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Path-integral treatment of the liquid-gas transition: From simple fluids to microemulsions

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We propose a unified field-theoretic path-integral treatment of the liquid-gas transition occurring in simple neutral fluids, neutral monodisperse polymer solutions, and monodisperse neutral microemulsions. The theoretical results obtained indicate that all three systems belong to the same Ising-type universality class, which is strongly supported by the most recent experimental results on liquid-gas transitions.

I. INTRODUCTION

Since the work of Lee and Yang,[1] it has become customary to describe the liquid-gas transition in simple fluids by using the isomorphism between the lattice-gas model of fluids and the Ising model.[2] Much less obvious is that more complicated fluids like polymer solutions also exhibit a liquid-gas transition that is characterized by Ising-type critical exponents.[3,4] Existing polymer-magnet analogies[5] suggest, however, that polymer solutions must be described by the $n \rightarrow 0$ limit of the classical Heisenberg model. This then formally puts polymer solutions in a universality class *other* than Ising. In order to understand better the nature of the liquid-gas transition in polymer solutions, it is essential to develop the theory of this transition for polymers along the same lines as for simple fluids. The necessity to develop the theory for polymers along the same lines as that for fluids is dictated by experimental observations,[3,4] strongly indicating that all neutral polymer solutions belong to the Ising universality class. The existing theories of liquid-gas phase transitions for polymers[6-8] so far have been unable to produce Ising-type critical exponents, whereas the existing theories of liquid-gas transitions for simple fluids[9-12] are not well adopted for extension to the case of polymer solutions. Here, we present a new field-theoretic formulation of the liquid-gas phase transition for simple liquids which allows a natural extension not only to the case of polymer solutions, but also to microemulsions, where the most recent experiments also indicate Ising-type critical behavior.[13,14]

Our present treatment of the liquid-gas transition is the continuation of our earlier efforts[15-17] aimed at the reformulation of the classical statistical mechanics systems into the field-theoretic form which is the most convenient for treatments of possible phase transitions in the above systems. A brief account of the presented below results is given in Ref. 18.

This work is organized as follows. In Sec. II we provide a brief pedagogical account of the Landau-type theories of liquid-gas transition for simple lattice models of neutral fluids, polymer solutions and microemulsions. This mean-field treatment serves as a useful guideline to the more sophisticated field-theoretic path integral treatments of the above systems presented in Sec. III. We construct the path integrals for simple fluids, polymers and microemulsions in such a way that the saddle-point method applied to these integrals brings us back the mean-field results of Sec. II. The requirement to reproduce the mean-field results of Sec. II is imposed in accordance with the similar requirement for the magnetic systems.[19] The fluctuation corrections are discussed in Sec. IV where we explicitly demonstrate that the above three systems belong to the same Ising-type universality class. This is supported by the recent experiments discussed in Sec. V. We also discuss there the universal ratios obtained from our analysis of the available experimental data. Our theoretical findings are in excellent agreement with the existing experimental data presented in this section. Finally, Sec. VI is devoted to the discussion of the obtained results and to some, yet unsolved, problems to be considered in future works.

II. THE LANDAU-TYPE ANALYSIS OF THE SIMPLE LATTICE MODELS

A. The case of simple fluids

Let N_0 be the total number of lattice cells of some simple hypercubic d dimensional lattice. If we assume that each lattice cell of size a^d (in the subsequent, without loss of generality, we put $a=1$) can be occupied by just one atom (molecule), and the binary interaction energy per lattice site is U_0/N_0, the free energy is given by

$$\frac{F}{TN_0}=\frac{U_0}{2T}n^2+n\ln n+(1-n)\ln(1-n)\ , \tag{2.1}$$

where $n=\tilde{N}/N_0$, $\tilde{N}$ is the total number of atoms (molecules). Without loss of generality, we can consider as well a two component system for which the free energy can be written as

$$\frac{F}{TN_0}=-\frac{1}{2T}[n^2V_{11}+2n(1-n)V_{12}+(1-n)^2V_{22}]$$
$$+\frac{V_{22}}{2T}+n\ln n+(1-n)\ln(1-n) \ . \tag{2.2}$$

Then, if we choose $V_{11}=-V_{12}=-V_{22}=U_0/2$ we obtain back Eq. (2.1). The sign "minus" in front of the interaction term is chosen for future convenience, as well as an extra term $V_{22}/2T$ which do not affect the thermodynamics. Knowledge of the free energy permits us to obtain the pressure of the system P as ($a^d=1$)

$$P=-\frac{\partial F}{\partial N_0}=-\frac{n^2}{2}(V_{11}-2V_{12}+V_{22})-T\ln(1-n) \ . \tag{2.3}$$

This then produces the equation for the spinodal

$$\frac{\partial P}{\partial n}=0=-4T_c n+T[1/(1-n)] \ , \tag{2.4}$$

where we have introduced $T_c=\frac{1}{4}(V_{11}-2V_{12}+V_{22})$. The critical point is obtained now as the simultaneous solution of Eq. (2.4) and $\partial^2P/\partial n^2=0$, i.e.,

$$(1-n)^2=T/T_c \ . \tag{2.5}$$

The solution of Eqs. (2.4) and (2.5) is found to be $n=n_c=\frac{1}{2}$, $T=T_c$. Following Baxter,[2] we introduce an order parameter m via the equation

$$n=\tfrac{1}{2}(1+m)\equiv n_c(1+m) \ . \tag{2.6}$$

For sufficiently small m (i.e., near the critical point), we can obtain the following expansion for the free energy

$$\frac{F}{TN_0}=-\frac{T_c}{2T}-\ln 2-\frac{1}{4T}(V_{11}-V_{22})m$$
$$+\tfrac{1}{2}\tau m^2+\tfrac{1}{12}m^4+\cdots \ , \tag{2.7}$$

where $\tau=(T-T_c)/T$. This expression, although formally looks like the correct Landau expansion, *cannot* be used for the investigation of the behavior in the vicinity of the critical point. Indeed, following Landau and Lifshitz[20] we have to rewrite *first* the expression for the pressure in terms of the order parameter m. Defining the reduced variables $p=P-P_c$ and $t=T-T_c$ we obtain

$$h=tm+\tfrac{1}{2}tm^2+\frac{T}{3}m^3+\frac{T}{4}m^4+\cdots \ , \tag{2.8}$$

where the "magnetic field" h is defined by $h=p-t\ln 2$. Second, according to Landau, we should write for the "free energy" functional the following result

$$\mathcal{F}=\hat{\mathcal{F}}(\tau,m)-\hat{h}m$$
$$=\frac{\Phi(p,t)}{T}+\tfrac{1}{2}\tau m^2+\tfrac{1}{6}\tau m^3+\tfrac{1}{12}m^4+\tfrac{1}{20}m^5-\hat{h}m+\cdots \ , \tag{2.9}$$

where $\hat{h}=h/T$. A functional $\mathcal{F}$ defined in this way is designed to automatically reproduce the result (2.8) if we use the equation

$$\hat{h}=\frac{\partial\hat{\mathcal{F}}}{\partial m} \text{ or } \frac{\partial\mathcal{F}}{\partial m}=0 \ . \tag{2.10}$$

According to Landau and Lifshitz, the cubic term in Eq. (2.9) can be dropped by means of redefining the order parameter $m\rightarrow m+\text{const}\tau$. Although at the mean-field level the above redefinition is completely harmless, inclusion of fluctuation corrections makes the above simple replacement nontrivial. Furthermore, as it can be seen from Eq. (2.9) the term of order m^2h, mentioned in Sec. 153 of Ref. 20, are *not* present in the expansion (2.9). These terms according to the same reference are needed in order to account for the asymmetry of the coexistence curve. We would like to argue here that the terms of order m^2h are *not* necessary in order to explain the asymmetry of the coexistence curve. We shall demonstrate under what conditions they might be actually included in the expansion (2.9).

Begin with the equation of state (2.8). In the limit $h\rightarrow 0$ we obtain approximately

$$m^2+\tfrac{3}{2}\tau m+3\tau=0 \ . \tag{2.11}$$

If the cubic term in the expansion (2.9) could be ignored, then we would obtain from Eq. (2.11) the result $m_0=\pm\sqrt{3(-\tau)}$. If, however, we want to keep the cubic term, then we obtain from Eq. (2.11) the following result

$$m=\tfrac{3}{4}(-\tau)\pm[\tfrac{9}{16}\tau^2+3(-\tau)]^{1/2}$$
$$\approx m_0+\tfrac{3}{4}(-\tau), \ \tau\rightarrow 0 \ . \tag{2.12}$$

This expression can be also rewritten as

$$m=\pm|B|(-\tau)^{\beta}+c_1(-\tau)^{1-\alpha} \ , \tag{2.13}$$

where the exponents β and α are the usual mean-field exponents,[20] i.e., $\beta=\frac{1}{2}$, $\alpha=0$ and the constants B and c_1 are given by Eq. (2.12). Using Eq. (2.6) and introducing $\eta_l=n-n_c$, $\eta_g=n_c-n$ as the relative densities of liquid and gas phases, respectively, we obtain from Eq. (2.13) the following results

$$\frac{\eta_l+\eta_g}{n_c}=2c_1(-\tau)^{1-\alpha} \ , \tag{2.14}$$

$$\frac{\eta_l-\eta_g}{n_c}=2|B|(-\tau)^{\beta} \ . \tag{2.15}$$

Equations (2.14) and (2.15) coincide with that given in Ref. 21 [see Eqs. (1.20) and (1.21), Chap. 3] and Ref. 22. The above calculations have demonstrated that the fluid diameter,[10] Eq. (2.14), which is responsible for the asymmetry of the liquid-vapor coexistence curve, *originates from the cubic term* in the expansion (2.9). The cubic term in the expansion (2.9) can be actually replaced with the help of an extra term proportional to m^2h in the expansion (2.9). Indeed, if instead of Eq. (2.9) we write

$$\mathcal{F}=\frac{\Phi_0}{T}-\hat{h}m+\frac{1}{2}\left[\tau+\frac{\hat{h}}{2}\right]m^2+\tfrac{1}{12}m^4+\cdots \ , \tag{2.16}$$

then the anticipated result, Eq. (2.12), can be obtained from Eq. (2.16) with help of Eq. (2.10) and assuming $\hat{h}$ to be weak.

To clarify the meaning of the constants $|B|$ and c_1 it is instructive to rewrite $\mathcal{F}$, Eq. (2.9), in the scaling form. Below T_c we have[20] after a simple algebra

$$\hat{\mathcal{F}}(\tau,\hat{h})=\frac{\Phi_0}{T}-\frac{3}{4}(-\tau)^{2-\alpha}\left[1+\frac{4}{\sqrt{3}}\frac{\hat{h}}{(-\tau)^{\nu/\mu}}+\cdots\right], \tag{2.17}$$

where ν and μ are known mean-field exponents, $\mu=\frac{1}{3}$, $\nu=\frac{1}{2}$. Notice, however, that Eq. (2.17) is formally correct *beyond* the mean-field level and this observation is essential for the subsequent development. Obtained results permit us to determine now the universal ratios and, whence, the meaning of constants c_1 and $|B|$. We would like to notice that, although the actual values of the universal ratios in the theory which includes the fluctuations are different from that obtained at the mean field level, their universality is preserved. Following Aharony and Hohenberg,[23] all universal ratios needed for our purposes can be constructed with the help of the universal equation of state

$$\hat{h}=m^{\delta}f(x)\;, \tag{2.18}$$

where $x=\tau|m|^{-1/\beta}$. Near the critical point we have

$$m=B(-\tau)^{\beta},\quad \tau<0,\ \hat{h}=0\;, \tag{2.19}$$

$$\chi=\begin{cases}C^{+}\tau^{-\gamma}, & \tau>0,\ \hat{h}=0\;,\\ C^{-}(-\tau)^{-\gamma}, & \tau<0,\ \hat{h}=0\;,\end{cases} \tag{2.20}$$

$$C_s=\begin{cases}(A^{+}/\alpha)\tau^{-\alpha}, & \tau>0,\ \hat{h}=0\;,\\ (A^{-}/\alpha)(-\tau)^{-\alpha}, & \tau<0,\ \hat{h}=0\;,\end{cases} \tag{2.21}$$

$$\hat{h}=\mathcal{D}m^{\delta},\quad \tau=0\;, \tag{2.22}$$

where χ is the susceptibility and C_s is the singular portion of the specific heat. Aharony and Hohenberg[23] show how Eq. (2.18) can be used to obtain the critical amplitudes defined above. The table of universal ratios is given, for example, in the book by Amit[24] or in the original papers by Aharony and Hohenberg[23] and by Berviller.[25] Notice, however, that Brezin *et al.*[26] give a somewhat different definition of the ratio A^{+}/A^{-}. Given these ratios, we can construct an infinite number of other universal ratios by considering the combinations of those given in the above references. Using Eqs. (2.10), (2.12), (2.16), and (2.17) we conclude that the presence of cubic term in the expansion, Eq. (2.9), does not change the value of the coefficient B, see Eq. (2.13). At the same time, using Eqs. (2.12), (2.13), and (2.17) we conclude that the coefficient $c_1=\frac{3}{4}$ is related to the coefficient A^{-} in view of Eqs. (2.17) and (2.21). Using the fact that the specific heat is given by $C=-\partial^2\mathcal{F}/\partial\tau^2$ we obtain $A^{-}/\alpha=\frac{3}{4}(2-\alpha)(1-\alpha)$ or

$$c_1=\frac{A^{-}}{\alpha(1-\alpha)(2-\alpha)}\;, \tag{2.23}$$

where A^{-}/α is *not* affected by the presence of the cubic term in the expansion (2.9). Finally, we can rewrite Eq. (2.14) in the following equivalent form:

$$\frac{\eta_l+\eta_g}{n_c}=\frac{2A^{-}}{\alpha(1-\alpha)(2-\alpha)}(-\tau)^{1-\alpha}\;. \tag{2.24}$$

The actual situation is somewhat more complicated than that reflected in Eq. (2.24) as will become apparent from Sec. V. The meaning of the constant $|B|$ in Eq. (2.15) is the same as in Eq. (2.19). The above results are correct only if the term of order m^5 in Eq. (2.9) can be neglected. We anticipate that this should be the case. In order to test the above statement experimentally, the following universal ratios may be studied:

$$R_1=\frac{A^{-}C^{+}}{\alpha B^2},\quad R_2=\frac{A^{-}C^{-}}{\alpha B^2}\;. \tag{2.25}$$

These ratios are going to be further discussed below. Given analysis can be easily extended now to the polymer solutions.

B. The case of polymer solutions

Flory-Huggins lattice gas model[5] can be defined as before on some d-dimensional hypercubic lattice. Assuming that each lattice cell of size a^d can be occupied by just one atom (monomer or solvent molecule) and that only the binary nearest-neighbor interactions are important, the free energy of an assembly of $\tilde{N}$ monomers can be written just as in the case of the lattice-gas model discussed above, i.e.,

$$\frac{F}{TN_0}=-\frac{1}{2T}[n^2V_{11}+2n(1-n)V_{12}+(1-n)^2V_{22}]+\frac{V_{22}}{2T}+\left[\frac{n}{N}\right]\ln\left[\frac{n}{N}\right]+(1-n)\ln(1-n)\;, \tag{2.26}$$

where $n=\tilde{N}/N_0$, N is the length of the polymer chain. The potentials V_{11}, V_{12}, and V_{22} represent the strength of polymer-polymer, polymer-solvent, and solvent-solvent interactions respectively. As before, the sign "$-$" in front of the interaction term is chosen for further convenience as well as the term $V_{22}/2T$. By analogy with the case of simple fluids, we obtain the expression for osmotic pressure as ($a^d=1$)

$$\begin{aligned}P&=-\frac{\partial F}{\partial N_0}\\&=-\tfrac{1}{2}(V_{11}-2V_{12}+V_{22})n^2\\&\quad-T\left[\left[1-\frac{1}{N}\right]n+\ln(1-n)\right]\;.\end{aligned} \tag{2.27}$$

The equation for spinodal now reads as $\partial P/\partial n=0$, or $T/T_c=(-n)/[1-1/N-1/(1-n)]$, where $T_c=V_{11}-2V_{12}+V_{22}$. The critical point is determined from the simultaneous solution of Eq. (2.27) and $\partial^2P/\partial n^2=0$, i.e., $(1-n)^2=T/T_c$. A little algebra shows that the critical temperature is equal to T_c and the critical density $n_c=1/(\sqrt{N}+1)$. An order parameter m can now be defined as in Eq. (2.6). For small m (i.e., near the critical point) the free energy, Eq. (2.16), can be rewritten as

$$\frac{F}{TN_0}=-\frac{T_c}{2T}n_c-\frac{(V_{12}-V_{22})}{T}n_c+n_c^3\ln\left[\frac{n_c}{N}\right]+\frac{1}{2}\left[1+\frac{2}{\sqrt{N}}-\frac{T_c}{T}\right]n_c^2m^2+\tfrac{2}{3}n_c^4m^3+\tfrac{1}{12}n_c^3m^4+\cdots\,. \tag{2.28}$$

As before, the above free energy cannot be used in the liquid-gas calculations. By analogy with Eq. (2.8), we obtain

$$\hat{h}=\tau m n_c^2+\tfrac{1}{2}\tau n_c^2m^2+\tfrac{1}{3}n_c^3m^3+\tfrac{1}{4}n_c^4m^4+\cdots\,, \tag{2.29}$$

where $\hat{h}=h/T$ and $h=p+tn_c$. The Landau-Lifshitz functional can now be written as

$$\mathcal{F}=\hat{\mathcal{F}}(\tau,m)-\hat{h}m=\frac{\mathcal{F}_0}{T}-\hat{h}m+\frac{\tau}{2}n_c^2m^2+\frac{\tau}{6}n_c^2m^3+\tfrac{1}{12}n_c^3m^4+\tfrac{1}{20}n_c^4m^5+\cdots\,. \tag{2.30}$$

The equation analogous to (2.13) can be obtained with constants B and c_1 being replaced by $B_p=\pm\sqrt{3/n_c}$ and $c_{1p}=(3/4)n_c^{-1}$. The cubic term in Eq. (2.30) can be eliminated, as in the case of simple liquids, with replacement $\tau\rightarrow\tau+\frac{1}{2}\hat{h}/n_c^2$ so that Eq. (2.16) can be replaced with

$$\mathcal{F}=\frac{\mathcal{F}_0}{T}-\hat{h}m+\frac{1}{2}\left[\tau+\frac{\hat{h}}{2n_c^2}\right]n_c^2m^2+\tfrac{1}{12}n_c^3m^4+\cdots\,. \tag{2.31}$$

Evidently, this replacement is possible only if the quintic term ($\sim m^5$) is ignored which we shall assume unless the otherwise is specified. In case of simple fluids we have defined the universal ratios R_1 and R_2. We would like now to demonstrate that in case of polymers the above universal ratios within the approximations made [i.e., without the quintic term in expansion (2.30)] are the same as for simple fluids, at least at the mean-field level. To this end using Eq. (2.29) and equation analogous to (2.17) which is

$$\mathcal{F}=\frac{\mathcal{F}_0}{T}-\tfrac{3}{4}[\sqrt{n_c}(-\tau)]^{2-\alpha}\times\left[1+\frac{4}{\sqrt{3}}\frac{\hat{h}}{[n_c(-\tau)]^{\nu/m}}+\cdots\right] \tag{2.32}$$

we obtain $A^-/\alpha=n_c^{(2-\alpha)/2}\frac{3}{4}(2-\alpha)(1-\alpha)$ and $C^-=(2n_c^2)^{-1}$, $C^+=n_c^{-2}$. Using the already obtained value of Bp we obtain (at the mean-field level)

$$R_1=2R_2=\tfrac{1}{2}\,, \tag{2.33}$$

which is the same as for simple fluids. This result can be used in order to study the role of quintic interactions in liquid-gas transition for polymers and will be further discussed in Sec. V.

C. The case of monodisperse microemulsions

Recently, Widom have proposed a model of microemulsion[27] which is the most suitable for the present study. Here, we adopt his model in the form discussed by Goldstein[28] because of its connection with the above discussed Flory-Huggins model. For an assembly of monodisperse micelles with the mean aggregation number σ (i.e., the average number of surfactants per micelle) we have instead of Eq. (2.26) the following result

$$\frac{F}{TN_0}=-\frac{1}{2T}[n^2V_{11}+2n(1-n)V_{12}+(1-n)^2V_{22}]+\frac{V_{22}}{2T}+\left[\frac{n}{M\sigma}\right]\ln\left[\frac{n}{M\sigma}\right]+(1-n)\ln(1-n)\,, \tag{2.34}$$

where M is the average length of the surfactant molecule, and V_{11},V_{12},V_{22} are responsible for the surfactant-surfactant, solvent-surfactant, and solvent-solvent interactions, respectively. It is assumed that $M\ll N$ and that all surfactant molecules for a given micelle reside on its surface. (For more details see Ref. 14.) Under such assumption we can effectively put $M\sim1$ and if the area of the micelle is A, then $\sigma=A/a_0$ where a_0 is the area per surfactant.[29] Evidently, we can always choose the system of units such that $a_0=1$ which we are going to assume in the subsequent. It is evident that for such defined model it is possible to repeat all calculations of the previous subsection without any change (except $N\rightleftarrows A$) so that we anticipate that the liquid-gas transition for micelles should also belong to the Ising universality class. This indeed was decisively demonstrated recently in real experiments by Dietler and Cannell[13] (see also Ref. 14).

Here we would like to prove, guided by the above analysis, that the liquid-gas transition is to a large extent universal phenomenon for liquids, polymers, and microemulsions.

III. PATH INTEGRAL FIELD-THEORETIC FORMULATION OF THE PARTITION FUNCTION FOR LIQUIDS, POLYMERS, AND MICROEMULSIONS. GENERAL REQUIREMENTS AND THE MEAN-FIELD RESULTS

Statistical mechanics for pointlike particles is by now a well developed discipline. Much more difficult is the study of statistical mechanics of extended objects using the standard formalism. The general problem can be formulated as follows.[18]

(1) Begin with an assembly of pointlike particles.

(2) Consider then an assembly of extended particles of *fixed* topology and having *rigid* surfaces.

(3) The same as above, but the particles having a *flexible surfaces.*

(4) Finally, the same as above but the particles, in addition, have a different topology.

The statistical mechanics of the first level of problems is by now a well developed subject. The second level of problems requires already the use of integral equation methods. The third and fourth levels cannot be solved with the use of traditional methods of statistical mechanics and the field-theoretic methods become indispensable for this task. Previously one of us, ALK, has applied field-theoretic methods to the problem of phase transition in symmetric[16] and asymmetric[17] electrolytes (see also Ref. 18). Presented below formalism can be considered, in part, as an extension of the above ideas.

A. The case of simple fluids

Begin with the grand partition function for a classical gas with two-body interaction potential placed in the external auxiliary field $U(\mathbf{r})$. We have

$$Z=\sum_{n=0}^{\infty}\frac{\lambda^n}{n!}Q_n\ , \tag{3.1}$$

where

$$Q_n=\int\prod_{i=0}^{n}d^dr_i\exp\left[-\beta\sum_{(i<j)}V(\mathbf{r}_i-\mathbf{r}_j)-\beta\sum_{i=0}^{n}U(\mathbf{r}_i)\right] .$$

λ is related to the chemical potential in a usual way and $\beta=T^{-1}$. In order to convert Eq. (3.1) into the field-theoretic form, we introduce the collective variable $\rho(\mathbf{r})$ which represents the local density of fluid (or gas)

$$\rho(\mathbf{r})=\sum_i\delta(\mathbf{r}-\mathbf{r}_i)\ . \tag{3.2}$$

Following Negele and Orland[19] it is convenient also to use the identity

$$\int d\rho(\mathbf{r})\delta\left[\rho(\mathbf{r})-\sum_i\delta(\mathbf{r}-\mathbf{r}_i)\right]=1 \tag{3.3}$$

valid for any $\mathbf{r}$. Using Eq. (3.3) the grand partition function can be rewritten as

$$\begin{aligned}Z=\sum_{n=0}^{\infty}\frac{\lambda^n}{n!}\int\mathcal{D}[\rho(\mathbf{r})]\int\mathcal{D}[\phi(\mathbf{r})]\exp&\left[\int d^dr\phi(\mathbf{r})\rho(\mathbf{r})-\frac{\beta}{2}\int d^dr\int d^dr'\rho(\mathbf{r}')V(\mathbf{r}'-\mathbf{r})\rho(\mathbf{r})\right.\\&\left.-\beta\int d^dr\ U(\mathbf{r})\rho(\mathbf{r})\right]\int\prod_{i=0}^{n}d^dr_i\exp\left[-\sum_i\phi(\mathbf{r}_i)\right]\\=\mathcal{N}\int\mathcal{D}[\phi(\mathbf{r})]\exp&\left[-\frac{\beta}{2}\int d^dr\int d^dr'(\phi-U)V^{-1}(\phi-U)+\lambda\int d^dr\exp(-\beta\phi)\right]\ .\end{aligned} \tag{3.4}$$

Here, the integral representation of the δ function was used along with the rotation to the imaginary axis and rescaling of the field ϕ. The normalization factor $\mathcal{N}$ appears as a result of Gaussian-type integration over ρ-variable. As already was noticed in Ref. 19, there is a close analogy between the partition function presented earlier and the partition function for the Ising model in external magnetic field H_i which can be written as

$$Z_{\text{Ising}}=\mathcal{N}\int\mathcal{D}[\phi]\exp(-\beta S[\phi,H])\ , \tag{3.5}$$

where

$$\begin{aligned}S[\phi,H]=&\tfrac{1}{2}\sum_{i,j}(\phi_i-H_i)\mathcal{J}_{ij}^{-1}(\phi_j-H_j)\\&-\frac{1}{\beta}\sum_i\ln[2\cosh(\beta\phi_i)]\end{aligned} \tag{3.6}$$

with $\mathcal{J}_{ij}$ being the usual nearest-neighbor coupling constant. Because of this analogy, we expect that the treatments of both models should follow the same steps. In particular, we will *require* that the Bragg-Williams approximation for the Ising model should correspond to Eq. (2.1) for the lattice gas. Indeed, the Bragg-Williams approximation for the Ising model can be obtained, on one hand, from the combinatorial arguments similar to that which lead to Eq. (2.1).[30] On the other hand, it can be easily obtained from the path integral, Eq. (3.5), by a saddle-point method, as described in Ref. 19. Application of *the same* saddle procedure as for the Ising model to the functional integral, Eq. (3.4), produces the following result

$$\frac{F}{TN_0}=\frac{U_0}{2T}n^2+n\ \ln n \tag{3.7}$$

to be compared with Eq. (2.1). To reproduce the important missing term $(1-n)\ln(1-n)$ we are forced to somehow modify the functional integral, Eq. (3.4), in such a way that the connection with Eq. (3.1) remains intact.

Some time ago Hubbard and Schofield[9] had proposed a field-theoretic formulation which implicitly accounts for the above missing term. Their treatment, however, is difficult to extend to polymers and microemulsions and, whence, we develop here an alternative formalism which automatically explicitly reproduces Eq. (2.1) and is easily extendable to the case of polymers and microemulsions. Moreover, should we use Eq. (3.4) in order to compute the fluctuation corrections to the mean-field result, Eq. (3.7), we would obtain totally wrong answer. Reformulation of the result (3.4) not only restores the missing term

$(1-n)\ln(1-n)$ but also produces the correct result for the fluctuation corrections to be discussed in Sec. IV.

Begin with observation that Eq. (2.1) can be written in the equivalent form, Eq. (2.2), characteristic for the binary system. Therefore we can, without loss of generality, consider from the outset the binary system. For such system we can write the grand partition function, by analogy with Eq. (3.4), as

$$Z=\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}\frac{\lambda_1^{N_1}}{N_1!}\frac{\lambda_2^{N_2}}{N_2!}\times\int\mathcal{D}[\lambda]\int\mathcal{D}[\rho]\int\mathcal{D}[\boldsymbol{\phi}]\exp(S[\lambda,\boldsymbol{\rho},\boldsymbol{\phi}])\ , \tag{3.8}$$

where

$$S[\lambda,\boldsymbol{\rho},\boldsymbol{\varphi}]=-\int d^dr\,\lambda(\mathbf{r})[1-\rho_1(\mathbf{r})-\rho_2(\mathbf{r})]+\int d^dr\,\boldsymbol{\phi}\cdot\boldsymbol{\rho}-\frac{\beta}{2}\int d^dr\int d^dr'\boldsymbol{\rho}^T(\mathbf{r})\underline{V}^{-1}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')$$
$$-\beta\int d^dr\,\mathbf{U}\cdot\boldsymbol{\rho}+\ln\left[\left[\int d^dr\exp[-\phi_1(\mathbf{r})]\right]^{N_1}\left[\int d^dr\exp[-\phi_2(\mathbf{r})]\right]^{N_2}\right] \tag{3.9}$$

and $\boldsymbol{\rho}\cdot\boldsymbol{\phi}=\rho_1\phi_1+\rho_2\phi_2$, etc. The matrix $\underline{V}(\mathbf{r}-\mathbf{r}')$ is given by

$$\underline{V}(\mathbf{r}-\mathbf{r}')=\begin{bmatrix}V_{11} & V_{12}\\ V_{21} & V_{22}\end{bmatrix},\quad V_{12}=V_{21}$$

with obvious spatial dependence for potentials $V_{ij}, i,j=1,2$. The auxiliary fields $U_{1,2}$ and the extra constraint on densities which introduces a new field $\lambda(\mathbf{r})$ are absolutely *essential* for the subsequent development. The summation over N_1 and N_2, the Gaussian integration over ρ_1 and ρ_2, the trivial rescaling and shifts for fields ϕ_1 and ϕ_2 produce the final result for Z as

$$Z=\int\mathcal{D}[\lambda]\exp\left[-\int d^dr\,\lambda(\mathbf{r})\right]\mathcal{L}[\lambda(\mathbf{r})] \tag{3.10}$$

where

$$\mathcal{L}[\lambda(\mathbf{r})]=\int\mathcal{D}[\phi]\exp(-\beta S[\boldsymbol{\phi},\lambda]) \tag{3.11}$$

and

$$S[\boldsymbol{\phi},\lambda]=\frac{1}{2}\int d^dr\int d^dr'(\boldsymbol{\phi}-\hat{\boldsymbol{\mathcal{U}}})^T\underline{V}^{-1}(\boldsymbol{\phi}-\hat{\boldsymbol{\mathcal{U}}})$$
$$-\frac{1}{\beta}\int d^dr\exp[-\beta(\phi_1-\lambda)]$$
$$-\frac{1}{\beta}\int d^dr\exp[-\beta(\phi_2-\lambda)]\ . \tag{3.12}$$

Also, $\hat{\mathcal{U}}_i=U_i-\mu_i$ with μ_i being a chemical potential for ith component, $\lambda_i=a^{-d}\exp\beta\mu_i$, $a^d=1$ and all normalization factors are adsorbed into the functional integral measure. Following Ref. 19 we shall use a saddle-point method in order to evaluate Z. Minimization of $S[\boldsymbol{\phi},\lambda]$ produces after a little algebra

$$\begin{bmatrix}\bar{\phi}_1(\mathbf{r})\\ \bar{\phi}_2(\mathbf{r})\end{bmatrix}=\begin{bmatrix}\hat{\mathcal{U}}_1(\mathbf{r})\\ \hat{\mathcal{U}}_2(\mathbf{r})\end{bmatrix}-\int d^dr'\underline{V}(\mathbf{r}-\mathbf{r}')\begin{bmatrix}\exp[-\beta(\bar{\phi}_1-\bar{\lambda})]\\ \exp[-\beta(\bar{\phi}_2-\bar{\lambda})]\end{bmatrix}, \tag{3.13}$$

where the overbars for ϕ_1, ϕ_2, and λ indicate that these are the mean fields so that, in general, $\phi_i=\bar{\phi}_i+\delta\phi_i$, etc.; on another hand, using Eqs. (3.8) and (3.9) we obtain

$$\langle\rho\rangle=-\frac{1}{\beta}\frac{\delta}{\delta\mathbf{U}(\mathbf{r})}\ln Z \tag{3.14}$$

which in the saddle-point approximation produces

$$\langle\bar{\rho}\rangle=\int d^dr\underline{V}^{-1}(\bar{\boldsymbol{\phi}}-\hat{\boldsymbol{\mathcal{U}}})\ . \tag{3.15}$$

Combining Eq. (3.15) with Eqs. (3.13) and (3.16) produces

$$\bar{\rho}_i=\exp[-\beta(\bar{\phi}_i-\bar{\lambda})]\ . \tag{3.16}$$

From here, we obtain as well

$$\bar{\phi}_i=-\frac{1}{\beta}\ln\bar{\rho}_i+\bar{\lambda}\ . \tag{3.17}$$

The obtained results should now be supplemented by the saddle-point equation for λ field. Using Eqs. (3.10)–(3.12), we easily obtain

$$1=\exp[-\beta(\bar{\phi}_1-\bar{\lambda})]+\exp[-\beta(\phi_2-\bar{\lambda})]$$

or, in view of Eq. (3.16),

$$\bar{\rho}_1+\bar{\rho}_2=1\ . \tag{3.18}$$

The saddle-point approximation for the thermodynamic potential Ω can now be written as

$$\Omega=-\frac{1}{\beta}\ln Z$$
$$=S[\bar{\boldsymbol{\phi}},\bar{\lambda}]+\frac{1}{\beta}\int d^dr\,\bar{\lambda}(\mathbf{r})\ . \tag{3.19}$$

Using the known connection[20] between Ω and the free energy F, $F=\boldsymbol{\mu}\cdot\mathbf{N}+\Omega$, we can write for the free energy F the following result:

$$F=S[\bar{\phi},\bar{\lambda}]+\frac{1}{\beta}\int d^dr\,\bar{\lambda}(\mathbf{r})-\int d^dr\,\hat{\boldsymbol{\mathcal{U}}}\cdot\bar{\boldsymbol{\rho}}\ , \tag{3.20}$$

where we took into account that for $\mathbf{U}=0$, $\hat{\boldsymbol{\mathcal{U}}}=-\boldsymbol{\mu}$, and $\int\rho\,d^dr=\mathbf{N}$. The combined use of Eqs. (3.13)–(3.19) produces

$$F=-\frac{\beta}{2}\int d^d r\int d^d r'\bar{\rho}^{\,T}\underline{V}\bar{\rho}+\int d^d r\,\bar{\rho}\ln\bar{\rho}+\int d^d r(1-\bar{\rho})\ln(1-\bar{\rho})\ , \tag{3.21}$$

where, in view of Eq. (3.18), we put $\bar{\rho}\equiv\rho_1$. In the case when Eq. (3.13) admits homogeneous solution Eq. (3.21) is reduced to Eq. (2.2) *as required* (recall $a^d=1$). The developed formalism now can be extended to the case of polymer solutions rather straightforwardly.

B. The case of polymer solutions

In case of polymers we have a complication, compared to the simple liquids case, which comes from the necessity to account for the connectivity effects. The monomer units along the polymer chain are no longer free to move independently, as in the simple fluids: they are connected with each other by means of chemical bond. Microscopically, polymers can be described by a variety of models but, as was pointed out by DeGennes,[5] beyond a certain length scale $\sim l$ their properties become very much independent of the nature of chemical composition and at such scales and beyond polymers can be modeled by random walks on some lattices. The random walk model is further complicated by the necessity to consider an excluded volume problem: the walk is not allowed to intersect itself. Such random walk model with excluded volume constraint *cannot* be solved exactly and the treatment of the model resembles very much that known in quantum many-body theory. For a simple polymer chain, the partition function can be written as[31]

$$Z_p=\mathcal{N}\int\mathcal{D}[\mathbf{r}(\tau)]\exp\left[-\frac{d}{2l}\int_0^N d\tau\left[\frac{dr}{d\tau}\right]^2-\int_0^N d\tau\int_0^N d\tau' V(\mathbf{r}(\tau)-\mathbf{r}(\tau'))\right]\ , \tag{3.22}$$

where the variable $\mathbf{r}(\tau)$ represents the spatial position of the polymer segment which has the contour position τ along the chain, $0\leq\tau\leq N$. The first term in the exponent of the functional integral represents just a simple random walk in d dimensions, whereas the second term accounts for the excluded volume effects. Usually, the potential is taken to be equal to $v\delta(\mathbf{r}(\tau)-\mathbf{r}(\tau'))$ (Ref. 31) with v being the excluded volume adjustable parameter. The normalization conditions for the above path integral we choose in such a way that when the excluded volume is being put equal to zero $Z_p^0=V$ where V is the volume of the system. This convention is commonly used in the literature.[31] Equation (3.22) can be conveniently rewritten in the following equivalent, symbolic form:

$$Z_p=\left\langle\exp\left[-\frac{1}{2}\int d^d r\int d^d r'\rho(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')\right]\right\rangle_p\ , \tag{3.23}$$

where we have introduced, by analogy with Eq. (3.2), the polymer density[32]

$$\rho(\mathbf{r})=\int_0^N d\tau\delta(\mathbf{r}-\mathbf{r}(\tau))\ . \tag{3.24}$$

Extension to the many chains case can be accomplished now rather straightforwardly[32] so that instead of Eqs. (3.10) and (3.11) we now obtain, in the grand canonical formalism, the following result for the partition function of the monodisperse (the same N for all chains) solution of polymers

$$Z=\int\mathcal{D}[\lambda]\exp\left[-\int d^d r\,\lambda(\mathbf{r})\right]\mathcal{L}[\lambda(\mathbf{r})]\ , \tag{3.25}$$

where

$$\mathcal{L}[\lambda(\mathbf{r})]=\int\mathcal{D}[\boldsymbol{\phi}]\exp(-\beta S[\boldsymbol{\phi},\lambda])\ ,$$

$$S[\boldsymbol{\phi},\lambda]=\frac{1}{2}\int d^d r\int d^d r'(\boldsymbol{\phi}-\hat{\mathbf{U}})^T\underline{V}^{-1}(\boldsymbol{\phi}-\hat{\mathbf{U}})-\frac{1}{\beta}\int d^d r\exp[-\beta(\phi_2-\lambda)]-\frac{\mathcal{N}}{\beta}\int\mathcal{D}[\mathbf{r}(\tau)]\exp\left[-\frac{d}{2l}\int_0^N d\tau\left[\frac{d\mathbf{r}}{d\tau}\right]^2-\beta\int_0^N d\tau[\phi_1(\mathbf{r}(\tau))-\lambda(\mathbf{r}(\tau))]\right]\ , \tag{3.26}$$

and the matrix $\underline{V}$ has the same form as in the case of simple fluids with V_{11}, V_{12}, V_{22} being polymer-polymer, polymer-solvent, and solvent-solvent interaction potentials, respectively. The application of saddle-point method to Eqs. (3.25) and (3.26) proceeds along the same lines as for the case of simple fluids. Therefore, we provide here only few important new details. In particular, instead of Eq. (3.13) we now obtain

$$\bar{\boldsymbol{\phi}}=\hat{\mathbf{U}}-\int\underline{V}\begin{bmatrix}N\exp[-N\beta(\bar{\phi}_1-\bar{\lambda})]\\ \exp[-\beta(\bar{\phi}_2-\bar{\lambda})]\end{bmatrix}\ , \tag{3.27}$$

and instead of Eq. (3.16) we now have

$$\bar{\rho}_1=N\exp[-N\beta(\bar{\phi}_1-\bar{\lambda})],\quad\bar{\rho}_2=\exp[-\beta(\bar{\phi}_2-\bar{\lambda})]\ , \tag{3.28}$$

where the obvious spatial dependence was suppressed. The rest of the calculation proceeds in the same fashion as before thus producing the final result

$$\beta F=-\frac{\beta}{2}\int\int\bar{\rho}^T\underline{V}\bar{\rho}+\int\left[\frac{\bar{\rho}}{N}\right]\ln\left[\frac{\bar{\rho}}{N}\right]+\int(1-\bar{\rho})\ln(1-\bar{\rho}) \tag{3.29}$$

to be compared with Eq. (2.26) for homogeneous densities. Above we used $\bar{\rho}_1=\bar{\rho}$, $\bar{\rho}_2=1-\bar{\rho}$. This accomplishes our mean-field (saddle-point) treatment for the case of monodisperse polymer solutions.

C. The case of microemulsions

In Sec. II, we have described in some detail the Flory-Huggins-type model of the monodisperse (the same aggregation number for all micelles) microemulsion. We have specified there that the surfactant molecules are located on the surfaces of droplets (micelles) all of which having the same area A. These droplets are *not* assumed to be rigid. By analogy with polymers, we have now to consider first the path integral for a single micelle which should come as a direct generalization of the Z_p given by Eq. (3.22). This can be accomplished by generalization of the model of crumpled manifolds (or tethered surfaces) proposed some time ago by Kardar and Nelson[33] and subsequently considered by other authors.[34,35] By analogy with polymers, they write the following partition function for the self-avoiding tethered surface:[36]

$$Z_{\mathrm{CM}}=\mathcal{N}\int\mathcal{D}[\mathbf{r}(\mathbf{x})]\times\exp\left[-\frac{k}{2}\int d^Dx\,\nabla\mathbf{r}\cdot\nabla\mathbf{r}-\frac{b}{2}\int d^Dx\int d^Dx'\,\delta^d(\mathbf{r}(\mathbf{x})-\mathbf{r}(\mathbf{x}'))\right], \tag{3.30}$$

where $\mathbf{r}(\mathbf{x})$ is the spatial position of some segment of the surface which can be described by the coordinate $\mathbf{x}$ in the internal space of surface (which is D dimensional) just like $\mathbf{r}(\tau)$ for the polymer segment which has the contour position τ along the chain [see Eq. (3.22)]. In this model, it is assumed that the space of internal coordinates $\mathbf{x}=\{x_1,x_2,\ldots,x_D\}$ represents a bounded domain $\wp\in R^D$ and that the shape of the domain should be assigned *by hand in advance.*

For the case of microemulsions we actually have only one restriction that the area A of the droplet remains the same.[37] This then *makes unnecessary* to assign the domain $\wp$ in advance, instead, it should be determined self-consistently as we shall demonstrate below in Sec. IV. With these remarks, we arrive at the following generalization of the model given by Eq. (3.30):

$$Z_m=\mathcal{N}\int\mathcal{D}[g;\mathbf{r}(\xi)]\delta\left[\int d^2\xi\sqrt{g}-A\right]\exp\{-\beta S[\mathbf{r}(\xi);g]\}, \tag{3.31}$$

where

$$S[\mathbf{r}(\xi);g]=\frac{\gamma_0}{2}\int d^2\xi\sqrt{g}\,g^{\alpha\beta}\partial_\alpha\mathbf{r}\cdot\partial_\beta\mathbf{r}+\frac{b}{2}\int d^2\xi\sqrt{g}\int d^2\xi'\sqrt{g}\,\delta^d(\mathbf{r}(\xi)-\mathbf{r}(\xi')) . \tag{3.32}$$

For locally flat surfaces we have $g^{\alpha\beta}=g_{\alpha\beta}=\delta_{\alpha\beta}$ and we obtain back Eq. (3.30). Here g is the determinant of the matrix $\partial_\alpha r^\mu\partial_\beta r_\mu$ representing the induced metric of surface (in terminology taken from the mathematical literature[38]), $\alpha,\beta=1,2$, $r_\mu=r_\mu(\xi)$, $\mu=1-d$, the summation over the repeated indices is assumed, $\xi=\{\xi_1,\xi_2\}$ represents the internal space of the surface imbedded in d dimensional external space, γ_0 is the bare surface tension. Functional integral (3.31) has been considered some time ago by Zamolodchikov[39] (without the self-interaction term) who considered only the surface of genus zero (i.e., spheres) as solutions of the minimization problem which determines the metric $g^{\alpha\beta}$ self-consistently as it will be explained below. Extension of his results to surfaces of higher genus (e.g., torus, etc.) is presented in Ref. 40. The model based on Eqs. (3.31) and (3.32) can be complicated by inclusion of the rigidity terms in addition to the elastic term given by the first term in the right-hand side of Eq. (3.32). The inclusion of the rigidity terms may or may not play any significant role as will become apparent from the subsequent. Moreover, it can be shown[41] that, at least for the case of spherical geometry, there is no need to impose *in addition* to the constraint of area conservation the constraint of volume conservation because the last constraint is satisfied automatically if the first is imposed. The extension of the results (3.31) and (3.32) to the case of many surfaces now can be accomplished in exactly the same way as for polymers. Following Ref. 42, introduce the covariant density

$$\rho(\mathbf{r})=\int d^2\xi\sqrt{g}\,\delta^d(\mathbf{r}-\mathbf{r}(\xi)) \tag{3.33}$$

to be compared with Eq. (3.24). Use of Eq. (3.33) permits us to write, instead of Eqs. (3.25) and (3.26), the following result for the grand partition function for the monodisperse solution of interacting droplets:

$$Z=\int\mathcal{D}[\lambda]\int\mathcal{D}[\boldsymbol{\phi}]\exp(-\beta S[\boldsymbol{\phi},\lambda]) , \tag{3.34}$$

where

$$S[\boldsymbol{\phi},\lambda]=\frac{1}{\beta}\int d^dr\,\lambda(\mathbf{r})+\frac{1}{2}\int\int(\boldsymbol{\phi}-\hat{\mathbf{U}})^T\underline{V}^{-1}(\boldsymbol{\phi}-\hat{\mathbf{U}})-\frac{\mathcal{N}}{\beta}\int\mathcal{D}[g;\mathbf{r}(\xi)]\delta\left[\int d^2\xi\sqrt{g}-A\right]\times\exp\{-\beta S[\mathbf{r}(\xi),g;\phi_1,\lambda]\}-\frac{1}{\beta}\int d^dr\exp[-\beta(\phi_2-\lambda)] , \tag{3.35}$$

and

$$S[\mathbf{r}(\xi),g;\phi_1,\lambda]=\frac{\gamma_0}{2}\int d^2\xi\sqrt{g}\,g^{\alpha\beta}\partial_\alpha\mathbf{r}\cdot\partial_\beta\mathbf{r}+\int d^2\xi\sqrt{g}\,[\phi_1(\mathbf{r}(\xi))-\lambda(\mathbf{r}(\xi))] . \tag{3.36}$$

Application of the saddle-point method to the path integral, Eq. (3.34), proceeds in complete analogy with case of polymers thus producing the final mean-field result analogous to Eq. (3.29) with N being replaced by A, (some additional details are given in Sec. IV). In case of homogenous solution of the Eq. (3.27) (modified accordingly for the present case) we arrive at the result (2.34), as expected. We do not include the irrelevant finite (or infinite) constants in the final answer because they are not affecting the thermodynamics. Presented results accomplish our mean-field treatment.

IV. COMPUTATION OF THE FLUCTUATION CORRECTIONS TO THE MEAN-FIELD RESULTS

Inclusion of fluctuations in the computation of path integrals is absolutely necessary for several reasons. First, as in the saddle-point theory for ordinary integrals, not all saddle-point solutions should be accepted but only those which maximize the function in the exponent of the integral. Second, in the case of quantum field theory, accounting for fluctuation corrections permits us to distinguish between the different universality classes. In our case we have strong experimental evidence, discussed briefly in the Introduction and further discussed in Sec. V, that the simple fluids, polymers, and microemulsions all belong to the same Ising-type universality class. Although this is rather obvious for the simple liquids because of Lee's and Yang's work on the subject,[1] it is much less obvious for polymers and microemulsions. In the last case the conflicting results were reported quite recently.[43,44] Here we would like to demonstrate that, indeed, all three systems belong to the Ising model universality class. This, however, does not exclude some differences between these systems which might be seen if the crossover regime is studied as it will become apparent from our derivations, which we plan to present in a forthcoming publication. See also Sec. V.

A. The case of simple fluids

Use of the functional integral, Eqs. (3.11)–(3.13) along with substitution of the fields $\phi_i=\bar{\phi}_1+\delta\phi_i$, $i=1,2$, and $\lambda=\bar{\lambda}+\delta\lambda$ produces with accuracy up to quadratic terms the following fluctuation matrix $\|M\|$ defined as

$$\|M\|=\begin{vmatrix} \dfrac{\delta^2 S}{\delta\phi_1^2} & \dfrac{\delta^2 S}{\delta\phi_1\delta\phi_2} & \dfrac{\delta^2 S}{\delta\phi_1\delta\lambda} \\ \dfrac{\delta^2 S}{\delta\phi_2\delta_1} & \dfrac{\delta^2 S}{\delta\phi_2^2} & \dfrac{\delta^2 S}{\delta\phi_2\delta\lambda} \\ \dfrac{\delta^2 S}{\delta\lambda\delta\phi_1} & \dfrac{\delta^2 S}{\delta\lambda\delta\phi_2} & \dfrac{\delta^2 S}{\delta\lambda^2} \end{vmatrix} . \quad (4.1)$$

Actual use of the Ising-type action, Eq. (3.12), produces for the matrix $\|M\|$ the following result (the obvious spatial dependence is suppressed):

$$\|M\|=\begin{vmatrix} V_{11}^{-1}-\dfrac{\bar{\rho}}{T} & V_{12}^{-1} & \dfrac{\bar{\rho}}{T} \\ V_{12}^{-1} & V_{22}^{-1}-\dfrac{1-\bar{\rho}}{T} & \dfrac{1-\bar{\rho}}{T} \\ \dfrac{\bar{\rho}}{T} & \dfrac{1-\bar{\rho}}{T} & -\dfrac{1}{T} \end{vmatrix} . \quad (4.2)$$

It is convenient to write Eq. (4.2) in the alternative form as

$$\|M\|=\underline{A}\left[\underline{I}-\frac{1}{T}\underline{A}^{-1}\cdot\underline{B}\right] , \quad (4.3)$$

where the matrix $\|A\|$ is given by

$$\|A\|=\begin{vmatrix} V_{11}^{-1} & V_{12}^{-1} & 0 \\ V_{12}^{-1} & V_{22}^{-1} & 0 \\ 0 & 0 & \dfrac{-1}{T} \end{vmatrix} , \quad (4.4)$$

and the matrix $\|B\|$ is defined by

$$\|B\|=\begin{vmatrix} \bar{\rho} & 0 & -\bar{\rho} \\ 0 & 1-\bar{\rho} & -(1-\bar{\rho}) \\ -\bar{\rho} & -(1-\bar{\rho}) & 0 \end{vmatrix} . \quad (4.5)$$

In arriving at the result (3.10)–(3.12) ρ integration was performed which produced the infinite normalization factor which has been absorbed in the normalization of measure as it was explained after Eq. (3.12). Now we can eliminate this factor by using the properties of the functional determinants (retention of the quadratic in $\delta\phi_i$ and $\delta\lambda$ terms in the exponent leads us to the consideration of the functional determinants[26]). The infinite factor coming from ρ integration is, in fact, the functional determinant which cancels the functional determinant coming from the matrix $\|A\|$. Whence we are left with the computation of the functional determinant of the matrix $\|Q\|$ defined by

$$\|Q\|=\underline{I}-\frac{1}{T}\underline{A}^{-1}\cdot\underline{B}=\begin{vmatrix} 1-\dfrac{V_{11}\bar{\rho}}{T} & -\dfrac{V_{12}(1-\bar{\rho})}{T} & \dfrac{V_{11}\bar{\rho}+V_{12}(1-\bar{\rho})}{T} \\ -\dfrac{V_{12}\bar{\rho}}{T} & 1-\dfrac{V_{22}(1-\bar{\rho})}{T} & \dfrac{V_{21}\bar{\rho}+V_{22}(1-\bar{\rho})}{T} \\ -\bar{\rho} & -(1-\bar{\rho}) & 1 \end{vmatrix} . \quad (4.6)$$

The determinant of the matrix $\|Q\|$ can be easily computed by using the Fourier transform and known formula $\ln\det\|Q\| = \operatorname{tr}\ln\|Q\|$. In terms of order parameter m defined by Eq. (2.6) the final result for the fixed wave vector $\mathbf{k}$ is given by (omitting an unimportant overall constant)

$$\det\|Q\|_{\mathbf{k}} = \left[\frac{T}{T_c(\mathbf{k})} - 1 + m^2\right] , \tag{4.7}$$

where $T_c(\mathbf{k}) = \frac{1}{4}(V_{11} - 2V_{12} + V_{22})(\mathbf{k})$. Making usual expansion $T_c(\mathbf{k}) \approx T_c(0) - \alpha k^2$ where α can be put equal to one by proper rescaling we obtain

$$\det\|Q\|_{\mathbf{k}} = (k^2 + \tau + m^2) , \tag{4.8}$$

with τ is being defined after Eq. (2.7). Combining Eq. (2.7) with the results of computation of the fluctuation corrections, Eq. (4.8), we finally obtain

$$\frac{F}{TN_0} = \frac{\Phi_0}{T} + \tfrac{1}{2}\tau m^2 + \tfrac{1}{12}m^4 + \tfrac{1}{2}\int \frac{d^dk}{(2\pi)^d}\ln(k^2 + \tau + m^2) \tag{4.9}$$

to be compared with the standard result of the ϕ^4 (Ising) field theory given in the book by Amit[24] [see his Eq. (6.25)]. Comparison with his book suggests that his $\lambda/4! = \frac{1}{12}$, which produces $\lambda/2 = 1$ in the fluctuation correction term, as anticipated. This concludes the formal treatment of fluctuations for fluids.

B. The case of polymers

Although the treatment of fluctuation corrections for polymers proceeds formally along the same lines as that for simple fluids, there are some important differences between these two cases. As before, we start with the fluctuation matrix (4.1). This time, however, we decompose the fields ϕ_i and λ as follows: $\phi_i = \bar{\phi}_i + (1/\sqrt{N})\delta\phi_i$, $\lambda = \bar{\lambda} + (1/\sqrt{N})\delta\lambda$. In view of Eqs. (3.26) and (4.1) we can write the following result:[31]

$$\begin{aligned}\int \mathcal{D}[\mathbf{r}(\tau)]\exp\left[-\frac{d}{2l}\int_0^N d\tau\left[\frac{d\mathbf{r}}{d\tau}\right]^2 - \beta\int_0^N d\tau[\phi_1(\mathbf{r}(\tau)) - \lambda(\mathbf{r}(\tau))]\right] \\ \approx \exp\{-\beta N[\bar{\phi}_1(\mathbf{r}) - \bar{\lambda}(\mathbf{r})]\}\left[N_0 - \frac{\sqrt{N}}{T}\int d^dr[\delta\phi_1(\mathbf{r}) - \delta\lambda(\mathbf{r})]\right. \\ \left. + \frac{1}{NT^2}\int d^dr\int d^dr'[\delta\phi_1(\mathbf{r}) - \delta\lambda(\mathbf{r})]S_0(\mathbf{r}-\mathbf{r}';N)[\delta\phi_1(\mathbf{r}') - \delta\lambda(\mathbf{r}')] + \cdots\right] ,\end{aligned} \tag{4.10}$$

where [see Eq. (4.20)] we used the conventions $Z_\rho^0 = V = N_0a^d$; $a^d = 1$ and also

$$S_0 = \int_0^N d\tau\int_0^\tau d\tau' G_0(\mathbf{r}-\mathbf{r}';\tau-\tau') , \tag{4.11}$$

where G_0 is usual Gaussian propagator.[31] The combined use of Eqs. (3.26), (4.10), and (4.11) ultimately produces the following result for the fluctuation matrix $\|M\|$ (the explicit spatial dependence is omitted as before):

$$\|M\| = \begin{bmatrix} V_{11}^{-1} - \dfrac{\bar{\rho}}{NT}2S_0 & V_{12}^{-1} & \dfrac{2S_0}{NT}\bar{\rho} \\ V_{12}^{-1} & V_{22}^{-1} - \dfrac{1-\bar{\rho}}{T} & \dfrac{1-\bar{\rho}}{T} \\ \dfrac{2S_0}{NT}\bar{\rho} & \dfrac{1-\bar{\rho}}{T} & -\dfrac{1}{T}\left[1 - \bar{\rho} + \dfrac{2S_0}{N}\bar{\rho}\right] \end{bmatrix} \tag{4.12}$$

to be compared with Eq. (4.2). Here $\bar{\rho}$ was defined after Eq. (3.21). Following the same steps as before, we arrive at the matrix $\|Q\|$, which in polymer's case can be written (for the case of homogeneous density $\bar{\rho} = n$) as

$$\|Q\| = \begin{bmatrix} 1 - \dfrac{2S_0}{NT}V_{11}n & -\dfrac{V_{12}(1-n)}{T} & \dfrac{1}{T}\left[2S_0V_{11}\dfrac{n}{N} + V_{12}(1-n)\right] \\ -\dfrac{2S_0}{NT}V_{12}n & 1 - \dfrac{V_{22}}{T}(1-n) & \dfrac{1}{T}\left[2S_0V_{12}\dfrac{n}{N} + V_{22}(1-n)\right] \\ -\dfrac{2S_0}{1-n}\dfrac{n}{N} & -1 & 1 + \dfrac{2S_0}{1-n}\dfrac{n}{N} \end{bmatrix} . \tag{4.13}$$

Use of Fourier transform methods[26] permits us to calculate the determinant of the matrix $\|Q\|$ in a straightforward way. For the fixed wave vector $\mathbf{k}$ we obtain, with accuracy up to an overall unimportant multiplicative constant, the following result:

$$\det\|Q\| = \frac{N}{2S_0(\mathbf{k})} + n_c\left[1 - \frac{T_c(\mathbf{k})}{T}\right] + n_c m\left[1 - \frac{T_c(\mathbf{k})}{T}\right] + n_c^2(1+2m) + n_c^2 m^2 \, , \tag{4.14}$$

where we have used Eq. (2.6) which defines the order parameter m and defined $T_c(\mathbf{k}) = (V_{11} + V_{22} - 2V_{12})(\mathbf{k}) \sim T_c - \alpha k^2$ with α being chosen to be equal to one by the proper choice of system of units. Using a known result for $S_0(\mathbf{k})$,[45]

$$\frac{2S_0(\mathbf{k})}{N} \approx \begin{cases} N(1-k^2R_g^2/d), & R_g|\mathbf{k}| \ll 1 \\ 2N/k^2R_g^2, & R_g|\mathbf{k}| \gg 1 \, , \end{cases} \tag{4.15}$$

where $R_g^2 = Nl^2/2d$ and, in view of Eq. (2.28), we conclude that, in order for the polymer solutions to belong to the same universality class as simple fluids, the following *additional* steps should be made. First, the order parameter should be redefined as $m \to \sqrt{n_c}m = \mu$; second, only the long-wavelength limit for $S_0(\mathbf{k})$, Eq. (4.15), should be used in order to achieve the correct renormalization scheme in view of Eq. (2.28); third, a new critical temperature $T_c^* = T_c/(1+2/\sqrt{N})$ should be introduced; fourth, to eliminate the linear (in m) terms in Eq. (4.14) the shifted order parameter variable $\hat{m}$ should be introduced via equation $m = \hat{m}/2 + c$, where $c = -\hat{\tau}/n_c$, $\hat{\tau} = (T - T_c^*)/T$. This shift, accordingly, should be made in Eq. (2.28). After these steps are made the expression for the free energy functional, Eq. (2.28), which includes the fluctuation corrections can be written as

$$\frac{F - F_0}{TN_0} = \tfrac{1}{2}\hat{\tau} n_c \mu^2 + \frac{n_c}{12}\mu^4 + \frac{1}{2}\int \frac{d^dk}{(2\pi)^d}\ln(k^2 + n_c\tau + n_c\mu^2) \tag{4.16}$$

and in Landau's style the terms $\sim\mu^2\tau$, etc., were ignored at the mean-field level. Evidently, this expression belongs to the Ising universality class by virtue of the same arguments as were made for fluids. This concludes the treatment of the polymer solutions case.

C. The case of monodisperse microemulsions

Because the model microemulsion described by Eq. (2.34) can be treated in exactly the same way as the Flory-Huggins model for polymers, we expect that the computation of fluctuation corrections for this model should also demonstrate that the uncharged (neutral) microemulsions belong to the Ising-type universality class. This conjecture is strongly supported by the recent experiments described in more detail in Sec. V. Here we provide only a sketch of the proof of the conjecture made above. The complete treatment will be presented in the forthcoming papers. A close analogy between polymers and microemulsions suggests that in computation of fluctuation corrections the only difference between these two cases will emerge from the difference in the actual form of the expansion (for microemulsions) analogous to Eq. (4.10) for polymers. We would now like to demonstrate that, in spite of this difference, the computation essentially proceeds along the same steps in both cases. In Sec. III we have already noticed the close similarity between the models of tethered surfaces, Eq. (3.30), and microemulsions, Eqs. (3.31) and (3.32). The model based on Eqs. (3.31) and (3.32) is reduced to (3.30) for $g^{\alpha\beta} = \delta^{\alpha\beta}$. In turn, the development of the model (3.30) proceeds in close analogy with the development of the analogous model for polymers.[34,36] In both cases we can define the zeroth order distribution function G_0 via

$$G_0(\mathbf{r}(\tau_1) - \mathbf{r}(\tau_2)) = \langle \delta^d(\mathbf{r}(\tau_1) - \mathbf{r}(\tau_2) - \mathbf{r}) \rangle_{N(A)} \, , \tag{4.17}$$

where, for the case of polymers, we have

$$\langle \cdots \rangle_N = \mathcal{N}\int \mathcal{D}[\mathbf{r}(\tau)]\exp\left[-\frac{d}{2l}\int_0^N d\tau \left[\frac{d\mathbf{r}}{d\tau}\right]^2\right] \cdots \tag{4.18}$$

and for the case of surfaces

$$\langle \cdots \rangle_A = \mathcal{N}\int \mathcal{D}[g;\mathbf{r}(\xi)]\delta\left[\int d^2\xi\sqrt{g} - A\right] \times \exp\{-\beta S[\mathbf{r}(\xi), g; 0,0]\} \cdots \tag{4.19}$$

with τ_1 and τ_2 for polymers being replaced by ξ_1 and ξ_2 for microemulsions. The last case is reduced to that for tethered surfaces when $g^{\alpha\beta} = \delta^{\alpha\beta}$. For $\tau_1 = N$ we have $\mathbf{r}(N) \equiv \mathbf{R}_1$, and for $\tau_2 = 0$ we have $\mathbf{r}(0) = \mathbf{R}_2$. The partition function Z_p^0, defined in comments preceeding Eq. (3.23), can be redefined now as ($a^d = 1$)

$$Z_p^0 = \int d^dR_1 \int d^dR_2 G_0(\mathbf{R}_1 - \mathbf{R}_2; N) = V = N_0 \, , \tag{4.20}$$

where we have used the property of translational invariance and the normalization of G_0. Expansion, Eq. (4.10), can be written now in the following equivalent form:[31]

$$\begin{aligned} \text{Eq. (4.10)} = {} & \exp[-\beta N(\bar{\phi}_1 - \bar{\lambda})] \\ & \times \Bigg[N_0 - \frac{1}{T\sqrt{N}}\int d^dR_1 \int d^dR_2 \int_0^N d\tau \int d^dr G_0(\mathbf{R}_1 - \mathbf{r}; N-\tau)\delta\Phi(\mathbf{r}(\tau))G_0(\mathbf{r} - \mathbf{R}_2; \tau) \\ & + \frac{1}{2NT^2}\int d^dR_1 \int d^dR_2 \int_0^N d\tau \int_0^N d\tau' \int d^dr \int d^dr' G_0(\mathbf{R}_1 - \mathbf{r}; N-\tau)\delta\Phi(\mathbf{r}(\tau))G_0(\mathbf{r} - \mathbf{r}'; \tau - \tau') \\ & \times \delta\Phi(\mathbf{r}(\tau'))G_0(\mathbf{r}' - \mathbf{R}_2; \tau') + \cdots \Bigg] \, , \end{aligned} \tag{4.21}$$

where $\delta\Phi=\delta\phi_1-\delta\lambda$. This form is ideally suited for the generalization to the case of surfaces. In the case of surfaces we need only to replace $\int_0^N d\tau\cdots$ by $\int d^2\xi\sqrt{g}\cdots$ and make the expansion for ϕ_i and λ fields as $\phi_i=\bar{\phi}+(1/\sqrt{A})\delta\phi_i$, $\lambda=\bar{\lambda}+(1/\sqrt{A})\delta\lambda$. Instead of $S_0(\mathbf{k})$ for polymers we now have to consider its analogue for surfaces. To do so, it is useful to consider first more general **k**-space n-point function:

$$G(\mathbf{k}_1,\ldots,\mathbf{k}_n)=\left\langle\prod_{i=1}^{n}\int d^2\xi_i\sqrt{g_i}e^{i\mathbf{k}_i\cdot\mathbf{r}(\xi_i)}\right\rangle_A \tag{4.22}$$

This function was calculated some time ago by Polyakov[46] with the result (for the case of sphere and with the use of conformal gauge $g_{\alpha\beta}=\delta_{\alpha\beta}\exp[\phi(\mathbf{z})]$, $\mathbf{z}=(\xi_1,\xi_2)$,

$$\begin{aligned}G(\mathbf{k}_1,\ldots,\mathbf{k}_n)={}&\mathcal{N}\int\mathcal{D}[\phi]\exp\left[-\frac{26-d}{48\pi}S_L[\phi]\right]\\&\times\int\prod_{i=1}^{n}d^2\xi_i\exp\left[\phi(\mathbf{z}_i)-\frac{1}{\beta\gamma_0}\sum_{i,j}^{n}\mathbf{k}_i\cdot\mathbf{k}_jG(\mathbf{z}_i,\mathbf{z}_j,\phi)\right]\delta\left[\int d^2\xi\exp[\phi(\mathbf{z})]-A\right],\end{aligned} \tag{4.23}$$

where the Green's function G can be written as

$$G(\mathbf{z},\mathbf{z}';\phi)=\begin{cases}-\dfrac{1}{4\pi}\ln|\mathbf{z}-\mathbf{z}'|^2, & z\neq z'\\[2mm] \dfrac{\phi(z)}{4\pi}-\dfrac{1}{4\pi}\ln\epsilon, & z=z'\end{cases} \tag{4.24}$$

with ϵ being some cutoff, just like a in Eq. (A9) of Ref. 36. Function $G(\mathbf{k}_1,\ldots,\mathbf{k}_n)$ is nonzero only for $\sum_i\mathbf{k}_i=0$ as in the case of tethered surfaces[36] which is just the consequence of transitional invariance. For $d=26$ and for the points $\{\xi_i\}$ which belong to the surface of area A the result (4.23) *coincides exactly* with Eq. (A10) of Ref. 26 for tethered surfaces (in case of their $D=2$). The difference with the present case lies in the fact that the restriction of constant surface area for the microemulsions automatically selects the shape of the surface *self-consistently* unlike the case of tethered surfaces where the domain $\mathcal{V}\in R^D$ is chosen *in advance,* see Eq. (3.30). To determine the shape self-consistently, we have to solve the variational problem[39,40] of finding an extremal solution of the equation

$$\frac{\delta S_L[\phi]}{\delta\phi}=0 \tag{4.25}$$

subjected to constraint

$$\int d^2\xi\exp[\phi(\mathbf{z})]=A\ , \tag{4.26}$$

where the action $S_L[\phi]$ is defined by

$$S_L[\phi]=\frac{1}{2}\int d^2\xi[\nabla\phi(\mathbf{z})]^2\ . \tag{4.27}$$

Variation of S_L produces

$$\delta S_L=\int d^2\xi(-\nabla^2\phi)\delta\phi\ , \tag{4.28}$$

while the variation of the constraint produces

$$\int d^2\xi\, e^{\phi}\delta\phi\ . \tag{4.29}$$

Now, if $\nabla^2\equiv\Delta$ is the flat-space Laplacian and Δ_g is the Laplacian in the curved space with metric tensor $g_{\alpha\beta}$, then it can be shown[40] that

$$R(e^{\phi}g)=e^{-\phi}R(g)+e^{-\phi}\Delta_g\phi\ , \tag{4.30}$$

with $R(g)$ being the scalar curvature[38,40,41] of the above curved space. For the flat space $g_{\alpha\beta}=\delta_{\alpha\beta}\equiv\hat{g}$ so that $R(\hat{g})=0$. Use of this property in Eq. (4.30) produces

$$e^{\phi}R(e^{\phi})=\Delta\phi\ . \tag{4.31}$$

Combining Eqs. (4.28) and (4.29) with (4.31), we obtain

$$\int d^2\xi[R(e^{\phi})+\lambda]e^{\phi}\delta\phi=0\ , \tag{4.32}$$

where λ is usual Lagrange multiplier (perhaps rescaled). Equation (4.32) implies

$$-R(e^{\phi})=\lambda=\text{const}=-R\ . \tag{4.33}$$

Combining Eqs. (4.31) and (4.33) produces famous Liouville equation[38,46]

$$\Delta\phi+Re^{\phi}=0\ , \tag{4.34}$$

which for R being constant immediately admits solution[38]

$$\phi_c(\mathbf{z})=\ln\left[\frac{4r^4}{[r^2+|\mathbf{z}|^2]^2}\right], \tag{4.35}$$

which is an equation for the metric of the sphere of radius $r=R^{-1}$. Here, the complex z plane coordinates were introduced via stereographic projection[38] with $\bar{z}$ being a complex conjugate of z so that $|z|^2=|\bar{z}\cdot z|$. The use of Eq. (4.35) now produces

$$\int d^2z\, e^{\phi_c}=A\ , \tag{4.36}$$

which determines the Lagrange multiplier λ in view of Eq. (4.33). Whence, the variational problem is solved completely and, if it is necessary, we can also consider the fluctuations around the spherical shape. Given above formalism can be extended to the case of more complicated surfaces, in principle.[40] Here we shall restrict ourself only with the case of sphere. Going back to Eq. (4.22) and using the obtained results we have

$$G(\mathbf{k}_1)=A\,\delta(\mathbf{k}_1)\ , \tag{4.37}$$

which produces essentially the same first two terms as in the square brackets of Eq. (4.10) with $\sqrt{N}$ being replaced by $\sqrt{A}$. Instead of $2S_0(\mathbf{k})/N$ we now have

$$\frac{1}{A}G(\mathbf{k}_1,\mathbf{k}_2)=\frac{1}{A}G(\mathbf{k},-\mathbf{k})\equiv\frac{2\hat{S}(\mathbf{k})}{A}$$
$$=\frac{A}{(4\pi)^2}\int d^2z_1\int d^2z_2\exp\left[\phi_1(z_1)+\phi_1(z_2)-\frac{k^2}{4\pi\beta\gamma_0}\phi_1(z_1)-\frac{k^2}{4\pi\beta\gamma_0}\phi_1(z_2)-\frac{k^2}{2\pi\beta\gamma_0}\ln|z_1-z_2|^2\right]\ , \tag{4.38}$$

where we have introduced the metric $\phi_1(\mathbf{z})$ instead of $\phi_c(\mathbf{z})$. The metric $\phi_1(\mathbf{z})$ is the metric of the sphere of *unit* radius so that $\phi_c=\phi_1+\ln(A/4\pi)$ as can be easily seen by the direct substitution of the last equation into Eq. (4.36). When the actual computations of Eq. (4.38) are made, we have to remember that $z_1\neq z_2$ for the logarithmic term in view of Eq. (4.24). These computations are rather lengthy so that we present here only the final result leaving the details of this and other computations, which we mention in Sec. VI, for the forthcoming papers. As in the case of polymers,[45] the final result is rather cumbersome and can be well approximated by the following interpolation formula:

$$\frac{2\hat{S}(\mathbf{k})}{A}\simeq\frac{A}{(1+k^2/2\beta\gamma_0)^{1/2}}\ , \tag{4.39}$$

to be compared with the analogous interpolation formula, Eq. (2.83) of Ref. 45, for polymers valid for all k's. The rest of the calculations proceed exactly in the same fashion as for polymers, see Eqs. (4.12)–(4.16) with N being replaced by A. This calculation assumes, of course, that the surface tension of the single droplet interface is nonzero. Inclusion of the effects of rigidity will effectively change the surface tension and might cause the surface transitions[37,42] in which case the whole above picture becomes invalid. This situation requires separate study to be considered in the future, whence we conclude that inclusion of the density fluctuations in the case of microemulsions produces the same result as Eq. (4.16) with $n_c\sim 1/\sqrt{N}$ for polymers being replaced by $n_c\sim 1/\sqrt{A}$ for monodisperse microemulsions. Therefore, the liquid-gas transition for microemulsions also belongs to the Ising universality class. This conclusion is strongly supported by the recent experiments on microemulsions to be considered next.

V. COMPARISON WITH EXPERIMENT

Up to date analysis of the experimental data for the case of simple fluids can be found in the recent paper by Goldstein and Parola.[47] These authors acknowledge that in case of simple neutral fluids the effects of cubic and quintic terms (see our Sec. II) which exhibit themselves through the singularity in fluid diameter, Eq. (2.14), are rather weak and require sophisticated equipment to be reliably detected. There is an entirely different situation for the polymers where the asymmetry of the coexistence curve is very pronounced.

In Sec. II we provided a mean-field analysis for the simple fluids, polymers and microemulsions. The results of the mean-field analysis suggested to us that, although the cubic and quintic terms might be important, almost *all* experimentally measurable results can be with good accuracy be explained *solely* on the basis of standard ϕ^4 field theory.[24,26] This statement remained a plausible conjecture until Sec. IV where the fluctuation corrections were explicitly computed. This computation revealed the correctness of our conjecture as far as the Ising-type critical exponents are of interest. For the case of simple fluids, these were known for some time.[1] For the case of polymers these exponents were determined in the accurate experiments by Dobashi *et al.*[4] to be discussed in some detail. More recent data for other polymer systems can be found in Ref. 3. For the case of microemulsions a much less clear situation existed only quite recently.[43,44] The authors of Ref. 43 found critical exponents γ and ν which vary continuously from the Ising to much smaller values. This observation, in turn, initiated the theoretical investigation[44] aimed to explain why the exponents are continuously varying. The most recent *independent* experiments[13,14] indicate, however, that the critical exponents do belong to the three-dimensional Ising universality class which is in full agreement with the results of our findings. Because the actual experimental methods of measurements for the polymers and the microemulsions are very similar, we shall spend most of the remainder of this section on the discussion of the polymer solutions case. For the system polystyrene in methylcyclohexane Dobashi *et al.*[43] experimentally found the functional dependence of the critical concentration (volume fraction) $\phi_c=n_c$ on the molecular weight $M_w(M_w\propto N)$. Assuming the simple dependence $\phi_c\propto M_w^{\omega}$, based on their Table I, it is easy to find $\omega\sim -0.38\pm 0.01$. Similar results were subsequently obtained in Refs. 48 and 49. The exponent ω *cannot* be predicted from the theory of critical phenomena for the same reason as the critical temperature T_c which is also *not* universal quantity.[24] The discrepancy with the Flory-type result, $n_c\sim N^{-1/2}$, can be attributed, for example, to the presence of the extra

TABLE I. The experimental data taken from the work by Dobashi *et al.*[4]

System	$M\times10^{-4}$	$\ln M$	B	$\ln B$	A	$\ln A$
a	1.02	9.23	1.44±0.05	0.365	1.41±0.22	0.33±0.19
b	1.61	9.69	1.29±0.02	0.255	1.19±0.21	0.16±0.18
c	1.73	9.76	1.27±0.05	0.239	1.22±0.07	0.20±0.05
d	2.02	9.91	1.25±0.02	0.223	0.91±0.10	−0.10±0.10
e	3.49	10.46	1.10±0.01	0.104	1.08±0.09	0.07±0.08
f	4.64	10.75	1.09±0.01	0.086	1.14±0.06	0.13±0.05
g	10.9	11.60	0.99±0.001	−0.010	1.22±0.04	0.20±0.03
h	18.1	12.11	0.84±0.02	−0.150	1.29±0.06	0.25±0.05
i	71.9	13.49	0.75±0.03	−0.288	1.59±0.09	0.47±0.06

higher-body interactions terms absent in the model based on Eq. (2.26). This was already suggested by Muthukumar.[6] We would like to demonstrate here that the presence of these extra higher-body terms will not affect the quantities which are universal, e.g., the critical exponents and the universal ratios, (see Sec. II). Dobashi *et al.*[4] measured the concentration difference $\phi^+-\phi^-$ and concentration sum $\phi^++\phi^-$ of two coexisting phases. They conjectured that

$$\phi^+-\phi^-=B\tau^{\beta} \tag{5.1}$$

and

$$\tfrac{1}{2}(\phi^++\phi^-)-\phi_c=A\tau^{\mu} \tag{5.2}$$

with A, B, β, and μ being adjustable parameters. The results of their measurements are presented in Table II of their work. Analysis of their results for the exponents β and μ strongly indicates the Ising-type values associated normally with the Ising exponents β and $1-\alpha$, respectively. In Sec. II we have introduced the universal ratios R_1 and R_2 defined by Eq. (2.25), while in Eq. (2.33) we have demonstrated *at the mean-field* level that these ratios are just pure numbers *independent of the molecular weight of the chain.* Now we are ready to demonstrate that this remains true in the real experiments. To this end, in addition to the results of Table II we need to use the results for the osmotic compressibility $\chi=C^{\pm}|\tau|^{-\gamma}$. [See Eq. (2.20).] The osmotic compressibility (and hence the exponent γ) can be obtained from the light scattering experiments on the basis of Eq. (3) of Ref. 49. From the same light scattering experiments the exponent ν and the correlation length can be obtained [see Eq. (2) of Ref. 49]. The results presented in that paper suggest that $C^{\pm}\propto M_w^{0.48\pm0.03}$. Given this result, we reanalyzed the results of Table II of Ref. 4, reproduced here as Table I, in order to obtain the molecular weight exponents for A and B defined by Eqs. (5.1) and (5.2). Our results are presented in Figs. 1 and 2. We found $A\propto M_w^{0.17}$, $B\propto M_w^{-0.150}$.

To understand the meaning of these numbers the following observations are helpful. First, in accordance with Eq. (4.16) we must choose the appropriate set of variables to achieve the correspondence with standard ϕ^4 field theory.[24] These are $\tau\rightleftarrows\tau n_c$, $m\rightleftarrows m\sqrt{n_c}$, $\lambda/4!\rightleftarrows n_c/12$. Second, to check the correctness of this choice, it is sufficient to consider the experimental data for the correlation length ξ. From Ref. 49 we obtain $\xi=\xi_0\tau^{-\nu}$ with $\xi_0\propto M_w^{0.28\pm0.03}$ and $\nu=0.63$. Using the results of Ref. 26 and the above identification we obtain

$$\xi\propto(\tau n_c)^{-\nu}=n_c^{-\nu}\tau^{-\nu}\ .$$

According to Ref. 49 $n_c\propto M_w^{-0.4\pm0.02}$, which produces $\xi_0\propto M_w^{0.25\pm0.02}$. This result is in excellent agreement with experimentally observed data. Third, using the relation between the correlation length and the static magnetic susceptibility[5,20] (osmotic compressibility) we have $\tau^{-\gamma}\sim\tau^{-\nu(2-\eta)}$ which in our case gives

$$(\tau n_c)^{-\gamma}\sim(\tau n_c)^{-\nu(2-\eta)}\ .$$

This produces

$$C^{\pm}\propto M_w^{0.4\nu(2-\eta)}\sim M_w^{0.488}\ ,$$

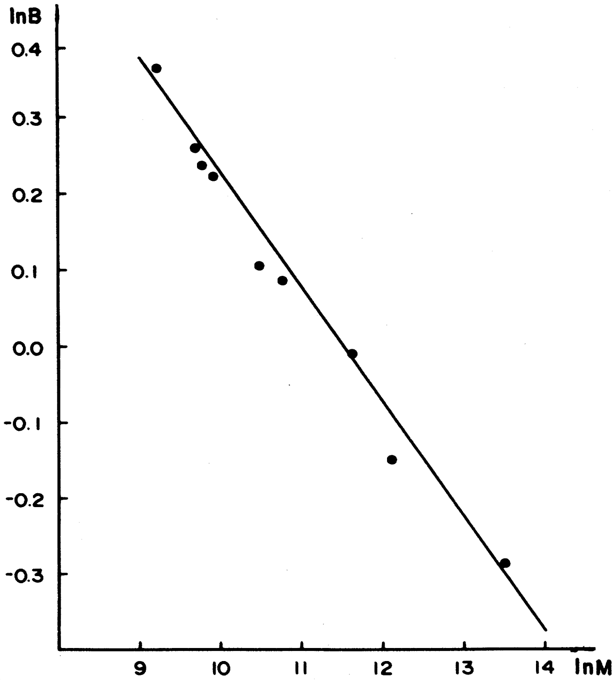

FIG. 1. Log-log plot for the coefficient B, defined in Eq. (5.1), based on data taken from Table I.

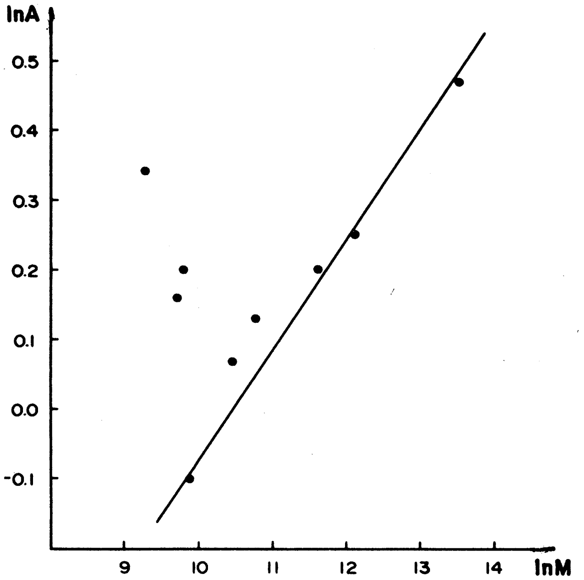

FIG. 2. Log-log plot for the coefficient A, defined in Eq. (5.2), based on data taken from Table I.

which is in perfect agreement with the already-cited result. Fourth, using Eq. (2.19) and the variables just determined, we obtain $m=(n_c)^{-1/2}B(n_c\tau)^{\beta}$, where the amplitude B [not to be confused with that given in Eq. (5.1)] may or may not depend on n_c. To check if B really depends on n_c it is sufficient to use the mean-field result [see the discussion following Eq. (2.30)], which is $B_p \propto n_c^{-1/2}$. This gives us two options for B, $B \propto n_c^{-\beta}$ and $B \propto n_c^{-1/2}$, in order to reach an accord with the mean-field results. To decide which of these two options is actually correct, the universal ratios, Eqs. (2.25) and (2.33), are of some help. In order to utilize them, several further steps are necessary. The reader should remember, that in Eqs. (2.19)–(2.22) the reduced temperature τ should be replaced by $\tau n_c \equiv T$ and that χ, C_s, etc., are given as derivatives of the free energy with respect to the rescaled variables, i.e., μ and T, while the universal ratios R_1 and R_2 are given in terms of original, i.e., nonrescaled, variables. In terms of *these* variables we actually have

$$\chi=n_c^{-1/2}\hat{C}^{\pm}(n_c\tau)^{-\gamma}$$

and

$$C_s=n_c^2\frac{A^{\pm}}{\alpha}(n_c\tau)^{-\alpha}$$

(to be compared with the previous expression for m). Using Eq. (2.32) and the following discussion, we obtain that at the mean-field level $\hat{C}^{\pm}$ defined earlier are equal to $n_c^{-1/2}$, while $A^{\pm}/\alpha \propto n_c^{-1}$. Notice that the experimental results for $C^{\pm}$ discussed earlier are actually related to the combination χn_c. It is this quantity which the authors of Ref. 49 identify with the osmotic compressibility. Notice also that the result $C^{\pm} \propto M_w^{0.48\pm 0.03}$ just quoted indicates that $\hat{C}^{\pm}$ *remains the same* even beyond the mean-field level. Because of this observation, we conjecture that the result $A^{\pm}/\alpha \propto n_c^{-1}$ is also not going to change. To be consistent, we must require finally that the amplitude B defined earlier remains the same as at the mean-field level, i.e., $B \propto n_c^{-1/2}$. With these assumptions, the universal ratios R_1 (or R_2) are given by

$$R_{1,2}\sim\frac{n_c^{1-\alpha}n_c^{-1-\gamma}}{n_c^{-2+2\beta}}\rightarrow \text{pure number}\ ,$$

which provides strong support to our conjecture. Another support is obtained from experiment. Dividing both sides of Eq. (5.1) by ϕ_c, we obtain $B_p \propto M_w^{0.23}$ (in view of our estimate $B \propto M_w^{-0.15}$). Using our conjectured value for B, $B \propto n_c^{-1/2}$, we easily obtain $B_p \propto M_w^{0.26}$, which is in good agreement with experiment.

To test the role of terms $\propto m^3$ we need to recall Eqs. (2.31) and (2.32) to be considered in the limit $\hat{h}\rightarrow 0$. At the mean-field level we have demonstrated that these terms can be reproduced (within the standard ϕ^4 field theory) by making a shift in the reduced temperature

$$\tau\rightarrow\tau+\frac{1}{2}\frac{\hat{h}}{n_c^2}\ .$$

If the fluctuation corrections are included, we conjecture that this replacement should be modified to $\tau\rightarrow\tau+\frac{1}{2}\hat{h}/n_c^{2+\psi}$, where the exponent ψ should reflect the importance of the fluctuation corrections. Because Eq. (2.32) is expected to be correct beyond the mean-field level, we can make this replacement for τ in order to obtain

$$(\eta_l+\eta_g)/n_c \propto \left.\frac{\partial F}{\partial \hat{h}}\right|_{\hat{h}\rightarrow 0}\ .$$

Actual calculation produces

$$(\eta_l+\eta_g)/n_c \propto n_c^{-1-\alpha/4-\psi}\tau^{1-\alpha}\ ,$$

which is in agreement with what we have already obtained at the mean-field level [see the discussion following Eq. (2.30)]. Dividing both sides of Eq. (5.2) by ϕ_c we obtain, on the other hand,

$$(\eta_l+\eta_g)/n_c \propto M_w^{0.55}\tau^{1-\alpha}\ ,$$

where we have used our result for A. If $\alpha\sim 0.12$, then we obtain

$$n_c^{-1-\alpha/4-\psi} \propto M_w^{0.3914+0.38\psi}\ ,$$

which, in view of our previous result, produces $\psi\sim 0.417$. The obtained result clearly indicates the importance of cubic terms for polymer solutions and poses for the theory the problem of explaining the value of the exponent ψ.

For the case of microemulsions[13,16] the obtained experimental values for γ and ν practically coincide with that for polymers.[49] More data are needed to test the corresponding universal ratios.

VI. DISCUSSION

We have presented here a new unified field-theoretic treatment of liquid-gas transition which, we think, is the most natural extension of the phenomenological Landau mean-field theory of such transition.[20] Being guided, on one hand, by the experimental data and, on the other, by the consistency with the previously known theoretical results our treatment is able to explain why such supposedly different systems as simple liquids, polymers and microemulsions exhibit the same kind of critical behavior. In spite of already good agreement with experiment for the above systems, many questions still need to be clarified. First, we would like to understand better the role of the higher-body interactions on nonuniversal critical parameters. Muthukumar[6] already have noticed that inclusion of the three-body interaction term in the Flory-Huggins theory changes the critical concentration from $n_c \propto N^{-1/2}$ to $n_c \propto N^{-1/3}$ to be compared with the experimentally observed $n_c \propto N^{-0.4}$. The theoretical problem lies in explaining why the explicit inclusion of higher-body terms into Hamiltonian does not affect the critical behavior observed experimentally (i.e., it is necessary to demonstrate that these higher-order terms are irrelevant in the renormalization group sense). This problem is closely related to the problem of the choice of renormalization scheme for our already developed theoretical formalism. Indeed, on one hand, comparison between Eqs. (4.9) [or (4.16)] and that given in the book by Amit[24] [see Eq. (6.25) in Amit's book] suggests that the renormalization should proceed *exactly* as in the standard ϕ^4 field theory; on another hand, the free energy (4.9) [or (4.16)] is *not* the free energy of Landau theory of liquid-gas transition as it was explained in Sec. III. If we follow the same steps as in this section starting with Eqs. (4.9) [or (4.16)] then we will arrive at the renormalization scheme close to that which was discussed by Nicoll and Zia.[11] The detailed study of the above situations are already underway and will be presented in the forthcoming publications. The renormalization scheme of Nicoll and Zia does not affect the leading critical exponents or universal ratios. It affects, however, the description of the crossover regime to the noncritical behavior. More data are needed from the experimentalists in order to distinguish between the above described possibilities.

For the case of microemulsions we need not only to provide the detailed derivation of the result (4.39) but also to study how the rigidity may alter this result. Helpful experimental and theoretical information in this regard can be found in the paper by Meunier[50] (see also Ref. 51). Finally, it is necessary to account for the effects of polydispersity (in case of polymers *and* microemulsions) and, in addition, of different topology[52] (in case of microemulsions).

Note added. After this work was completed we became aware of some recent works on Polyakov's bosonic string in noncritical dimensions (i.e., below $d=26$). Khizhnik, Polyakov, and Zamolodchikov[53] (KPZ) have reanalyzed the earlier result of Zamolodchikov, Ref. 39. Their new results were independently rederived by David[54,55] and Diestler and Kawai.[56] According to these authors, the results presented in our Sec. IV correspond to the semiclassical approximation ($d=-\infty$), while for *finite d* Polyakov's bosonic string with area constraint, Ref. 39, exist only for $d \leq 1$ and $d \geq 25$. For $1 \leq d \leq 25$ results of KPZ are *not* in agreement with the corresponding Monte Carlo simulations by Kazakov and Migdal[57] which, on another hand, *do* support their findings for $d \leq 1$. The above authors earlier found[58] that in $d=3$ the same Monte Carlo algorithm produces *meaningful results* for Polyakov-Zamolodchikov model, Ref. 39. Because of this observation, authors of Ref. 57 concluded that the correct description of the model in the region $1<d<25$ is still missing. Our semiclassical results presented in Sec. IV represent only the *leading* contribution which is in agreement with both Refs. 39 and 53. The current problem lies in the computation of systematic corrections to the above semiclassical results. The most recent Monte Carlo simulations on bosonic strings with rigidity in noncritical dimensions[59] indicate that, just as in the case of polymers,[5] the rigidity effects are not important at distances considerably larger than the persistence length so that the nonrigid Zamolodchikov model[39] is quite adequate at such distances.

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