem are necessarily different from those obtained from the RPA free energy. While considering that difference, we discuss an error which we believe is present in most of the work employing exact instability ideas to describe phase transitions. The paper is concluded in Sec. VI, where possible explanation of the RPA catastrophe is discussed. It appears that the unphysical behavior is related to the fact that short-ranged correlations are described incorrectly by RPA; when this inadequacy is removed from RPA, the approximation does not violate the second law of thermodynamics.

II. A TWO-COMPONENT FLUID AND THE RPA

We consider a binary fluid of \( N_A \) molecules of mass \( m_A \) and \( N_B \) molecules of mass \( m_B \), contained in a volume \( V \). The thermodynamic particle densities of the two species are

\[
\rho_A = \frac{N_A}{V}, \quad \rho_B = \frac{N_B}{V}. \tag{2.1}
\]

We assume that the potential energy of the fluid is a sum of pair-potentials, that two like molecules do not interact at all, and two unlike molecules interact with a radially symmetric, purely repulsive potential. Thus, the total potential energy can be expressed as

\[
U = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} u(|\mathbf{r}_i - \mathbf{R}_j|), \quad u(r) \geq 0. \tag{2.2}
\]

Here \( \mathbf{r}_i \) denotes the position of the \( i \)th \( A \) molecule and \( \mathbf{R}_j \) denotes the position of the \( j \)th \( B \) molecule. One further restriction is made on the potential energy: The two-particle potential has a Fourier transform. As a concrete example, we consider the Yukawa potential

\[
u(r) = (\epsilon / \alpha r) \exp(-\beta r), \tag{2.3}
\]

where \( \epsilon \) and \( \alpha \) are constants with the dimensions of energy and inverse length, respectively. The precise form of \( u(r) \) will not alter the principal conclusions of this paper (we discuss this further in Sec. IV). The particular choice exhibited in Eq. (2.3) is made for computational convenience and to facilitate comparison with Ref. 1.

The quantity we are interested in calculating for the system defined above is the Helmholtz free energy. This is given by the canonical ensemble partition function

\[
\exp(-\beta A) = \langle \exp(-\beta U) \rangle, \tag{2.4}
\]

where \( \beta = 1/k_B T \), \( k_B \) Boltzmann’s constant times the temperature, \( A \) is the excess free energy—that is, the Helmholtz free energy of the interacting system minus the Helmholtz free energy of an ideal gas at the same temperature and densities—and the brackets \( \langle \cdots \rangle \) denote the unweighted configurational average

\[
\langle \cdots \rangle = \frac{1}{\Omega(V,N_A,N_B)} \int d\mathbf{r}^{N_A} d\mathbf{R}^{N_B} \langle \cdots \rangle. \tag{2.5}
\]

From very general statistical mechanical theorems, we know that the fluid defined by Eq. (2.2) is well behaved in the thermodynamic limit \( (N_A, N_B, V \to \infty ; \rho_A, \rho_B \text{ finite}) \). In particular, the limiting Helmholtz free energy per unit volume exists and is differentiable. Furthermore, because of the simple nature of the potential, we would expect the exact statistical treatment of this fluid to indicate that any phase transition be a separation into two phases of equal total density but different concentrations of \( A \) and \( B \). This is the type of phase transition considered by Deutch and Zwanzig. In the remainder of this section we express the configurational partition function [Eq. (2.4)] in terms of a collective coordinate representation. Once this is done, the RPA can be defined.

Since the Fourier transform of the two-particle potentials exists, the total potential energy can be written in terms of the Fourier components of the particle densities. By applying periodic boundary conditions in a cubic volume, the origin at the center of the cube, Eq.
(2.2) can be expressed as
\[ U = V^{-1} \sum_{k} \tilde{a}(k) q_{A}(k) q_{B}(-k), \]  
(2.6)
where
\[ \tilde{a}(k) = \int_{V} u(r) \exp(-ik \cdot r) \, dr \]  
(2.7)
and the \( q_{A}(k) \) and \( q_{B}(k) \) are the Fourier components of the particle densities of \( A \) and \( B \) molecules,
\[ q_{A}(k) = \sum_{i=1}^{N_{A}} \exp(-ik \cdot r_{i}), \quad q_{B}(k) = \sum_{j=1}^{N_{B}} \exp(-ik \cdot r_{j}). \]  
(2.8)
The vectors \( k \) take on the values
\[ k = (n, m, l) 2\pi V^{-1/3} \quad (n, m, l = 0, \pm 1, \pm 2, \cdots). \]  
(2.9)
In terms of these Fourier transforms, Eq. (2.4) for the excess free energy can be written as
\[ \beta \Delta A / V = \beta \phi_{A} 0 \]  

\[ -V^{-1} \ln \left[ \prod_{k} \exp \left\{ -\beta \tilde{a}(k) V^{-1} \left[ q_{A}(k) q_{B}(-k) \right. \right. \right. \]  

\[ + \left. q_{B}(k) q_{A}(-k) \right] \} \right], \]  
(2.10)
where \( \prod_{k'} \) denotes a product over half of \( k \) space with \( k = 0 \) omitted. This equation relates the excess free energy to the collective coordinates \( q_{A}(k) \) and \( q_{B}(k) \). The first term on the right-hand side of Eq. (2.10) is the mean field (van der Waals) contribution to \( \beta \Delta A / V \). The remaining term gives the contributions due to fluctuations.

The argument of the logarithm in Eq. (2.10) is an average of an infinite product. The RPA writes this averaged product as a product of averages. That is, the excess free energy in RPA is defined by the equation
\[ \beta \Delta A_{RPA} / V = \beta \phi_{A} 0 \]  

\[ -V^{-1} \sum_{k} \ln \langle S(k) \rangle, \]  
(2.11)
where
\[ S(k) = \exp \left\{ -\beta \tilde{a}(k) V^{-1} \left[ q_{A}(k) q_{B}(-k) \right. \right. \right. \]  

\[ + q_{B}(k) q_{A}(-k) \} \right]. \]  
(2.12)
Thus, RPA neglects the correlations between density Fourier components with different wave vectors. Diagrammatically, \( \Delta A_{RPA} \) is the contribution to the free energy due to all pair-potential ring diagrams in the usual cluster expansion for \( \Delta A \). The approximation \( \Delta A \approx \Delta A_{RPA} \) is intimately related to the assumption that the free energy is a quadratic functional of the density fluctuations (which is one way of hypothesizing GFT). The relationship is discussed in Appendix B.

One further note is in order concerning RPA. We could consider the general situation in which the total pair interactions are sums of a "reference" part \( u_{ij}^{0} \) between species \( i, j \) (\( i, j = A, B \)) and a perturbation part \( u_{ij} \). In that case RPA is given by Eq. (2.11) with \( \Delta A \) now representing the excess free energy with respect to the "reference system" (the system in which the total pair interactions are the \( u_{ij}^{0} \)). The mean field term is then \( \beta \sum_{i<j} \rho_{i} \rho_{j} \delta_{ij} / 2 \), the function \( S(k) \) is replaced by \( \exp \left\{ -\beta \sum_{i<j} \delta_{ij} (q_{i} q_{j}^{*} - \delta_{ij} N_{i} / V) \right\} \) and (\( \cdots \)) represents the canonical ensemble average in the reference system. While we will not present any explicit calculations for this general RPA, we will occasionally state some pertinent results that are obtained from it. The methods used in calculating the general RPA, its relation to graphical methods, and the systematic corrections to it are discussed in the literature.

In the next two sections of this paper, we discuss the evaluation of \( \Delta A_{RPA} \) for the simple binary model and the consequences of accepting \( \Delta A_{RPA} \approx \Delta A \) as a good approximation. Because the results we obtain are pathological in certain regions, we shall exercise great care in evaluating the required integrals in order to ensure that the nonphysical behavior is due solely to RPA, and not subsequent approximations.

### III. EVALUATION OF THE FREE ENERGY

In order to obtain \( \Delta A_{RPA} \) in Eq. (2.11) we must calculate the quantities
\[ \langle S(k) \rangle = V^{-N_{A}-N_{B}} \int d^{N_{A}} r d^{N_{B}} \]  

\[ \times \exp \left\{ -\beta \tilde{a}(k) V^{-1} \left[ q_{A}(k) q_{B}(-k) \right. \right. \right. \]  

\[ + q_{B}(k) q_{A}(-k) \} \right] \]  
(3.1)
at nonzero \( k \). For any fixed \( V, N_{A}, N_{B} \) the two terms in the argument of the exponential are uniformly absolutely bounded, and the integrations are over a finite range, so the exponential may be expanded in the double infinite series
\[ S(k) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \left[ -\beta \tilde{a}(k) / V \right]^{n+m} \]  

\[ \times \left[ q_{A}^{m}(k) q_{B}^{n}(-k) q_{B}^{m}(k) q_{A}^{n}(-k) \right] \]  
(3.2)
and the average of \( S(k) \) may be performed term by term. The quantity \( q_{A}^{m}(k) q_{B}^{n}(-k) \) is a function of the coordinates of \( A \)-type particles only, and \( q_{B}^{m}(k) q_{B}^{m}(k) q_{A}^{n}(-k) \) is a function of those of \( B \)'s only, so the average of \( S(k) \) becomes [recall Eq. (2.5)]
\[ \langle S(k) \rangle = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \left[ -\beta \tilde{a}(k) / V \right]^{n+m} \]  

\[ \times \left[ q_{A}^{m}(k) q_{B}^{n}(-k) \right] \]  

\[ \langle q_{B}^{m}(k) q_{B}^{m}(k) q_{A}^{n}(-k) \rangle \]  
(3.3)
The second equality is a consequence of the periodic
boundary conditions, which imply
\[ V^{-1} \int_V \, dt \exp(i\mathbf{k} \cdot \mathbf{r}) = 1, \quad \mathbf{k} = 0 \]
\[ = 0, \quad \mathbf{k} \neq 0. \]  \hfill (3.4)

The averages \( \langle q^a_{\mathbf{k}}(\mathbf{k}) q^{a*}_{\mathbf{k}}(\mathbf{-k}) \rangle \) and \( \langle q^a_{\mathbf{k}}(\mathbf{k}) q^{a*}_{\mathbf{k}}(\mathbf{-k}) \rangle \)
are just integer functions of \( n, N_A \) and \( n, N_B \) respectively. Their evaluation is a purely combinatorial problem. It is straightforward (see Appendix A) to show that these averages are given exactly by
\[ \langle 1/n \rangle \langle q^a_{\mathbf{k}}(\mathbf{k}) q^{a*}_{\mathbf{k}}(\mathbf{-k}) \rangle = M(n, N_A), \quad \mathbf{k} \neq 0 \]
\[ \langle 1/n \rangle \langle q^a_{\mathbf{k}}(\mathbf{k}) q^{a*}_{\mathbf{k}}(\mathbf{-k}) \rangle = M(n, N_B), \quad \mathbf{k} \neq 0 \]  \hfill (3.5)
with
\[ M(n, N) = \sum_{\{f_i\}} \left[ \prod_{i=1}^n f_i^2 \cdots (f_n!^2) \right], \]  \hfill (3.6)
where the symbol \( \sum_{\{f_i\}} \) denotes the sum over all choices of the nonnegative integers \( f_i \) \( (i = 1, 2, \cdots, N) \) subject to the constraint that \( \sum_{i=1}^N f_i = n \).

To the best of our knowledge, \( M(n, N) \) is not known exactly in terms of simple functions. However, it is easy to obtain upper and lower bounds for it which are sufficiently precise for our purposes. Clearly the sum in Eq. (3.6) will be increased if each \( (f_i!)^2 \) is replaced by \( (f_i!) \). On the other hand, the sum itself is surely greater than the sum over the subset of terms for which each \( f_i \) is either zero or one. Combining these facts, we have the inequalities
\[ N^e \geq M(n, N) \geq \left( \begin{array}{c} N^e \\n \end{array} \right) \geq (N-n)^e, \quad n < N \]
\[ \geq 0 \quad n > N. \]  \hfill (3.7)

We may also observe that the sum in Eq. (3.6) constitutes a subset of the terms in the multinomial expansion for \( N^{2N}/n! \), so that
\[ M(n, N) \leq N^{2N}/n!, \]  \hfill (3.8)
which guarantees that the sum for \( \langle S(k) \rangle \) converges for any finite \( N_A, N_B, V \).

It is often stated,\(^2\) on the basis of central limit theorem arguments and/or erroneous combinatorial reasoning, that \( M(n, N) = N^e \). From Eq. (3.7), we see that this result is asymptotically correct when \( N > n \). However, the sum in Eq. (3.5) runs over all integers \( n \) for fixed \( N_A, N_B, V \), and as \( n \) tends to infinity, \( N^e \) diverges while \( M(n, N) \to 0 \) by Eq. (3.8). In practice the use of the approximation \( M(n, N) = N^e \) for all \( n \) leads to correct (RPA) results, provided the system is well behaved in the (RPA) thermodynamic limit.

Substituting the results of Eqs. (3.5), (3.6), and (3.8) into Eq. (3.3), we obtain the inequalities for
\[ \langle S(k) \rangle(k \neq 0) \]
\[ \sum_{n=0}^{\min(N_A, N_B)} \left[ \beta a(k) \right]^{\rho_{\text{RPA}} B} \left( 1 - \frac{n}{N_B} \right) \leq \langle S(k) \rangle \]
\[ \leq \sum_{n=0}^{\infty} \left[ \beta a(k) \right]^{\rho_{\text{RPA}} B}, \]  \hfill (3.9)
where the sum of the left-hand side runs from zero thru the smaller of \( N_A \) and \( N_B \). For the purpose of obtaining bounds on the thermodynamic free energy when \( N_A, N_B, V \to \infty \) it will be useful to replace the lower bound in Eq. (3.9) by a weaker bound in which the summation index appears only as an exponent. Let \( R(N_A N_B) \) be the nearest integer to \( + \left( \min(N_A, N_B) \right)^{1/2} \) and define
\[ \rho_A^* = \rho_A \left[ 1 - \left( \frac{R(N_A N_B)}{N_A} \right) \right], \]
\[ \rho_B^* = \rho_B \left[ 1 - \left( \frac{R(N_A N_B)}{N_B} \right) \right]. \]  \hfill (3.10)

Equation (3.9) then implies the weaker inequality
\[ R(N_A N_B) \]
\[ \sum_{n=0}^{R(N_A N_B)} \left[ \beta a(k) \right]^{\rho_A^* \rho_B^*} \leq \langle S(k) \rangle \]
\[ < \sum_{n=0}^{\infty} \left[ \beta a(k) \right]^{\rho_{\text{RPA}} B}. \]  \hfill (3.11)

We must now consider two possibilities [\( \beta a(0) \leq \rho_{\text{RPA}} \leq 1 \) or \( \beta a(0) > \rho_{\text{RPA}} > 1 \).]

(i). \[ \beta a(0) \leq \rho_{\text{RPA}} \leq 1. \] In this case, for every \( k \neq 0, \]
\[ \left[ \beta a(k) \right]^{\rho_{\text{RPA}}} < 1, \] and the geometric series in Eq. (3.11) can be summed analytically to give
\[ 1 - \left[ \beta a(k) \right]^{\rho_{\text{RPA}}} \leq \langle S(k) \rangle \]
\[ \leq \left[ 1 - \left[ \beta a(k) \right]^{\rho_{\text{RPA}}} \right]^{-1}, \quad k \neq 0. \]  \hfill (3.12)

In the thermodynamic limit, as \( N_A, N_B, V \to \infty \) with \( \rho_{\text{RPA}} \) constant, the upper and lower bounds in Eq. (3.12) rapidly approach a common value, and the limiting RPA free energy is given exactly by [see Eqs. (2.9) and (2.11)]
\[ \beta a_{\text{RPA}} := \lim_{N_A N_B V \to \infty; \rho_{\text{RPA}} \text{ const}} \langle \beta \Delta A_{\text{RPA}}/V \rangle \]
\[ = \beta \rho_{\text{RPA}} a(0) + [1/(2 \pi^2)] \]
\[ \times \int \, d\mathbf{k} \ln \left[ 1 - \rho_{\text{RPA}} \beta a(0) \right], \]  \hfill (3.13)
where
\[ a_\infty(k) = \lim_{n \to \infty} \int_V \exp(i\mathbf{k} \cdot \mathbf{r}) u(x) \, dx. \]  \hfill (3.14)

For the Yukawa potential in Eq. (2.3), \( a_\infty(k) \) is given by
\[ a_\infty(k) = \left[ 4 \pi e / (\alpha^2 + k^2) \right] \] (Yukawa potential)  \hfill (3.15)
and the integral in Eq. (3.13) is easily evaluated by standard techniques. In terms of the dimensionless densities \(y_A, y_B\) and dimensionless inverse temperature \(\beta\) defined by
\[
y_A = \rho_A / \alpha^3, \quad y_B = \rho_B / \alpha^3, \quad \beta = \alpha t_0(0) / \alpha = 4\pi t_0\beta
\] (3.16)
the free energy for the Yukawa potential is found to be
\[
\beta \Delta a_{\text{RPA}} / \alpha^3 = \tilde{y}_A y_B - (1/12\pi) \left[ \left( 1 + \tilde{y}_A y_B \right)^{1/\beta} \right]^{12} + \left[ 1 - \tilde{y}_A y_B \right]^{12} - 2.
\] (3.17)
Clearly this result is meaningful only when
\[
\left[ \beta \tilde{a}_0(0) \right]_{\text{RPA}} > 1.
\]

(ii) \([\beta \tilde{a}_0(0)]_{\text{RPA}} > 1\). In this case, the RPA free energy per unit volume, which exists for each finite \(V, N_A, N_B\), does not possess a finite thermodynamic limit, but diverges to \(\to -\infty\) as \(N_A, N_B, V \to \infty\) with the product \(\rho_A \rho_B\) constant. As the size of the container grows, the allowed values of \(k\) pack closer together [Eq. (2.9)], so that for \(V\) sufficiently large there will be some allowed \(k^*\) (say, \(2\pi V^{1/3} [1, 0, 0]\)) for which \(\beta \tilde{a}_k(0) \geq 0\). In this case, the upper bound to \(\left< S(k) \right>\) in Eq. (3.11) diverges. Both the lower bound in Eq. (3.12) and \(\left< S(k) \right>\) itself are finite, however, as guaranteed by Eq. (3.7). But as \(V, N_A, N_B \to \infty\) the lower bound in (3.12) varies as some number greater than 1 raised to a power which goes to infinity so that \(\left< S(k) \right>\) diverges, and so does \(\beta \Delta a_{\text{RPA}} / \alpha^3\).

Thus, in the thermodynamic limit, when
\[
[\beta \tilde{a}_0(0)]_{\text{RPA}} = (\tilde{\beta})^3 y_A y_B < 1
\]
the free energy per unit volume given by Eq. (3.17), and when \((\tilde{\beta})^3 y_A y_B > 1\), it is negatively infinite.

IV. THERMODYNAMIC BEHAVIOR OBTAINED FROM THE FREE ENERGY

The total Helmholtz free energy per unit volume corresponding to Eq. (3.7) is given by
\[
\beta a / \alpha^3 = y_A \ln y_A + y_B \ln y_B + y_A \left[ \ln(y_A^*) - 1 \right]
+ y_B \left[ \ln(y_B^*) - 1 \right] + \tilde{y}_A y_B - (1/12\pi)
\times \left[ \left( 1 + \tilde{y}_A y_B \right)^{1/\beta} \right]^{12} + \left[ 1 - \tilde{y}_A y_B \right]^{12} - 2,
\]
where \(y_A, y_B, \tilde{\beta}\) are defined by Eq. (3.16), and where
\[
\lambda_i^* = \kappa_i / (2\pi m_i k_B T)^{1/2}, \quad i = A, B.
\] (4.2)
This is a concave function of \(\tilde{\beta}\), as demanded by thermodynamic stability, with second derivative given by
\[
c_i / k_B = -\tilde{\beta} \left( \partial^2 \beta a / \alpha^3 \right) / \partial \tilde{\beta}^2 \bigg|_{y_A,y_B}
= 1/2 \left( y_A + y_B \right) + \left( \tilde{\beta} \right)^2 y_A y_B / 12\pi
\times \left[ \left( 1 + \tilde{y}_A y_B \right)^{1/\beta} - 1 \right] - \left[ 1 - \tilde{y}_A y_B \right]^{12} - 1/2.
\] (4.3)

Thus the heat capacity per unit volume, \(c_i\), is positive, and diverges [as \((T - T_c)^{-1/2}\) for fixed \(y_A y_B\)] at the surface \(\tilde{y}_A y_B = 1\), which Deutch and Zwanzig identify as the coexistence surface. Thermodynamic stability, however, requires that the free energy also be a convex function of \(y_A\) and \(y_B\) taken together at fixed \(\tilde{\beta}\), and we shall see that this condition is violated for lower densities than the “catastrophe” surface \(\tilde{y}_A y_B = 1\).

In discussing the isothermal stability and phase equilibria of our hypothetical RPA fluid we find it convenient to introduce the renormalized densities and chemical potentials
\[
\tilde{y}_A = \tilde{y}_A y_A, \quad \tilde{y}_B = \tilde{y}_B y_B
\]
\[
\bar{y} = (\tilde{y}_A / \tilde{y}_B)^{1/3}, \quad x = (\tilde{y}_A / \tilde{y}_B)^{1/3}
\]
\[
\bar{\mu}_A = \beta \bar{\mu}_A - \ln\left[ \lambda_i^* / \tilde{\beta} \right], \quad \bar{\mu}_B = \beta \mu_B - \ln\left[ \lambda_i^* / \tilde{\beta} \right].
\] (4.4)

From Eq. (4.1) we obtain for these activities
\[
\bar{\mu}_A = \ln \tilde{y}_A + \tilde{y}_B \left[ 1 - \tilde{y}_A F'(\tilde{y}_B) \right],
\]
\[
\bar{\mu}_B = \ln \tilde{y}_B + \tilde{y}_A \left[ 1 - \tilde{y}_B F'(\tilde{y}_A) \right],
\] (4.5)
where
\[
F(x) = \left[ 1 / 16 \pi (x) \right]^{1/2} \left[ \left( 1 + x^2 \right)^{1/2} - \left( 1 - x^2 \right)^{1/2} \right]
= (16\pi)^{-1} \sum_{n=0}^{\infty} \left( 4n + 3 \right) \left( -4n + 3 \right)^{2n} (2n + 1)^{-1}
\] (4.6)
is a function with the following properties:

(i) \(F(x) \geq 0\) \((x \leq 0 \leq 1)\),

(ii) \(F'(x) \geq 0\) \((x \leq 0 \leq 1)\),

(iii) \(F(1)\) exists and is nonzero,

(iv) \(F'(x) \to \infty\) as \(x \to 1\),

(v) \(F(0), F'(0)\) are nonzero, finite constants.

Convexity of \(\bar{\beta} a / \alpha^3\) in \(y_A\) and \(y_B\) is equivalent to the condition
\[
D_{AB} = \left[ \frac{\partial \bar{\mu}_A}{\partial \tilde{y}_A} - \frac{\partial \bar{\mu}_B}{\partial \tilde{y}_B} \right]^2 
\geq 0.
\] (4.7)

From Eq. (4.5),
\[
D_{AB} = \tilde{y}^2 \left[ 1 - \beta F'(\tilde{y}) \right] F - \tilde{y} \tilde{y} \left( x + x^2 - 1 \right) F'(\tilde{y})
- (\tilde{y})^2 F'(\tilde{y}) F'(\tilde{y}).
\] (4.8)

While this is positive for \(\tilde{y}\) sufficiently small, the coefficient of \(F'(\tilde{y})\) is negative for all \(x\) when \(\tilde{y} \leq 1\) so that, from property (iv) of \(F(\tilde{y})\), \(D_{AB}\) must become negative at some \(\tilde{y} < 1\) for any given value of \(x\). Thus the spinodal surface, at which thermodynamic stability breaks down, lies strictly outside the catastrophe surface \(\tilde{y} = 1\) and this latter surface cannot in any sense be construed as the coexistence surface. Specifically, the line \(\tilde{y}_A = \tilde{y}_B = 1\) lies in the unstable region, and cannot be taken as the plait-point curve, so the “square-root” divergence of \(c_i\) there is meaningless. (That this type of square-root divergence is nonphysical has been suspected for some time in the context of the pure fluid
liquid–vapor transition because it also arises as the first contribution in a systematic expansion scheme all higher-order terms of which are even more divergent.\(^{18}\)

Despite the catastrophically bad results given by RPA when \(\tilde{y} \geq 1\), one might optimistically hope that it would provide a reasonable description in the thermodynamically stable region where \(D_{AB} > 0\). In particular one might hope to find pairs of coexisting phases in this region, which would form a coexistence surface lying outside the spinodal and tangent to it along a plait-point curve. Such a coexistence surface would necessarily be described by classical critical exponents\(^a\)—specifically by a finite \(\epsilon_c\) at the plait-point curve—but might at least be a reasonably sensible extension of the mean field theories.

From the symmetry of the model we have chosen, one would expect this surface to be symmetric about \(y_A = y_B\) with pairs of coexisting phases \((\alpha, \beta)\) having the property that

\[
y_A^{(\alpha)} = y_B^{(\beta)}, \quad y_B^{(\alpha)} = y_A^{(\beta)} \tag{4.9}
\]

as well as the thermodynamically required

\[
\mu_A^{(\alpha)} = \mu_B^{(\beta)}, \quad \mu_B^{(\alpha)} = \mu_A^{(\beta)} \tag{4.10}
\]

Together these equations imply \(\mu_A = \mu_B\) on the coexistence surface which yields the equation

\[
(2 \ln x)/(x - 1/x) = y_0[1 - \beta F(\tilde{y})] \tag{4.11}
\]

The left-hand side of Eq. (4.11) is a nonnegative function of \(x\) on \([0, \infty]\), vanishes at \(x = 0\) and \(x = \infty\), and achieves a maximum value of 1 at \(x = 1\).

Conditions (ii) and (v) on the function \(F(\tilde{y})\) imply that there is a temperature given by \(\tilde{y} F(0) = 1\) below which there can be no solution to Eq. (4.11). For higher temperatures, solutions exist for sufficiently small (and large) \(x\), but at no temperature can there be a solution when \(x = 1\). Thus the coexistence surface becomes unstable before the coexisting phases become identical and there is no plait-point curve.

In fact, RPA implies that as an equimolar \((x = 1)\) mixture of \(A\) and \(B\) is compressed it neither splits into two phases at a plait point, nor comes into equilibrium with any other stable phase, but simply “collapses” into the disaster region, \(\tilde{y} > 1\). To see this, we note that in the absence of a plait-point curve, the only way an equimolar mixture can avoid collapsing is to come to simultaneous equilibrium with a pair of phases of higher density—one on each side of \(y_A = y_B\)—to form a three-phase region in the \(y_A y_B\) plane. From the symmetry of the free energy these two phases must lie on the coexistence surface determined above in Eq. (4.11). Along \(y_A = y_B\), the chemical potentials are

\[
\bar{\mu}_A = \bar{\mu}_B = \ln \tilde{y} + y_0[1 - \beta F(\tilde{y})] < 1, \tag{4.12}
\]

whereas on the coexistence surface we have, upon adding the (equal) expressions for \(\bar{\mu}_A\) and \(\bar{\mu}_B\) in Eq. (4.5) and making use of Eq. (4.11),

\[
\bar{\mu}_A = \bar{\mu}_B = \ln \tilde{y} + \left(1 + \frac{2x^2}{1 - x^2}\right) \ln \left(\frac{x}{1 - x}ight) \geq 1, \tag{4.13}
\]

Since the largest value of \(\bar{\mu}_A\) on the symmetry line is less than the smallest value on coexistence curve, there can be no three-phase equilibrium, and the equimolar solution will remain homogeneous until the stability criterion is violated and it collapses into the disaster region. By continuity, solutions which are sufficiently close to equimolar must exhibit the same behavior. Thus RPA fails to predict sensible phase equilibrium behavior even when supplemented by a Maxwell construction approach.

The results we have obtained may be summarized as follows. The RPA free energy predicts a surface in temperature-composition-density space (the “catastrophe” surface) at which the heat capacity \(c_v\) diverges with a square-root law. Inside this surface (higher densities, lower temperatures) the free energy predicted by RPA is negligibly infinite. This is precisely the surface Deutch and Zwanzig identify as the coexistence surface. Lying strictly outside the catastrophe surface is the spinodal surface at which thermodynamic stability breaks down. The entire catastrophe surface lies on the interior of the unstable region. For some temperature and composition ranges there exists a stable coexistence surface, but at no temperature is there a stable plait point. At every temperature there is a range of compositions, near equimolar, which upon compression do not separate into stable phases, but remain homogeneous until the spinodal surface is reached. Upon further compression, the system becomes unstable and can lower its free energy indefinitely by collapsing into the region of negatively infinite free energy.

The existence of a nonphysical region in which the free energy is unbounded is not, in itself, particularly upsetting. If a stable coexistence surface completely surrounded this region, one could discard the nonphysical behavior and choose for the free energy inside the coexistence curve a linear interpolation between its values in the coexistent phases. This would lead to a thermodynamically consistent description of a fluid. However, the fact that the coexistence surface, when it exists at all, does not completely surround the catastrophe region is a very serious failure of RPA, for it means that no sensible description can be obtained from RPA for the simple and easily understood model of a binary fluid proposed in Sec. II.

We deliberately chose a particularly simple model potential energy of interaction so that a complete analysis of the thermodynamic behavior would be tractable, and it is natural to ask if some minor modification in the model might restore physical sense to RPA. The answer appears to be no (see Sec. VI, how-
ever). The model may be modified in several ways without changing our results in any essential way. First, our results are quite insensitive to the specific form of the pair potential \( u(r) \): An exponential or Gaussian will lead to identical conclusions. Indeed, any nonnegative potential for which the Fourier transform \( \hat{d}_a(k) \) falls off as rapidly as \( 1/k^2 \) for large \( k \) and varies as \( A - Bk^2 \) for small \( k \) will approach \( A + Bk^2 \) for both positive and \( B \) finite values result in a new function \( F(R) \) in Eq. (4.6) but one which obeys conditions (i)–(v), from which all of our conclusions on stability and coexistence of phases follow. Thus, for example, the catastrophe is not due to the divergence of the Yukawa potential at \( r = 0 \).

Second, if in addition to the repulsive potential between \( A \)'s and \( B \)'s, a shorter-ranged Fourier-transformable repulsive potential is introduced which acts between every pair of particles, and the total potential energy is treated by RPA, the free energy can again be obtained in terms of an explicit integral. There is still a “catastrophe region” and it is easy to show that along the line \( \rho_A = \rho_B \) the compressibility becomes negative and diverges to \( -\infty \) as the catastrophe region is approached, whereas \( [\delta^2/\delta(\rho_A - \rho_B)^2]_{\rho_A = \rho_B} \) remains positive. A proof that no three-phase region can exist is mathematically intractable, but such behavior would be highly unphysical for a system with these potentials.

Third, if the molecules \( A \) and \( B \) are taken to be hard spheres with identical radii with an additional repulsion between \( A \)'s and \( B \)'s, an RPA free energy may be obtained by taking the averages in Secs. II and III over the allowed states of a reference system in which only the hard-core repulsions are present (see comments at the end of Sec. II). Here the RPA is the more general one in which the reference system is a hard-core fluid rather than the ideal gas. The formulas which relate the RPA free energy to the reference system and the perturbation are given in Ref. 13. The free energy in RPA is that of the hard-core reference system plus the mean field result, \( \beta F(0) \rho_A \rho_B \), plus an integral involving the repulsive potential between \( A \)'s and \( B \)'s and the two-particle distribution function \( g_0(r) \) for the hard-core reference system. By assuming that the Fourier transform of \( g_0(r) \) is nonsingular (which is reasonable as long as the reference system does not exhibit a phase transition in the thermodynamic region of interest), it can be shown here too that a catastrophe region exists and that along the line \( \rho_A = \rho_B \) the compressibility becomes negative and diverges to \( -\infty \) as the catastrophe region is approached while \( [\delta^2/\delta(\rho_A - \rho_B)^2]_{\rho_A = \rho_B} \) remains finite. Thus, including a short-ranged repulsion between all particles does not prevent the catastrophe in RPA.

V. THERMODYNAMIC BEHAVIOR OBTAINED FROM THE COMPRESSIBILITY THEOREM

In Secs. III and IV, we obtained the thermodynamic behavior of the model system by evaluating the Helmholtz free energy from the partition function in RPA. There are, however, other ways by which we might have arrived at the thermodynamics. In this section we use the compressibility theorem, which relates the fluctuations in density of the components to thermodynamic derivatives of densities with respect to chemical potentials. If the statistical mechanics is done exactly, two different methods of extracting the thermodynamics give identical results, but within RPA they need not. We shall now show that, in contrast to our first procedure, the use of the compressibility theorem leads to mean field results only with no additional contribution due to RPA. In particular no anomalous specific-heat singularity is observed.

Define the generalized “compressibility” \( \chi_{AB}(k) \)

\[
\chi_{AB}(k) = V^{-1} \langle q_A(k) q_B(-k) \rangle,
\]

\[
= \langle q_A(k) q_B(-k) \rangle \prod_{k'} \langle S(k') \rangle / \langle S(k) \rangle V,
\]

where \( \langle \cdot \rangle \) denotes total canonical ensemble average defined by the second equality. The compressibility theorem then states, as a rigorous equality, that

\[
\lim_{k \to 0} \chi_{AB}(k) = (\partial \rho_A / \partial \beta \mu_A)_{\mu_A T} - (\partial \rho_B / \partial \beta \mu_B)_{\mu_B T}.
\]

The quantities \( \chi_{AA}(k) \) and \( \chi_{BB}(k) \) are defined analogously by taking the thermodynamic average of \( q_A(k) q_A(-k) \) and \( q_B(k) q_B(-k) \), and they become equal in the limit of zero \( k \) to derivatives of \( \rho_A \) with respect to \( \beta \mu_A \) and of \( \rho_B \) with respect to \( \beta \mu_B \). In RPA we make the approximation of taking the product over \( k' \) outside the average in both numerator and denominator of Eq. (5.1). A straightforward extension of the methods presented in Sec. III yields for RPA

\[
\chi_{AB}(k) = -\beta (\beta^2 + 1) A_{AB}(k) \rho_A \rho_B / (1 - \beta^2 A_{AB}(k) \bar{\rho} A_{AB}(k) P) \]

or, in the notation introduced in Eq. (3.16),

\[
(\partial \rho_A / \partial \beta \mu_A)_{\mu_A T} = (\partial \rho_B / \partial \beta \mu_B)_{\mu_B T} = -\bar{\beta} y_A y_B / (1 - \bar{\beta}^2 y_A y_B).\]

Similarly, one finds

\[
(\partial \rho_B / \partial \beta \mu_A)_{\mu_A T} = (\partial \rho_B / \partial \beta \mu_B)_{\mu_B T} = -\bar{\beta} y_B y_B / (1 - \bar{\beta}^2 y_B y_B).\]

These relations are easily inverted using Jacobians to give the derivatives of the chemical potentials with respect to densities. The results are

\[
(\partial \beta \mu_A / \partial y_A)_{y_A T} = 1 / \bar{\mu} A,
\]

\[
(\partial \beta \mu_B / \partial y_B)_{y_B T} = 1 / \bar{\mu} B,
\]

\[
(\partial \beta \mu_A / \partial y_B)_{y_B T} = -\bar{\beta} y_A y_B / (1 - \bar{\beta}^2 y_A y_B),\]

from which we deduce

\[
\beta \mu_A = \beta \mu_A^0(T) + \ln y_A + \bar{\beta} y_B,
\]

\[
\beta \mu_B = \beta \mu_B^0(T) + \ln y_B + \bar{\beta} y_A,
\]
where \(\mu^A_0(T)\) and \(\mu^B_0(T)\) are nonsingular functions of \(T\) only which are determined by the ideal gas behavior of pure \(A\) and \(B\) at zero density. These equations are the mean field result and lead to classical behavior at a stable critical locus.

It is worth emphasizing that the behavior of the heat capacity, \(c_{eq}\), is determined to within a nonsingular function of \(T\) alone by Eq. (5.7) through the identities

\[
\left(\frac{\partial g_{AB}}{\partial \mu_A}\right)_{\rho_B T} = T\left(\frac{\partial \mu_A}{\partial T}\right)_{\rho_B T},
\]

\[
\left(\frac{\partial g_{AB}}{\partial \mu_B}\right)_{\rho_A T} = T\left(\frac{\partial \mu_B}{\partial T}\right)_{\rho_A T}.
\]

Provided that each pure component approaches ideal-gas behavior at low densities, there can be no possible singularity in \(c_{eq}\) as the plait point is approached except for the finite discontinuity arising from the mean field equations [Eqs. (5.7)].

As is the case with the thermodynamic behavior predicted from the free energy, the results we derived here from the compressibility theorem are a feature of RPA and not the particular model. The application of the general RPA to various two-component and one-component models which should exhibit phase transitions yield the same mean field type results when the compressibility theorem is used.

It might be tempting to the unwary to obtain the coexistence surface from the compressibility theorem through Eqs. (5.7), and then investigate \(c_{eq}\) by using the free energy obtained in Sec. III. This would lead to the conclusion that \(c_{eq}\) diverges at each point along the critical curve. This is inconsistent with the second law of thermodynamics, however, and is the result of having used two different free energies for one system. We note that precisely such arguments are responsible for the assignation of a square root divergence of \(c_{eq}\) and \(\chi_{eff}\) in RPA and GPT theories of single component critical points as well as for the infinite \(c_{eq}\) of Ref. 1, so that these results should be viewed with considerable skepticism.

**VI. REASON FOR THE CATASTROPHSE**

In this section we examine why RPA has the catastrophe discussed in Sec. III.

Consider the radial distribution function \(g_{AB}(r)\) between species \(A\) and \(B\). It is related to the free energy by a functional derivative,

\[
g_{AB}(r) = [\rho_B \mu_B]^{-1}\left[\frac{\delta \left(\beta \Delta A/V\right)}{\delta \mu_{AB}(r)}\right].
\]

By applying Eq. (6.1) to the RPA free energy for the simple binary fluid considered in Secs. II and III, we find

\[
g_{AB}(r) \mid_{\text{RPA}} = 1 - \left[\frac{1}{(2\pi)^2}\right] \int \delta \mu_{AB}(k) \times \left[1 - \beta^2 \rho_B \mu_B \delta \mu_{AB}(r)\right] \exp(-i k \cdot r) d\mathbf{k}.
\]

For the Yukawa potential in Eq. (2.3), the integral over wave vectors can be performed analytically.

Among other things, it is found that

\[
g_{AB}(r) \mid_{\text{RPA}} \rightarrow \pm \infty \quad \text{as} \quad r \rightarrow 0.
\]

This result is obviously unphysical. Since \(g_{AB}\) plays the role of a probability function, it must be positive. Furthermore, since the Yukawa potential becomes infinite (and positive) as \(r \rightarrow 0\), \(g_{AB}\) should approach \(0^+\) as \(r \rightarrow 0\).

We believe that the physically improper description of the short-ranged correlation is responsible for the RPA catastrophe. When the density becomes high enough that a significant number of configurations sample the short-ranged correlations, an incorrect description of these correlations may produce the catastrophic result obtained when \(\rho_B \mu_B \geq (\beta \mu(0))^{-1}\). This can be understood mathematically by considering a "test" system in which the pair potential is \(\lambda \mu_{AB}(r), 0 \leq \lambda \leq 1\). If \(g_{AB}(r, \lambda)\) is the radial distribution function in the test system, then differentiation and integration of the canonical partition function proves that

\[
\frac{\beta \Delta A}{V} = \rho_B \mu_B \int_0^1 d\lambda \int d^3r g_{AB}(r, \lambda) \mu_{AB}(r).
\]

If the RPA is used to yield \(g_{AB}(r, \lambda)\), as in Eq. (6.2), the \(\lambda\) integration of (6.4) produces the free energy given in Eq. (3.13). Equation (6.4) seems to provide a connection between the perverse behavior of \(g_{AB}\) exhibited in Eq. (6.3) and the RPA catastrophe in the free energy.

If the catastrophe is the result of the unphysical description of the short-ranged correlations, then it is reasonable to guess that the catastrophe could be avoided when proper account of these correlations is made. This is also suggested by unpublished work communicated to us by J. D. Weeks in which he considered a one-component fluid in which the pair interactions are hard-core repulsions, \(u^\alpha\), plus an attractive perturbation \(u\). Such a model should exhibit a liquid-gas phase transition. The appropriate RPA for this model is the general one in which the averages are taken over the allowed states in the hard-core reference system (see Ref. 13 and comments at the end of Sec. II). Due to the hard cores, we know that \(g(r) = 0\) for \(r < \sigma\) where \(\sigma\) is the hard-core diameter. But when RPA is applied in a straightforward manner, it is found that \(g(r) \rightarrow \pm \infty\) as \(r \rightarrow 0\) for this system. [This curious behavior is ascertained from the formula for the RPA \(g(r)\) cited in Appendix B and derived in Ref. 13.] Furthermore, a catastrophe line exists (identified by Broust as the limit of stability for the model). However, the physically correct condition

\[
\frac{2}{\rho^2} \left(\frac{\delta \left(\beta \Delta A/V\right)}{\delta \mu_{AB}(r)}\right) = g(r) = 0, \quad r < \sigma
\]

can be imposed on the RPA. This is done by forcing the RPA free energy to be stationary with respect to variations of the perturbation for distances smaller than \(\sigma\). When this procedure is applied numerically
to the particular system in which the perturbation is 
the attractive portion of the Lennard–Jones potential 
the following results are obtained: (1) By making 
Eq. (6.5) a supplementary condition to RPA, the RPA 
free energy is finite for all fluid densities. That is, 
the excluded volume condition “erases” the RPA cata-

trophe. (2) A Maxwell construction can be performed. 
The results obtained are classical. For example, near 
the critical point, the coexistence curve predicted by 
RPA in the temperature density plane is quadratic (rather 
than cubic).

Thus, it does seem reasonable that the RPA cata-

trophe is intimately related to the extremely unphysi-

cal description of short-ranged correlation usually 
afforded by RPA. In light of the usual justification 
for RPA, we find this tentative relationship interesting. 
Most workers have used RPA (in one guise or 

another) to describe phase transitions argue that des-

pite any incorrect predictions of short-ranged corre-

lations, RPA may describe the long-ranged correla-

tions correctly, and it is the nature of these latter correlations 
only that determine the nature of the critical singulari-

ties. One conclusion of the calculations presented in 
this paper is that this justification for RPA is not correct.

ACKNOWLEDGMENTS

We are grateful to J. M. Deutch for pointing out the 
thermodynamically inconsistent result in his van der 
Waals model calculations. A conversation between 
Dr. Deutch and one of us (J.C.W.) motivated this 
work. We thank J. D. Weeks for allowing us to quote 
results of his unpublished work and D. Shallit in for 
a valuable observation on the bounds in Eq. (3.7). We 
are also grateful to the Department of Chemistry, 
Harvard University, for its hospitality during the 
period in which this work was started.

APPENDIX A

We establish here the result quoted in Eq. (3.5). 
The average \( \langle a^*_n(k) a^*_n(-k) \rangle \) may be written in the 
form

\[
\langle a^*_n(k) a^*_n(-k) \rangle = \sum_{i_1=1}^{N_A} \cdots \sum_{i_{n-1}=1}^{N_A} \sum_{j_1=1}^{N_A} \cdots \sum_{j_{n-1}=1}^{N_A} V^{-N_A} \\
\times \int_V \prod_{i=1}^{N_A} \exp[ik \cdot (r_{i1} + \cdots + r_{in} - r_{j1} - \cdots - r_{jn})].
\]

(A1)

For any particular choice of \( i_1 \cdots i_n, j_1 \cdots j_n \), the 
integral in this sum will vanish unless the ordered row 
\( i_1 \cdots i_n \) can be rearranged to give the ordered row 
\( j_1 \cdots j_n \), in which case the contribution is exactly unity.

Thus \( \langle a^*_n(k) a^*_n(-k) \rangle \) is the number of distinct 
(ordered) pairs of ordered \( n \)-tuples \( (i_1 \cdots i_n; j_1 \cdots j_n) \), 
where the \( i \)'s and \( j \)'s are chosen from the integers 
\( 1, \cdots, N_A \), such that when viewed as unordered sets 
the \( n \)-tuples are the same. This number may be ob-
tained as follows. Suppose that in one such choice of 
the \( i \)'s and \( j \)'s there are \( f_l \) of the \( n \) indices equal to 
\( l \) \( (l=1, \cdots, N_A) \). Then

\[
\sum_{l=1}^{N_A} f_l = n,
\]

(A2)

and the number of distinct ways of displaying these as 
an ordered array is

\[
\frac{n!}{\prod_{l=1}^{N_A} f_l}.
\]

The number of distinct pairs of arrays is the square 
of this number summed over all choices of the set \( \{ f_l \} \) 
subject to (A2); that is,

\[
\langle a^*_n(k) a^*_n(-k) \rangle = \sum_{\{ f_l \}} (n! / \prod_{l=1}^{N_A} f_l)^2
\]

(A3)

in the notation of Sec. III, which is identical to Eq. (3.5).

APPENDIX B

In this Appendix we argue that the RPA as defined 
in Sec. II is equivalent to GFT. We consider a one-
component system (the generalization to two 
components is straightforward) and the general RPA in 
which \( \Delta A \) is the excess free energy with respect to that 
of a reference system with pair interactions \( u(r) \). The 
Fourier transform of the perturbation is \( \hat{u}(k) \).

We define the functions (see text for supplementary 
definitions)

\[
X_2(k) = \langle \langle q(k) \rangle^2 \rangle,
\]

and

\[
X_4(k_1, k_2) = \langle \langle q(k_1) \rangle^2 \langle q(k_2) \rangle^2 \rangle
\]

\[
- \langle \langle q(k_1) \rangle \langle q(k_2) \rangle \rangle \langle \langle q(k_1) \rangle \langle q(k_2) \rangle \rangle.
\]

(B1)

These functions are related to the free energy by the 
identities

\[
[\partial - \beta \Delta A / \partial \beta \hat{u}(k)] = X_2(k) / V
\]

and

\[
[\partial^2 - \beta \Delta A / \partial \beta \hat{u}(k_1) \partial \beta \hat{u}(k_2)] = X_4(k_1, k_2) / V^2.
\]

(B2)

A direct consequence of the quadratic functional form 
for \( \Delta A \) used in GFT is that

\[
X_4(k_1, k_2) = X_2(k_1) \langle \delta_{k_1, k_2} + \delta_{k_1, -k_2} \rangle.
\]

(B3)

where \( X_2(k) \) is frequently expressed in the form

\[
X_2(k) \equiv V / [1 - \rho C(k)]
\]

(B4)

and \( C(k) \) is the Fourier transform of what is usually 
called the direct correlation function. If GFT is to obey 
the identities (B2) and simultaneously (B3), then 
\( X_2(k) \) must satisfy a differential equation, the unique 
solution to which yields

\[
\rho C(k) = -\beta \rho \hat{u}(k) f(k) + g(k),
\]

(B5)

where \( f \) and \( g \) must be independent of the perturbation 
\( u(r) \). As a result, these functions can be determined
by noting that
\[ \chi_{\text{exact}}(k) \rightarrow N / [1 + \beta \rho \theta(k) - \rho C_\theta(k)] \]
as \( \alpha(k) \rightarrow 0. \)
\[ \text{(B6)} \]

Here \( C_\theta(k) \) denotes the Fourier transform of the direct correlation function in the reference system. Thus, if we require the GFT \( \chi_\theta(k) \) to obey (B6), we can make the identification
\[ f(k) = 1, \quad g(k) = \rho C_\theta(k). \]
\[ \text{(B7)} \]

By combining Eqs. (B4), (B5), and (B7) we obtain an equation for \( \chi_\theta(k) \) which is the general RPA formula:
\[ \chi_\theta^{RPA}(k) = N[1 + \beta \rho \theta(k) - \rho C_\theta(k)]^{-1}. \]
Thus, we have proved the GFT implies RPA.

The proof that RPA implies GFT follows from the formula for \( \chi_\theta^{RPA}(k) \) [or \( \Delta A_{RPA} \), which is obtained from \( \chi_\theta^{RPA}(k) \) by functional integration]. In particular, the application of the identities given in Eq. (B2) and similar formulas relating higher-order moments to higher-order derivatives of \( \Delta A \) yields in RPA
\[ \left( \prod_{i=1}^{\alpha} \left| q(k_i) \right| \right)^{\sigma} = \prod_{j=1}^{\alpha} \left| q(k_j) \right|^{\sigma} \]
\[ \text{(B8)} \]
where the product is over different wave vectors: \( k_i \neq \pm k_j \) and \( 1 \leq i, j \leq n \). Furthermore, it follows from the definition of RPA that all "odd" moments, such as \( \langle q(k_1)q(k_2)q(k_3) \rangle \), are zero in RPA since \( q(k) \)'s with different wave vectors are uncorrelated in that approximation and the symmetry in an isotropic system requires that \( \langle q(k_1)q(k_2) \cdots q(k_n) \rangle \) is zero unless \( k_1 + k_2 + \cdots + k_n = 0 \). (These facts are derivable as simple extensions of results cited in the literature.)

Thus, all the moments are specified in RPA. The only probability distribution for \( q(k) \) consistent with these moments is the GFT distribution (see, for example, Refs. 5 and 8). Since GFT amounts to nothing more or less than the specification of the GFT distribution for \( q(k) \), RPA implies GFT.

We point out that the arguments used above to prove that GFT implies RPA hinge on the requirements that GFT obey Eqs. (B2) and (B6). It is possible that one might want to claim that GFT need not obey these rigorous identities. In the proof that RPA implies GFT, we have assumed that the RPA free energy is well behaved in the thermodynamic limit. Thus the proof is valid for thermodynamic states outside of the RPA catastrophe region only.

* This research was supported by the National Science Foundation Grant GP 15429, and the American Chemical Society Petroleum Research Fund.


2 K. D. Mountain and R. Zwanzig, J. Chem. Phys. 48, 1451 (1968); R. D. Mountain, J. Phys. 52, 3852 (1970). Mountain argues in the second reference that the \( c_n \sim (T - T_\text{c})^{-n} \) predicted by GFT is due to an incorrect feature of the GFT prediction of correlations, and thus the prediction is probably not correct.

3 The calculations presented in Refs. 1 and 2 are presented therein as extensions of the interesting paper by N. G. van Kampen, Phys. Rev. 135, A362 (1964).


11 This restriction has recently been removed by C. Cohen and J. M. Deutch (Ref. 10). They find that this removal does not avoid the thermodynamic inconsistency found by Deutch and Zwanzig (Ref. 1).


16 It would arise from a Maxwell construction on a free-energy analytic at the critical point. For a discussion of such theories, see M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967).

17 J. D. Weeks (unpublished).