Critical Solution Behavior in a Binary Mixture of Gaussian Molecules

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(Received 10 June 1964)

We have examined in detail the cluster expansion for the mixing free energy of molecules whose repulsive interactions give rise to Ursell–Mayer cluster bonds of Gaussian form. By choosing the Gaussian width for unlike molecular pairs in a binary solution to exceed a common width assignment for like pairs, the resultant positive mixing free energy can produce phase separation at sufficiently high over-all density. Using the exact evaluation technique for any Gaussian cluster integral of arbitrary complexity, the set of free-energy contributions involving clusters of up to five particles were calculated and treated as input in a Padé approximant to estimate the width-ratio-dependent critical density. In the large unlike-to-like width-ratio limit, only the relatively restricted class of clusters corresponding to "bicolored" graphs needs to be considered, and the free-energy calculation may be easily extended to eight-particle clusters. A Padé analysis of the second composition derivative of free energy (related to composition fluctuations and solution turbidity in the critical region) yields results at variance with simple solution theories, but of the same type that may by analogy be inferred from recent three-dimensional Ising model susceptibility numerical analyses. A list is appended of the multiply connected mixture graphs through five points and bicolored graphs through eight points.

I. INTRODUCTION

THE only exact information available on models for cooperative behavior which are at all closely allied to physical systems exhibiting phase change, stems from the rigorously soluble two-dimensional Ising models. The fact that thermodynamically significant quantities (e.g., specific heat, susceptibility, long-range order) predicted by these soluble models exhibit singularities, at the critical point, of types unheralded by simple approximate theories, has continued to provide a challenge to the insight and ingenuity of theoreticians interested in the broader problem of critical phenomena.

Recently, several clever numerical analyses, some of which have employed the Padé approximant method, have succeeded in obtaining excellent estimates of the analogous three-dimensional model critical singularities. Undoubtedly these results will have considerable value in providing guidelines for future theory.

Although the Ising models doubtlessly provide an excellent description of binary alloy order–disorder mixing behavior, there is room for skepticism as to how closely their critical region predictions should apply even qualitatively to binary liquid solutions. Thus, one wishes to know to what extent freeing particle centers from a rigid space lattice might modify the nature of corresponding critical singularities.

This paper is therefore devoted to an exposition of a model fluid binary solution which exhibits a critical point for phase separation. The leading terms in the cluster series for the mixing free energy have been evaluated exactly, and the results for the second composition derivative of free energy (at the critical composition) have been analyzed by the Padé approximant method. This quantity's inverse has thus been shown to possess critical singular behavior of a branch point type, similar to that of the Ising model analog: the susceptibility.

It is therefore our conclusion that currently available approximate solution theories need fundamental revisions, so as to produce the correct critical region predictions, since for at least the one quantity investigated here, they are definitely in error.

In the following section we discuss the thermodynamics involved in the phase separation of a binary mixture, and present the Mayer cluster-theoretic formulas by which this phenomenon may be analyzed. The difficulty associated with such an analysis is twofold. First, the cluster integrals entering into the theory are usually difficult to evaluate. One model for which this is not the case is the system of Gaussian molecules,[1] i.e., a system for which the Mayer f function is taken to be a negative Gaussian. In the Ising model studies it is found that the nature of the critical point branch points is independent of certain features of the specific model, viz., independent of lattice type for a given dimensionality. Therefore, it is felt that in spite of certain nonphysical features, the Gaussian model should be investigated since the nature of the critical singularities may not be strongly potential dependent.[2] The second difficulty which is frequently encountered in a cluster analysis is the construction of the required diagrams. This problem is particularly acute for the binary mixture. Therefore, in addition to the necessarily limited analysis of the general Gaussian mixture presented below, a more extensive analysis has been made of a special limit in which the interactions be-

[1] (a) E. W. Montroll, T. H. Berlin, and R. W. Hart, *Changement de Phases* (Société de Chimie Physique, Presses Universitaires de France, 1952), p. 211. (b) G. E. Uhlenbeck and G. W. Ford in *Studies in Statistical Mechanics*, edited by J. DeBoer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962), Vol. 1, p. 123.
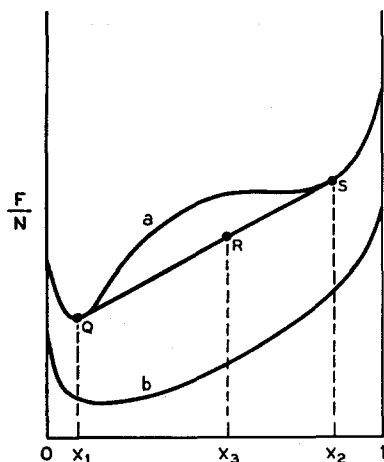
[2] M. F. Sykes and N. Dalton (to be published).

FIG. 1. Helmholtz free-energy curves (Curve a: high over-all density; Curve b: low over-all density) and the double tangent construction (Line QRS) for a general binary fluid mixture exhibiting phase separation.

tween molecules of unlike species are of long range compared with the interactions of like molecules. In passing to this limit we do not expect to encounter the limitations at the critical point which beset the cluster analysis of systems, all of whose forces are long range *and* weak.[3]

II. PHENOMENOLOGY

The phase stability of thermodynamic systems is determined by the free energy. Consider a binary system such that, in some sense, interactions between molecules of unlike species are energetically less favorable than between likes. Since it is the free energy which determines the state, it is possible that under certain conditions entropy of mixing will more than compensate the mixing energy term and a homogeneous state will result. Under other circumstances, however, a phase separation occurs. The three independent variables in the system are temperature, total density ρ, and composition (mole fraction). For reasons inherent in the Gaussian molecule model it is preferable in all that follows to consider temperature as a fixed variable and study changes induced by variation of the other two quantities.

Frequently statistical thermodynamic theories will yield values of the Helmholtz free energy F at all densities and mole fractions, even in thermodynamically unstable regions. That is the case in the present work. The thermodynamically stable situation is then determined by finding the state with minimum free energy. There is a well-known construction, called the double tangent construction, which facilitates this calculation.[4] Two schematic plots of free energy versus

[3] R. Brout, Phys. Rev. **118**, 1009 (1960); **122**, 469 (1961); P. C. Hemmer, J. Math. Phys. **5**, 75 (1964).

[4] J. S. Rowlinson, *Liquids and Liquid Mixtures* (Academic Press Inc., New York, 1959).

composition are given in Fig. 1. For Curve 1(a) it is possible to draw a double tangent, line QS. For any over-all composition between x_1 and x_2 the system will divide into two phases of composition x_1 and x_2. Actually no use has been made of the calculated free energy between Q and S, and so no questions regarding the validity or significance of the calculation in this region need be asked. For densities such that a curve like 1(b) applies, the system is homogeneous for all compositions.

A great deal of conceptual and computational simplicity is introduced by imposing a certain symmetry on the system: The interaction potential between two molecules of Type A is taken to be identical with that between two B's. In this case the free energy (now on a per particle basis) as a function of composition at various densities may appear as in Fig. 2. It is convenient in this symmetric case to introduce a new composition variable $y = 2x_A - 1$ which varies from -1 to $+1$. The free-energy curve always has an extremum at equimolar composition, $y = 0$. A double tangent construction is only possible if this extremum is a maximum. Thus the critical density is that ρ at which the second derivative of the free energy with respect to composition $(\partial^2 F / \partial y^2)_\rho$, vanishes (i.e., the extremum goes from a minimum to a maximum and two new minima develop at nonzero y). The object of our research is analysis of the manner in which this second derivative vanishes as a function of density as the critical density is approached from the single-phase side (low density).

Aside from the thermodynamic implications of the local shape of the F, y, ρ surface in the region of the critical point, the vanishing of the $(\partial^2 F / \partial y^2)_{\rho,V,T}$ leads to large composition fluctuations and hence critical opalescence. In order to examine this phenomenon let us consider the relation, as given by the Kirkwood–
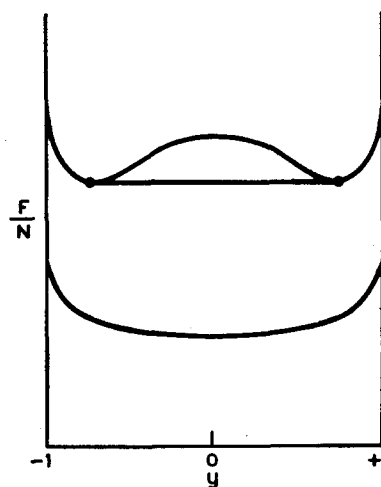

FIG. 2. Symmetrical version of Fig. 1 applicable to the Gaussian mixture model investigated in this article.

Buff[5] solution theory, between the second composition derivative of free energy and the radial distribution functions, $g_{ij}(r)$, between a pair of molecules of Species i and j

$$\frac{1}{NkT}\left(\frac{\partial^2 F}{\partial y^2}\right)_{\rho,V,T} = \frac{2+\rho[(1+y)^2 Q_{AA}+2(1-y^2)Q_{AB}+(1-y)^3 Q_{BB}]}{(1-y^2)+\rho(1-y)^2[(1+y)Q_{AA}+(1-y)Q_{BB}]+\rho^2(1-y^2)[Q_{AA}Q_{BB}-Q_{AB}^2]}, \quad (2.1)$$

where $N=N_A+N_B$,

$$Q_{ij}=\int [g_{ij}(r)-1]d\mathbf{r}$$

$$= V\left[\frac{\langle (N_i-\langle N_i\rangle)(N_j-\langle N_j\rangle)\rangle}{\langle N_i\rangle\langle N_j\rangle} - \frac{\delta_{ij}}{\langle N_i\rangle}\right], \quad (2.2)$$

and $\langle\ \rangle$ indicates grand canonical ensemble averages.

The intensity of light scattering in the limit of zero angle $I(0)$ is also proportional to an expression involving the Q's.

$$I(0) \propto f_A^2(1+y)^2 Q_{AA}+2f_A f_B(1-y^2)Q_{AB}$$
$$+f_B^2(1-y)^2 Q_{BB}, \quad (2.3)$$

where f_i is the scattering factor for a molecule of Species i. The inverse of $I(0)$ may be expected to have the same type of zero as a function of $\rho-\rho_c$ as is found for $(\partial^2 F/\partial y^2)_{\rho,VT}$ because of its common relation to the singularity of the Q's.

This identification of branch point singularities provides a convenient bridge between the present theory and experimental solution chemistry. It is preferable to study simple solutions such as carbon tetrafluoride–methane or fluoroform–xenon[4] so as to avoid extraneous effects associated with the internal degrees of freedom.

III. CLUSTER EXPANSION FOR THE HELMHOLTZ FREE ENERGY

Our study is based on a consideration of the density expansion for the Helmholtz free energy of a system

of N_A particles of A and N_B of B, $(N_A+N_B=N)$. The Mayer cluster theory (suppressing internal degrees of freedom) gives[6]

$$F/NkT=\tfrac{3}{2}\sum_{i=A,B}(N_i/N)\log(h^2/2\pi m_i kT)-1+\log\rho$$

$$+\tfrac{1}{2}(1-y)\log\tfrac{1}{2}(1-y)+\tfrac{1}{2}(1+y)\log\tfrac{1}{2}(1+y)$$

$$-\sum_{n_A,n_B\geq 0}\rho^{n_A+n_B-1}[\tfrac{1}{2}(1+y)]^{n_A}[\tfrac{1}{2}(1-y)]^{n_B}C(n_A,n_B). \quad (3.1)$$

$C(n_A,n_B)$ is a sum of cluster integrals corresponding to the labeled irreducible graphs $G_{n_A n_B}$ containing n_A vertices of type A and n_B vertices of type B

$$C(n_A,n_B)=\frac{1}{n_A!n_B!V}\sum_{G_{n_A n_B}}\int d\mathbf{r}_1\cdots d\mathbf{r}_{n_A+n_B}\prod_{G_{n_A n_B}}f_{ij}, \quad (3.2)$$

where the product is over such pairs ij as are connected by a bond in the graph $G_{n_A n_B}$. The Mayer f function is related to the potential of interaction $u_{ij}(r)$ between a pair of molecules of Species i and j by

$$f_{ij}(r)=\exp[u_{ij}(r)/kT]-1. \quad (3.3)$$

Symbolically the equation for the free energy may be written

(3.4)

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[5] J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **19**, 774 (1951).
[6] H. L. Friedman, *Ionic Solution Theory* (Interscience Publishers, Inc., New York, 1962), wherein a comprehensive set of references to the original literature may also be found.

The series is written in terms of unlabeled graphs. The fractions preceding the graphs are the inverse of the symmetry number (the order of the group) of each graph.

IV. GAUSSIAN MODEL

For real molecular potentials the cluster integrals are extremely difficult to evaluate when more than two or three vertices are involved. It has been realized in recent years that many problems in the fluid state are primarily associated with the packing geometry of the molecules, which is largely determined by the hard cores. Thus considerable attention has been directed to the rigid-sphere model, but even for this simplified interaction the cluster integrals are rather difficult to calculate.

Montroll, Berlin, and Hart[1] have pointed out that if the Mayer f function is written as the negative of a Gaussian then the cluster integrals are easily determined. This represents a purely repulsive potential and one a great deal "softer" in the sense of rapidity of rise of the repulsion than the rigid-sphere potential or even the inverse twelfth power. Proposals for modifications which add an attractive part to the potential[7] soon increase the number of steps involved in the calculation beyond practical limits; thus it is difficult to employ these modifications for a discussion of the liquid–gas transition.

Extensive studies of the thermodynamic properties and the pair correlation function[8] of a single-component system of Gaussian molecules have been carried out. Because the interactions are purely repulsive no liquid–gas transition is possible. This interaction can, however, lead to immiscibility in a mixture. Let us assume that the $A-A$ and $B-B$ interactions are such that

$$f_{AA}(r) = f_{BB}(r) = -\exp(-r^2) \qquad (4.1)$$

(the width of the Gaussian defines the unit of distance). The interaction between unlike molecules leads to

$$f_{AB} = -\exp(-\alpha r^2). \qquad (4.2)$$

For $0 < \alpha < 1$ the potential energy of an unlike pair is greater than that of a like pair, for a given distance. A phase separation, as discussed above, may occur.

The reason that the cluster integral corresponding to each graph is tractable for this Gaussian f function is that the product of f functions which forms the integrand becomes a multidimensional Gaussian form, and thus the integral is expressible in terms of a determinant. This determinant is formed in the following way. First construct a matrix M which for a p point graph is $p \times p$. For the off-diagonal elements $(i \neq j)$

let $M_{ij} = 0$ if the points i and j are not connected by a bond in the graph; let $M_{ij} = -1$ if i and j are connected and are a like pair (A–A or B–B); let $M_{ij} = -\alpha$ if i and j are connected and are an unlike pair (A–B). For the diagonal elements let M_{ii} be equal to the number of like bonds terminating at point i plus α times the number of unlike bonds, thus,

$$M_{ii} = -\sum_{j=1 \neq i}^{p} M_{ij}. \qquad (4.3)$$

By this definition the matrix M is singular but if the graph is connected the principle minors are nonsingular, and are all equal. Let us call the determinant representing one of the principle minors D. It is a generalization of the so-called graph complexity.[1b] D is a polynomial of degree $p-1$ in α, in general. The coefficient of α^n is the number of spanning Cayley trees with n unlike bonds which can be constructed from the bonds of the graph.[9] With these Gaussian f bonds it is easily shown that

$$\frac{1}{V}\int d\mathbf{r}_1 \cdots d\mathbf{r}_p \prod_G (-f_{ij}) = \pi^{\frac{3}{2}(p-1)} D^{-\frac{3}{2}}. \qquad (4.4)$$

V. LIMIT OF STRONG REPULSION BETWEEN UNLIKE PAIRS

A practical limitaton on the extent to which the coefficients of the density series for the free energy can be calculated is the difficulty of determining the graphs which enter. We have listed the mixture graphs of up to five points. As we see in the following section this is apparently inadequate, and it is questionable whether even going to six points would be sufficient. Going to seven points represents a major research problem and can only be contemplated in terms of clever application of a computer, since several thousand diagrams are probably involved.

There is one model limit for which it is possible, with a reasonable amount of effort, to obtain a significant extension of the density series for the free energy. Assume that the repulsion between unlikes is much stronger than between likes. Then the most important graphs of the cluster series are those which have bonds only between unlike vertices. These are called bicolored graphs, because the vertices can be colored with two colors in such a way that no two points of the same color are connected by a bond.[10] Examples from Eq. (3.4) are the second ρ graph, and the ninth ρ^3 graph. The numbers of unlabeled irreducible bicolored graphs up to eight points are: one two-point graph, one four-point graph, one five-point graph, five six-point graphs, eight seven-point graphs, and 42 eight-point graphs (graphs arising from interchange of A and B are not counted in this list, although this in general

[7] T. Tanaka, P. H. E. Meijer, and J. N. Fox, J. Chem. Phys. **36**, 731 (1962); H. N. V. Temperley (to be published) (proposes a linear combination of a negative and a positive Gaussian, the latter of longer range).

[8] E. Helfand and R. L. Kornegay, Physica (to be published).

[9] This is a corollary of a theorem due to H. M. Trent, Proc. Natl. Acad. Sci. U.S. **40**, 1004 (1954).

[10] F. Harary, Pacific J. Math. **8**, 745 (1958).

TABLE I. Residue γ and location (in parentheses) $\tilde{\rho}_c$ of the critical point singularity in the (m, n) Padé approximant to $d\ln(\partial^2 F/\partial y^2)_{\rho,\text{V},\text{T}}/d\tilde{\rho}$ at $y=0$, $\alpha \rightarrow 0$.

m	$n =$ 0		1		2		3		4		5	
1			1.515	(2.462)	1.178	(2.263)	1.590	(2.440)	1.570	(2.434)	1.527	(2.422)
2			1.292	(2.320)	1.355	(2.355)	1.571	(2.434)	1.604	(2.448)		
3			1.369	(2.361)	Complex pair		1.536	(2.424)				
4			1.595	(2.438)	1.588	(2.436)						
5			1.588	(2.436)								
6	1.724	(2.462)										

leads to a different graph). The bicolored graphs have previously arisen for the same reason as here in Zwanzig's study of the orientational transition in a system of thin rods.[11] In that paper the bicolored graphs through seven points were listed. We have gone to one more point.[12]

The limit of strong unlike repulsion corresponds to letting $\alpha \rightarrow 0$. In this limit the p-point bicolored graphs make contributions of order $\alpha^{-3p/2}$ while the contributions of other graphs are at least $\alpha^{\frac{3}{2}}$ smaller. The very large contribution of bicolored graphs indicates that we are concerned with low density; in fact, in the $\alpha \rightarrow 0$ limit the free energy depends on α and density in the combination

$$\tilde{\rho} = \pi^{\frac{3}{2}}\rho\alpha^{-\frac{3}{2}}, \qquad (5.1)$$

which we now make the independent variable. This shift to a density scale of order $\alpha^{\frac{3}{2}}$ is not surprising, since the important interactions enter through the unlike f function $-\exp(-\alpha r^2)$. In this function the scale of distance for unlike interactions is $\alpha^{-\frac{1}{2}}$, and the scale of density is $\alpha^{-\frac{3}{2}}$.

We are interested in the manner in which

$$(\partial^2 F/\partial y^2)_{\rho,\text{V},\text{T}}$$

vanishes at the critical density, $\tilde{\rho}_c$. The series for this function may be analyzed for zeros, poles, and branch points by means of Padé approximants. If a given function contains a singularity (or zero) of the type $(\tilde{\rho}-\tilde{\rho}_c)^{\gamma}$, then its logarithmic derivative will have a simple pole at ρ_c with residue γ, i.e., is of the form

$$[\gamma/(\rho-\rho_c)] + \text{a function regular at } \rho_c. \qquad (5.2)$$

We have therefore obtained Padé approximants to the series for $\partial[\log(\partial^2 F/\partial y^2)_{\rho,\text{V},\text{T}}]/\partial\rho$. The (m, n) Padé approximant is a ratio, $P_n(\tilde{\rho})/Q_m(\tilde{\rho})$, of an nth degree to an mth degree polynomial.[13,14] Thus allowance is made for m simple poles. The $n+m+1$ independent coefficients of P_n and Q_m are determined so that the first $n+m+1$ terms of the expansion of the (m, n) approximant are identical with the corresponding terms of the given function.

The values of the critical density, $\tilde{\rho}_c=\pi^{\frac{3}{2}}\rho_c\alpha^{-\frac{3}{2}}$, and γ, the power law index, for various Padé approximants are listed in Table I. These are, respectively, the location of the pole of the Padé approximant closest to the origin, and the value of the residue at that pole. One gleans from this table some idea of the manner in which the prediction is stabilized as higher approximants are employed.

The Padé approximant study as far as we have taken it also indicates that there are infinities in $(\partial^2 F/\partial y^2)_{\rho=\rho_c}$ of a branch point nature at $\tilde{\rho}=5.2 \exp[(0.36)(2\pi i)]$, $5.2 \exp[-(0.36)(2\pi i)]$, and 6.2. The $(4,1)$, $(4, 2)$, and $(5, 1)$ approximants are virtually identical; the $(4, 1)$ approximant is:

$$\left[\frac{\partial}{\partial\tilde{\rho}}\log\frac{\beta}{N}\left(\frac{\partial^2 F}{\partial y^2}\right)_{\rho,\text{V},\text{T}}\right]_{y=0}$$

$$= -(0.500+0.087\tilde{\rho})\left[\left(1-\frac{\tilde{\rho}}{2.438}\right)\left(1-\frac{\tilde{\rho}}{-3.527+4.005i}\right)\right.$$

$$\left.\times\left(1-\frac{\tilde{\rho}}{-3.527-4.005i}\right)\left(1-\frac{\tilde{\rho}}{6.092}\right)\right]^{-1}; \qquad (5.3)$$

the $(4, 2)$ approximant is

$$-(0.500+0.090\tilde{\rho}+0.001\tilde{\rho}^2)\left[\left(1-\frac{\tilde{\rho}}{2.436}\right)\left(1-\frac{\tilde{\rho}}{-3.431+3.956i}\right)\left(1-\frac{\tilde{\rho}}{-3.431-3.956i}\right)\left(1-\frac{\tilde{\rho}}{6.234}\right)\right]^{-1}; \qquad (5.4)$$

[11] R. Zwanzig, J. Chem. Phys. 39, 1714 (1963).
[12] The generation of the eight-point graphs was done manually by first listing all the bicolored graphs of eight points with enough lines against the number of such graphs predicted by Harary (Ref. 10) using the Polyá counting theorem. It is easy to select from this list those graphs which are irreducible. This task took about three days. We believe that with a month's effort the nine-point graphs can be listed. The 10-point bicolored graphs would take several months to find.
[13] H. Padé, Ann. Sci. Ecole Normale Supérieure (Paris) 9, Suppl. 1 (1892); G. A. Baker, Jr., and J. L. Gammel, J. Math. Anal. Applications 2, 21 (1961); G. A. Baker, Jr., J. L. Gammel, and J. G. Wills, J. Math. Anal. Applications 2, 405 (1961).
[14] G. A. Baker, Jr., Phys. Rev. 124, 768 (1961).

and the (5, 1) approximant is

$$-(0.500+0.083\tilde{\rho})\left[\left(1-\frac{\tilde{\rho}}{2.436}\right)\left(1-\frac{\tilde{\rho}}{-3.432+3.962i}\right)\right.$$

$$\left.\times\left(1-\frac{\tilde{\rho}}{-3.432-3.962i}\right)\left(1-\frac{\tilde{\rho}}{6.246}\right)\left(1-\frac{\tilde{\rho}}{77.450}\right)\right]^{-1}.$$

$$(5.5)$$

From these results we conclude that approaching the critical point from lower densities, $(\partial^2 F/\partial y^2)_{\rho,\mathrm{V},\mathrm{T}}$ approaches zero proportionate to $(2.44-\tilde{\rho})^{1.59}$.

Thus we have established a branch point character for the $\alpha\to 0$ limit of $(\partial^2 F/\partial y^2)_{\rho,\mathrm{V},\mathrm{T}}$. This does not necessarily imply a similar branch point behavior for $0<\alpha<1$. However, even this restricted result points out a weakness in application of simple solution theories (conformal, regular, perturbation, cell, etc.) to critical phenomena, since none of them can exhibit even limiting branch point behavior.

VI. GENERAL RATIO OF UNLIKE-TO-LIKE RANGE

For general α, one must return to a consideration of all the irreducible diagrams with vertices labeled A and B. The series through five-point diagrams has been determined. The required determinants were evaluated with the aid of the ALPAK program for algebraic manipulation on a digital computer.

Again the nature of the approach to zero of

$$(\partial^2 F/\partial y^2)_{\rho,\mathrm{V},\mathrm{T}}$$

at the critical density and along the $y=0$ line has been analyzed by forming Padé approximants to the logarithmic derivative. The results must be termed inconclusive in the sense that the results for the different Padé approximants which can be formed differ considerably. A study of the small α case where longer series are available indicates why. In the previous section it has been found that the results do not stabilize until allowance for at least four poles and one zero is made [(1, 4) approximant]. This requires the analysis of seven-point graphs. When allowance is only made for fewer poles and a low-degree polynomial is used in the numerator, one can see roughly how the resulting poles and residues are a compromise of the four important ones. However, this compromise tends to distort the value of $\gamma(\alpha)$ rather seriously.

VII. CONCLUDING REMARKS

It is of interest to consider the relation of this mixture system to magnetic systems. The correspondence involves replacement of the composition variable y by the magnetization M. M is defined as $\partial G/\partial H$, where G is the free energy of the magnetic system and H is the magnetic field. The susceptibility, $\chi=\partial M/\partial H$, is related to G by differentiating G at constant temperature twice with respect to H, and using the chain rule

$$\frac{\partial^2 G}{\partial H^2}=\chi=\chi^2\frac{\partial^2 G}{\partial M^2}=\chi\frac{\partial\chi}{\partial M}\frac{\partial G}{\partial M}. \qquad (7.1)$$

For $H=0$ above the Curie point

$$\chi(\partial G/\partial M)\equiv\partial G/\partial H\equiv M=0. \qquad (7.2)$$

(The analog $\partial F/\partial y$ is also equal to 0 in the mixture.) Thus

$$\partial^2 G/\partial M^2=[\chi(H=0)]^{-1}, \qquad T>T_c. \qquad (7.3)$$

To complete the analogy note that the forward-scattering intensity for zero field is proportional to χ or $(\partial^2 G/\partial M^2)^{-1}$.

An Ising-like magnetic analog of the above mixture would be the dilute ferromagnet. The susceptibility of this model as a function of concentration has not been studied. The most extensive investigations have been on the model wherein all the sites are occupied by the magnetic species, and temperature is the variable of interest. One finds in this case that the susceptibility diverges at the Curie point as $|T-T_c|^{-\frac{5}{4}}$ for the three-dimensional Ising model,[14,15] $|T-T_c|^{-\frac{4}{3}}$ for the three-dimensional Heisenberg model,[16] and $|T-T_c|^{-\frac{7}{4}}$ for the two-dimensional Ising model.[14,15] It is our strong suspicion, based on these Ising model results, that the mixture model for finite α retains its branch point character.

Finally, we would like to mention that we are addressing ourselves to the problem of the behavior of $(\partial^2 F/\partial\rho^2)_{\mathrm{T},\mathrm{V},y=0}$ for the mixture. The question of interest is whether this has a logarithmic singularity like the specific heat of a magnetic material.

ACKNOWLEDGMENT

APPENDIX

In Table II there is presented a list of the multiply-connected (irreducible) mixture graphs of five or less points. Under the heading "Graph" there appears a five-number code, a.b.c.d.e, which stands for:

(a) the number of A vertices;

(b) the number of B vertices;

[15] J. W. Essam and M. E. Fisher, J. Chem. Phys. **38**, 802 (1963).

[16] C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962).

TABLE II. Multiply connected mixture graphs.

| Graph	B Vertices	Symm. No.	Complexity	Graph	B Vertices	Symm. No.	Complexity
2.0.1.1.1	...	2	1	4.1.7.5.1	1	2	$4\alpha+10\alpha^2+6\alpha^3+\alpha^4$
1.1.1.1.1	1	1*	α	4.1.7.5.2	2	1	$16\alpha+5\alpha^2$
3.0.3.1.1	...	6	3	4.1.7.5.3	3	1	$9\alpha+10\alpha^2+2\alpha^3$
2.1.3.1.1	1	2	$2\alpha+\alpha^2$	3.2.7.5.1	2, 5	2	$12\alpha^2+8\alpha^3+\alpha^4$
4.0.4.1.1	...	8	4	3.2.7.5.2	1, 2	1	$4\alpha+10\alpha^2+6\alpha^3+\alpha^4$
3.1.4.1.1	1	2	$2\alpha+2\alpha^2$	3.2.7.5.3	2, 3	1	$9\alpha+10\alpha^2+2\alpha^3$
2.2.4.1.1	1, 2	2*	$2\alpha+2\alpha^2$	3.2.7.5.4	2, 4	1	$6\alpha^2+11\alpha^3+4\alpha^4$
2.2.4.1.2	1, 3	4*	$4\alpha^3$	3.2.7.5.5	3, 4	2	$4\alpha+10\alpha^2+6\alpha^3+\alpha^4$
4.0.5.2.1	...	4	8	3.2.7.5.6	1, 3	1	$6\alpha^2+11\alpha^3+4\alpha^4$
3.1.5.2.1	1	2	$3\alpha+4\alpha^2+\alpha^3$	5.0.7.6.1	...	4	24
3.1.5.2.2	2	2	$6\alpha+2\alpha^2$	4.1.7.6.1	1	4	$16\alpha+8\alpha^2$
2.2.5.2.1	1, 3	4	$4\alpha^2+4\alpha^3$	4.1.7.6.2	2	2	$9\alpha+12\alpha^2+3\alpha^3$
2.2.5.2.2	1, 2	1*	$3\alpha+4\alpha^2+\alpha^3$	4.1.7.6.3	3	2	$12\alpha+10\alpha^2+2\alpha^3$
4.0.6.3.1	...	24	16	3.2.7.6.1	1, 2	2	$9\alpha+12\alpha^2+3\alpha^3$
3.1.6.3.1	1	6	$9\alpha+6\alpha^2+\alpha^3$	3.2.7.6.2	1, 3	2	$6\alpha^2+14\alpha^3+4\alpha^4$
2.2.6.3.1	1, 2	4*	$4\alpha+8\alpha^2+4\alpha^3$	3.2.7.6.3	2, 5	4	$12\alpha^3+12\alpha^4$
5.0.5.1.1	...	10	5	3.2.7.6.4	2, 3	1	$4\alpha+11\alpha^2+8\alpha^3+\alpha^4$
4.1.5.1.1	1	2	$2\alpha+3\alpha^2$	3.2.7.6.5	3, 4	4	$4\alpha+12\alpha^2+8\alpha^3$
3.2.5.1.1	1, 2	2	$2\alpha+3\alpha^2$	5.0.8.7.1	...	4	40
3.2.5.1.2	1, 3	2	$4\alpha^3+\alpha^4$	4.1.8.7.1	1	4	$32\alpha+8\alpha^2$
5.0.6.2.1	...	2	11	4.1.8.7.2	2	2	$12\alpha+19\alpha^2+8\alpha^3+\alpha^4$
4.1.6.2.1	1	2	$8\alpha+3\alpha^2$	4.1.8.7.3	3	2	$24\alpha+14\alpha^2+2\alpha^3$
4.1.6.2.2	2	1	$3\alpha+6\alpha^2+2\alpha^3$	3.2.8.7.1	1, 2	2	$12\alpha+19\alpha^2+8\alpha^3+\alpha^4$
4.1.6.2.3	3	1	$6\alpha+5\alpha^2$	3.2.8.7.2	1, 3	2	$18\alpha^2+18\alpha^3+4\alpha^4$
3.2.6.2.1	2, 5	2	$4\alpha^2+6\alpha^3+\alpha^4$	3.2.8.7.3	2, 5	4	$8\alpha^2+20\alpha^3+12\alpha^4$
3.2.6.2.2	1, 2	1	$3\alpha+6\alpha^2+2\alpha^3$	3.2.8.7.4	2, 3	1	$5\alpha+16\alpha^2+15\alpha^3+4\alpha^4$
3.2.6.2.3	2, 3	1	$3\alpha+6\alpha^2+2\alpha^3$	3.2.8.7.5	3, 4	4	$12\alpha+20\alpha^2+8\alpha^3$
3.2.6.2.4	2, 4	1	$7\alpha^3+4\alpha^4$	5.0.8.8.1	...	8	45
3.2.6.2.5	3, 4	2	$6\alpha+5\alpha^2$	4.1.8.8.1	1	8	$16\alpha+20\alpha^2+8\alpha^3+\alpha^4$
3.2.6.2.6	1, 3	1	$4\alpha^2+6\alpha^3+\alpha^4$	4.1.8.8.2	2	2	$24\alpha+18\alpha^2+3\alpha^3$
5.0.6.3.1	...	12	12	3.2.8.8.1	1, 2	2	$5\alpha+18\alpha^2+18\alpha^3+4\alpha^4$
4.1.6.3.1	2	6	$3\alpha+6\alpha^2+3\alpha^3$	3.2.8.8.2	2, 3	2	$12\alpha+22\alpha^2+10\alpha^3+\alpha^4$
4.1.6.3.2	1	4	$8\alpha+4\alpha^2$	3.2.8.8.3	2, 4	4	$9\alpha^2+24\alpha^3+12\alpha^4$
3.2.6.3.1	2, 5	12	$12\alpha^4$	5.0.9.9.1	...	12	75
3.2.6.3.2	1, 2	2	$3\alpha+6\alpha^2+3\alpha^3$	4.1.9.9.1	1	4	$32\alpha+32\alpha^2+10\alpha^3+\alpha^4$
3.2.6.3.3	3, 4	4	$4\alpha^2+8\alpha^3$	4.1.9.9.2	2	6	$48\alpha+24\alpha^2+3\alpha^3$
5.0.7.4.1	...	12	20	3.2.9.9.1	1, 2	2	$15\alpha+34\alpha^2+22\alpha^3+4\alpha^4$
4.1.7.4.1	2	6	$4\alpha+9\alpha^2+6\alpha^3+\alpha^4$	3.2.9.9.2	1, 3	4	$6\alpha+25\alpha^2+32\alpha^3+12\alpha^4$
4.1.7.4.2	1	4	$16\alpha+4\alpha^2$	3.2.9.9.3	2, 5	12	$27\alpha^2+36\alpha^3+12\alpha^4$
3.2.7.4.1	2, 5	12	$8\alpha^3+12\alpha^4$	5.0.10.10.1	...	120	125
3.2.7.4.2	1, 2	2	$4\alpha+9\alpha^2+6\alpha^3+\alpha^4$	4.1.10.10.1	1	24	$64\alpha+48\alpha^2+12\alpha^3+\alpha^4$
3.2.7.4.3	3, 4	4	$12\alpha^2+8\alpha^3$	3.2.10.10.1	1, 2	12	$18\alpha+51\alpha^2+44\alpha^3+12\alpha^4$
5.0.7.5.1	...	2	21				
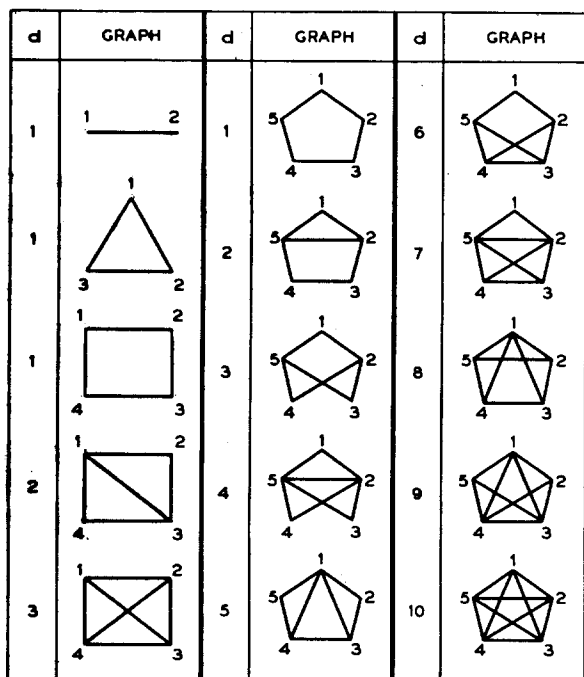
FIG. 3. Skeletal graph list numbers (d) and vertex labelings for entries in Table II.

(c) the number of bonds;

(d) the list number of the skeletal graph (no A and B assignment) as given by Hoover and De Rocco[17] and reproduced in Fig. 3;

(e) a new list number to distinguish the two-component graph.

In the second column are listed those vertices which are labeled B. Reference here is to the labeling shown in Fig. 3. The third column gives the symmetry number (order of the group) of the graph. Column 4 is the determinant D, the complexity, defined in Section 4. There are, strictly speaking, more graphs not listed, which follow by an interchange of A's and B's. Some graphs with equal numbers of A and B indices are unaltered upon interchanging A and B and others yield new graphs. Following the symmetry number of those which do not yield new graphs an asterisk has been placed (note that Graph 2.2.5.2.1 has no asterisk).

Because mixture problems, in a limit where use of only bicolored graphs is appropriate, can be carried

[17] W. G. Hoover and A. G. De Rocco, J. Chem. Phys. 36, 3141 (1962).

TABLE III. Multiply connected bicolored graphs.

Graph	Bonds	Symm. No.	Complexity $X\alpha^{1-p}$
1.1.1.1	1	1*	1
2.2.4.1	1111	4*	4
3.2.6.1	111111	12	12
4.2.8.1	11111111	48	32
3.3.6.1	101110011	6*	6
3.3.7.1	111110011	2*	15
3.3.8.1	101111111	4*	36
3.3.9.1	111111111	36*	81
5.2.10.1	1111111111	240	80
4.3.8.1	110110011101	4	20
4.3.9.1	110110111101	2	44
4.3.9.2	111110011101	6	50
4.3.10.1	110110111111	8	96
4.3.10.2	111111011101	4	105
4.3.11.1	111110111111	12	216
4.3.12.1	111111111111	144	432
6.2.12.1	111111111111	1440	192
5.3.10.1	101110011101101	12	56
5.3.10.2	101110011101110	8	64
5.3.11.1	101111011101101	6	116
5.3.11.2	101110111101110	8	128
5.3.11.3	111110011101101	4	140
5.3.12.1	101111111101101	24	240
5.3.12.2	111110111101110	4	276
5.3.12.3	101110011111111	12	294
5.3.13.1	111111111101101	24	540
5.3.13.2	111110011111111	12	567
5.3.14.1	111111111111101	48	1080
5.3.15.1	111111111111111	720	2025
4.4.8.1	1001110001100011	8*	8
4.4.9.1	1101110001100011	1*	23
4.4.9.2	1011110001100101	6*	27
4.4.10.1	1010110101111010	8*	64
4.4.10.2	1111110001100101	6*	54
4.4.10.3	1101110001110011	2*	56
4.4.10.4	1101111001100011	1*	66
4.4.10.5	1101110011100011	4	60
4.4.10.6	1111110001100011	2	56
4.4.11.1	1101110111100011	4*	153
4.4.11.2	1101110101110011	2	132
4.4.11.3	1101110001111011	2*	160
4.4.11.4	1111111001100011	1*	129
4.4.11.5	1010110111111010	4*	128
4.4.11.6	1111110001101011	2	145
4.4.12.1	1101111001111011	24*	384
4.4.12.2	1101110101111011	4	336
4.4.12.3	1101110001111111	1*	304
4.4.12.4	1101110101110111	16	288
4.4.12.5	1111111101100011	4	280
4.4.12.6	1111111011100011	4*	288
4.4.12.7	1010111111111010	16*	256
4.4.13.1	1111110101111011	6*	704
4.4.13.2	1111111011101011	4	624
4.4.13.3	1101110011111111	4*	576
4.4.14.1	1111111011111111	8*	1280
4.4.14.2	1111111011101111	24	1152
4.4.15.1	1111111111110111	36*	2304
4.4.16.1	1111111111111111	576*	4096

further in the density series than any other Mayer cluster expansion, it is perhaps of value to list the bicolored graphs. In Table III the multiply connected bicolored graphs of eight or less points are tabulated.

Column 1 is a four-number code, a.b.c.e. (as previously defined), which "names" the graph. Column 2 consists of a series of zeros and ones which designates the graph. A 1 indicates the presence of a bond while a 0 indicates its absence in the following order:

1A 1B graph: 1–2,

2A 2B graph: 1–3, 1–4, 2–3, 2–4,

3A 2B graph: 1–4, 1–5, 2–4, 2–5, 3–4, 3–5,

4A 2B graph: 1–5, 1–6, 2–5, 2–6, 3–5, 3–6, 4–5, 4–6,

3A 3B graph: 1–4, 1–5, 1–6, 2–4, 2–5, 2–6, 3–4, 3–5, 3–6,

5A 2B graph: 1–6, 1–7, 2–6, 2–7, 3–6, 3–7, 4–6, 4–7, 5–6, 5–7,

4A 3B graph: 1–5, 1–6, 1–7, 2–5, 2–6, 2–7, 3–5, 3–6, 3–7, 4–5, 4–6, 4–7,

6A 2B graph: 1–7, 1–8, 2–7, 2–8, 3–7, 3–8, 4–7, 4–8, 5–7, 5–8, 6–7, 6–8,

5A 3B graph: 1–6, 1–7, 1–8, 2–6, 2–7, 2–8, 3–6, 3–7, 3–8, 4–6, 4–7, 4–8, 5–6, 5–7, 5–8,

4A 4B graph: 1–5, 1–6, 1–7, 1–8, 2–5, 2–6, 2–7, 2–8, 3–5, 3–6, 3–7, 3–8, 4–5, 4–6, 4–7, 4–8,

where i–j indicates the bond between an A point i and a B point j. All bonds not included in the above list are of necessity excluded by the fact that the graph is bicolored. Column 3 of Table III contains the symmetry number. Again an asterisk indicates that interchange of A and B does not yield a new graph. Column 4 is the graph complexity, D. A factor of α^{p-1} has been omitted. Note that the complexities are numerically quite close together for a given number of A and B points and lines in the graph.