A free energy variational principle is proposed for the study of aggregation structures in amphiphile solutions. For nonionic amphiphiles the postulated free energy functional depends on the scalar concentration fields for solvophilic head groups \(H\) and solvophobic tail groups \(T\); it has a form appropriate for a binary mixture of head-group chains and tail-group chains supplemented by a term that enforces chemical bond connection between pairs of those chains. Numerical solutions to the Euler equations for the variational principle are presented for molecules with formal constitution \(\{(H)_n\,(T)_m\}\) under conditions of spherical aggregate symmetry. These solutions include globular micelles, hollow vesicles, and a type of point defect in a smectic A lamellar system.

\[ (H)_n (T)_m \]  

The final Sec. VI indicates how the present work can be extended to ionic amphiphiles. It also remarks on the need to embed the variational formalism in a more complete statistical mechanical context, and on the procedure for accomplishing that goal.

II. VARIATIONAL PRINCIPLE

To ensure maximal simplicity in the following, attention will be restricted to solutions of nonionic amphiphiles. The interesting and important attributes of these substances arise from the distinguishability of solvophilic head groups \(H\) and solvophobic tail groups \(T\). These are typically combined in each molecule as

\[ n_H + n_T \]

i.e., a sequence of \(n_H+n_T\) units, the first \(n_H\) of which are \(H\) followed by \(n_T T\) units. These are dissolved in a low-molecular-weight-solvent medium of molecules \(W\).

The various aggregation patterns that could spontaneously form in solution (spherical micelles, rods, layers of oriented molecules, bicontinuous phases, microemulsions) can be described economically in terms of the spatial distributions of head units, tail units, and solvent molecules. These distributions will be denoted by the scalar concentration fields \(c_H(r)\), \(c_T(r)\), and \(c_W(r)\). The major objective is to predict what fields are implied by a given set of molecular structures and interaction parameters, under given solvent, concentration, and temperature conditions.

The following simplifying assumption will be invoked for convenience (though it is not a necessity):

\[ c_H(r) + c_T(r) + c_W(r) = 1. \]  

Put most directly this implies that each of \(H\), \(T\), and \(W\) on average occupy the same volume, which the choice of units sets equal to 1. By this means we can eliminate \(c_W\) and thus consider only \(c_H\) and \(c_T\) to be independent fields.

Having adopted this point of view the next task is to identify a free energy functional \(F(c_H, c_T)\) whose extrema with respect to permissible variations in the
scalar fields will include physically relevant aggregation structures. This task (and thus \( F \) itself) will be separated into two parts. The first part amounts to regarding the system as a solution of disconnected \( H \) and \( T \) chains, for which the free energy functional will be denoted by \( F_1[c_H, c_T] \). The second part reconnects the \( H \) and \( T \) chains into intact amphiphile molecules, and so requires inclusion of \( F_2[c_H, c_T] \):

\[
F = F_1 + F_2. \tag{2.3}
\]

Nothing is present in \( F_1 \) to prevent external forces of modest strength from separating \( H \) chains from \( T \) chains over macroscopic distances; it is the role of \( F_2 \) to prevent absolutely such a possibility.

For \( F_1 \) the following form has been selected \((\beta = 1/k_B T)\):

\[
\beta F_1 = \int \! dr \left\{ \beta \left( c_T + \frac{c_H}{n_H} \right) \ln \left( \frac{c_T + \frac{c_H}{n_H}}{c_T + \frac{c_H}{n_H}} \right) + \left( c_T + \frac{c_H}{n_H} \right) \right\} + \left( 1 - c_T - c_T \right) \ln \left( 1 - c_T - c_T \right) + G_{HH}(\nabla c_H)^2 + G_{HT}(\nabla c_H \cdot \nabla c_T) + \frac{1}{2} J_{TT}(c_T)^2 + J_{HT}c_Hc_T + J_{TT}c_T^2 \right\}. \tag{2.4}
\]

The types of terms appearing here are quite standard for the theory of mixtures.\(^8,9\) First, there are interactions of \( H \) and \( T \) units, respectively, with external potentials \( u_H \) and \( u_T \). These are followed by mixing entropy terms of the Flory type. The terms quadratic in field gradients are of a type familiar in study of inhomogeneous fluids,\(^9,10\), their presence avoids spontaneous appearance of concentration discontinuities. Finally, the last three terms involve interactions between units with strengths specified by the parameters \( J_{\mu\nu} \).

Expression (2.4) certainly is not unique for the problem in hand. But it is perhaps the simplest form which retains essentials while avoiding triviality.

The connection-enforcing functional \( F_2 \) will be postulated to have a quadratic nonlocal character:

\[
\beta F_2 = \frac{1}{2} \int \! dr_1 \int \! dr_2 \left\{ c_T(r_1) I_{TT}(r_1) c_T(r_2) + c_H(r_1) I_{HT}(r_1) c_H(r_2) + \frac{1}{2} J_{TT} c_T(r_1) c_T(r_2) + \frac{1}{2} J_{HT} c_H(r_1) c_T(r_2) \right\}. \tag{2.5}
\]

The three integral kernels \( I_{\mu\nu} \) introduced here will be evaluated in Sec. IV, and the procedure leading to that evaluation will show that they have the requisite property of preventing macroscopic separation of \( H \) chains from \( T \) chains.

It is worth stressing that two length scales have been distinguished in the amphiphile aggregation problem. The shorter length scale is that of separation between neighboring units either along the same molecular chain, or on neighboring chains. Structural details on this scale are largely irrelevant for present purposes and have been suppressed by choosing \( F_1 \) to have the local form presented in Eq. (2.4). The larger length scale is the coherence length of the aggregation pattern, which is expected to be comparable to the length of the amphiphile molecules themselves. Because molecular reorientations can in fact lead to separation of \( H \) and \( T \) on this latter scale without violating chemical connectivity, it is mandatory that the operators in \( F_2 \) be nonlocal over at least the same scale.

### III. EULER EQUATIONS

The search for concentration fields that extremalize the free energy has to be carried out subject to fixed total numbers of \( H \) and \( T \) units throughout the system:

\[
\frac{\partial}{\partial n_H} \int c_H(r) \, dr = n_H^2 \int c_H(r) \, dr = N_H, \tag{3.1}
\]

\[
\text{where } N \text{ is the number of amphiphile molecules present. These conditions require the introduction of a pair of Lagrange multipliers } \lambda_H \text{ and } \lambda_T \text{ that must appear when the first variations of } \beta F \text{ with respect to } c_H \text{ and } c_T \text{ are set equal to zero. The Euler equations that result from this process are easily obtained. From the } c_H \text{ variation one finds:}
\]

\[
0 = \lambda_H + \beta \left( c_H(r_1) + 1 \ln \left( \frac{c_H(r_1)}{1 - c_H(r_1)} \right) \right) - 2G_{HH}(\nabla c_H)^2 - G_{HT}(\nabla c_H \cdot \nabla c_T) - 2J_{HH} c_H c_H + J_{HT} c_H c_T \tag{3.2}
\]

\[
+ \int \! dr_2 \left[ 1_{HH}(r_{12}) c_H(r_2) + 1_{HT}(r_{12}) c_H(r_2) \right].
\]

The \( c_T \) variation leads to the same type of equation, but with \( H \) and \( T \) subscripts interchanged.

It is not necessary to know the Lagrange multipliers \( \lambda_H \) and \( \lambda_T \) in order to compute the structure of spontaneously formed nonuniformities in the system, when \( u_H \) and \( u_T \) vanish. We can define the local concentration deviation \((\alpha = H, T)\):

\[
\delta c_{\alpha}(r) = c_{\alpha}(r) - c_{\alpha}^0,
\]

where \( c_{\alpha}^0 \) is the uniform concentration that obtains far from the nonuniformity. The \( c_{\alpha}^0 \) of course must satisfy Eq. (3.2) in the external-field-free case, which allows the \( \lambda_\alpha \) to be eliminated. The resulting equations are:

\[
\frac{\delta c_H(r_1)}{c_H^0} = \left[ 1 - c_H^0 + \frac{c_T^0 + \delta c_T}{1 - c_H^0 + \delta c_T} \right] \left[ 1 - c_H^0 + \frac{c_T^0 + \delta c_T}{1 - c_H^0 + \delta c_T} \right]^{-1}
\]

\[
\times \exp \left\{ 2G_{HH}(\nabla c_H \cdot \nabla c_T) + G_{HT}(\nabla c_H \cdot \nabla c_T) - 2J_{HH} c_H c_H - 2J_{HT} c_H c_T \right\} - 1,
\]

along with the corresponding relation that has \( H \) and \( T \) permuted.

After determining the integral kernels \( I_{\mu\nu} \) these last integrodifferential equations will be suitable for numerical study of aggregation forms.

### IV. LINEAR RESPONSE

We now consider the response of the initially homogeneous amphiphile solution to application of a weak ex-
ternal potential. In particular we begin by examining the case:

\begin{align}
  u_h(r_1) &= \epsilon \sin(k \cdot r_1), \\
  u_T(r_1) &= 0,
\end{align}

where \( \epsilon \) is small, and the wave vector \( k \) is arbitrary. The induced concentration changes will be proportional to \( \epsilon \) in this weak coupling regime, and will be spatially sinusoidal. Therefore we write the following expressions for the perturbed concentrations:

\begin{align}
  c_h(r_1) &= e_0 [1 + \epsilon \eta_h \sin(k \cdot r_1)], \\
  c_T(r_1) &= e_0 [1 + \epsilon \eta_T \sin(k \cdot r_1)].
\end{align}

The linear response coefficients \( \eta_h \) and \( \eta_T \) can be determined by substituting expressions (4.2) into Euler equation (3.2) and its H, T - T, H partner, linearizing with respect to \( \epsilon \), and then solving the resulting simultaneous linear equations. One finds

\begin{align}
  c_{h0}^{\eta_h} &= \frac{-bA_T(k)}{A_h(k)A_T(k) - B^2(k)}, \\
  c_{T0}^{\eta_T} &= \frac{bB(k)}{A_h(k)A_T(k) - B^2(k)},
\end{align}

where

\begin{align}
  A_h(k) &= \frac{1}{n_0 e_0} + \frac{1}{n_0 c_{h0}^{\eta_h}} + 2G_H H^2 + 2J_H H + L_H H(k), \\
  A_T(k) &= \frac{1}{n_0 c_{T0}^{\eta_T}} + \frac{1}{n_0 c_{h0}^{\eta_h}} + 2G_H T^2 + 2J_H T + L_H T(k), \\
  B(k) &= \frac{1}{1 - c_{h0}^{\eta_h} c_{T0}^{\eta_T}} + G_H T^2 + J_H T + L_H T(k).
\end{align}

Here we have introduced Fourier transforms for the integral kernels:

\begin{equation}
  L_{\mu
u}(k) = \int dr_1 \cos(k \cdot r_{12}) I_{\mu
u}(r_{12}).
\end{equation}

A similar calculation can be carried out for a linear perturbation opposite to that of Eq. (4.1), namely,

\begin{align}
  u_h(r_1) &= 0, \\
  u_T(r_1) &= \epsilon \sin(k \cdot r_1),
\end{align}

for which the local concentrations again have sinusoidal forms:

\begin{align}
  c_h(r_1) &= e_0 [1 + \epsilon \eta_h \sin(k \cdot r_1)], \\
  c_T(r_1) &= e_0 [1 + \epsilon \eta_T \sin(k \cdot r_1)].
\end{align}

By following the same procedure as before, one obtains

\begin{align}
  c_{h0}^{\eta_h} &= \frac{bB(k)}{A_h(k)A_T(k) - B^2(k)}, \\
  c_{T0}^{\eta_T} &= \frac{-bA_T(k)}{A_h(k)A_T(k) - B^2(k)}.
\end{align}

Linear response results (4.3) and (4.8) can also be achieved through an alternative route, namely direct statistical-mechanical calculation for intact molecules. If \( N \) amphiphile molecules are present in solution,
expanded to give
\[
S_{\nu}(k) = n_H n_T - \frac{1}{2} M_{\nu}^{(0)} k^2 + \frac{1}{8} \sum_{\mu \nu} M_{\mu \nu}^{(0)} k^4 - O(k^6),
\]
where we have introduced the mean moments
\[
M_{\nu}^{(0)} = \sum_{\nu = \mu} \langle |r_{1\nu} - r_{1\nu}|^2 \rangle_0, \text{ etc.}
\]
(4.17)

Thereupon, we have
\[
\Delta(k) = \Delta k^2 + \Delta k^4 + O(k^6),
\]
(4.19)

wherein
\[
\Delta_2 = -\frac{1}{6} \left( n_H n_T - 2 n_H n_T + n_H^2 \right),
\]
\[
\Delta_4 = \frac{1}{8} \left[ n_H n_T - 2 n_H n_T + n_H^2 \right] + \frac{1}{8} \left[ M_{\nu}^{(0)} M_{\mu}^{(0)} - (M_{\mu}^{(0)} M_{\nu}^{(0)})^2 \right].
\]
(4.20)

The small-\(k\) expansions of the \(L_{\nu\nu}\) are then found to be as follows:
\[
L_{HH}(k) = \frac{n_H^2}{c} \Delta k^2 - \frac{1}{c} \left[ \frac{M_{\nu}^{(0)}}{6 \Delta_2} + \frac{n_H \Delta_2}{\Delta_2} \right] + O(k^2),
\]
\[
L_{HT}(k) = -n_H n_T \Delta k^2 - \frac{1}{c} \left[ \frac{M_{\nu}^{(0)} + n_H \Delta_2}{6 \Delta_2} \right] + O(k^3),
\]
\[
L_{TT}(k) = \frac{n_T^2}{c} \Delta k^2 - \frac{1}{c} \left[ \frac{M_{\mu}^{(0)} + n_T \Delta_2}{6 \Delta_2} \right] + O(k^2).
\]
(4.21)

That each of the transforms \(L_{\nu\nu}\) has a double pole at the origin in \(k\) space implies that the \(l_{\nu\nu}\) are inversely proportional to distance in their asymptotic regimes, i.e., Coulombic in character. From Eq. (4.16) one readily establishes that
\[
l_{\nu\nu}(r_{12}) = \frac{q_{\nu}}{r_{12}},
\]
(4.22)

where the effective charges are given by:
\[
q_H = n_H/(4\pi \varepsilon_0 \Delta_2)^{1/2},
\]
\[
q_T = -n_T/(4\pi \varepsilon_0 \Delta_2)^{1/2}.
\]
(4.23)

The identification of the connectivity kernels as effective interactions with long-range Coulombic character is significant. It shows that the effects of covalent chemical binding between pairs of \(H\) chains and \(T\) chains can be regarded as a local electroneutrality condition familiar from electrochemistry. Just as macroscopic separation of anions and cations in an electrolytic solution is impossible, so too is it impossible to separate \(H\) chains and \(T\) chains over macroscopic distances.

This useful analogy can be reinforced by examining the Debye length \(\kappa^{-1}\) implied by our electrochemical transcription. Using Eqs. (4.23) and realizing that the effective dielectric constant is unity, we have
\[
\kappa^{-1} = (\frac{4\pi \varepsilon_0 n_H^2}{q_H},+c_2 q_T^2)^{1/2}
\]
\[
= \left[ \frac{\Delta_2}{n_H n_T (n_H + n_T)} \right]^{1/2}.
\]
(4.24)

The fact that the integral kernels are inversely proportional to concentration [Eq. (4.14)] is necessary for the Debye length to be concentration independent, since the length scale of intact molecules is fixed. Change in temperature and in solvent composition clearly can effect \(\Delta_2\) and this in turn will modify the effective Debye length. In any case we see that the latter quite properly is determined by the second moments of the amphiphile molecule configurational distribution.

V. NUMERICAL EXAMPLES

Now that the integral kernels have been identified we proceed to carry out a modest numerical exploration. For this purpose the point of view will be adopted that the asymptotic expressions (4.22) actually apply at all distances \(r_{12}\). The validity of this hypothesis is subject to later assessment of course, but the most important attribute of the kernels is certainly being retained.

For the sake of concreteness we will consider the case of a molecule \(H_8T_{10}\). In order to calculate effective charges (now equal in magnitude for \(H^\prime\)'s and for \(T^\prime\) 's), it will be supposed that moments \(M_{\nu}^{(0)}\) can be calculated using just the configuration where all 19 bonds are collinear and have unit length. This does not imply that the amphiphile molecules are invariably straight and rigid, but that their configurational fluctuations in pure solvent occur in a manner which produces second moments equal to those of the unit-bond-length linear form. Under this assumption the square of the \(H\) or \(T\) effective charge becomes:
\[
q^2 = 3/(40000\pi \varepsilon_0 c).
\]
(5.1)

In order to minimize the confusing effects of parameter variations, we will consistently set
\[
G_{HH} = G_{TT} = 0.5,
\]
\[
G_{HT} = -0.5.
\]
(5.2)

In the present context rather little molecular information is present to choose these quantities, but the values shown do not seem unreasonable. The common positive value selected for \(G_{HH}\) and \(G_{TT}\) should avoid discontinuities as discussed earlier. At the same time the negative value for \(G_{HT}\) is suggested by chemical structure, since antiparallel gradients of \(H\) and \(T\) are encouraged by the intramolecular "interface" between \(H\) and \(T\) chains.

The dimensionless local interaction parameters \(J_{\nu\nu}\) are decisive in producing aggregates. Hydrophobic interactions between tail units mediated by water as a solvent require \(J_{TT}\) to be negative. The sign of \(J_{HH}\) is less obvious and so the results from alternative choices are worth exploring, but in any case \(J_{HH}\) should not be more negative than \(J_{TT}\) to avoid micelle inversion. For simplicity we assume
\[
J_{HT} = 0.
\]
(5.3)

The Euler equations were solved numerically for several \(c\), \(J_{HH}, J_{TT}\) choices under conditions of spherical symmetry, which seemed appropriate for globular micelles. The radial coordinate \(r\) in the range \(0 < r < 20\) was subdivided into intervals of length 0.2, derivatives were represented as differences, and integrals carried out by the rectangle rule. Although many iterations typically were required to yield numerical convergence for the coupled integrodifferential equations, the task was basically simple enough that it could be carried out.
Frank H. Stillinger: Variational model for micelle structure

FIG. 1. Micelle structure computed from the Euler equations under the spherical symmetry constraint. For the case shown 
$c = 0.0010, J_{HH} = -1, J_{TT} = -2$.

on a programmable desktop calculator (HP 9825A).

Figure 1 shows the local density profiles $\delta c_T(r)$ and $\delta c_H(r)$ that were found for the case

$c = 0.001, J_{HH} = -1, J_{TT} = -2$. (5.4)

At this concentration the overall volume fraction of amphiphile is $20c = 0.05$. A small micellar aggregate obviously has formed with a core of $T$'s and an attenuated fringe of $H$'s. Consistent with previous remarks, the latter exactly counterbalance the former by forming a perfect "ion atmosphere." Solvent penetrates somewhat into the core region; specifically

FIG. 2. Spherical micelle structure for $c = 0.0010, J_{HH} = 4, J_{TT} = -2$.

$C = 0.0010$

\[ J_{TT} = -2, J_{HH} = +4 \]
\[ q^2 = 3/(40,000 \pi \beta C) \]
\[ C = 0.0010 \]

\[ J_{TT} = -2, J_{HH} = +4 \]
\[ q^2 = 3/(40,000 \pi \beta C) \]
\[ C = 0.0020 \]

We estimate (by integrating $c_T$ to its first zero) that the core region contains an average of approximately $102.8 T$ units. These may comprise only parts of $T$ chains, of course.

Figure 2 shows the effect of varying $J_{HH}$ while other parameters are held constant. In particular $J_{HH}$ is now set equal to four, representative of strong repulsion between the head groups. The resulting micelle is even smaller than before, with a dramatically extended fringe of $H$ units. Quite obviously the change has had the expected destabilizing influence. The continued ability of the aggregate to hold together at all stems from the geometric advantage of spherical geometry which allows mutually repelling $H$'s to fan out and avoid each other.

The influence of variable concentration is demonstrated by comparing Fig. 2 ($c = 0.001$) with Figs. 3 ($c = 0.002$), 4 ($c = 0.003$), and 5 ($c = 0.004$), wherein all other param-

FIG. 3. Spherical micelle structure for $c = 0.0020, J_{HH} = 4, J_{TT} = -2$.

\[ c_w(0) = 1 - c_H(0) - c_T(0) \]
\[ = 0.092. \] (5.5)

FIG. 4. Spherical micelle structure for $c = 0.0030, J_{HH} = 4, J_{TT} = -2$.

\[ c_w(0) = 1 - c_H(0) - c_T(0) \]
\[ = 0.092. \] (5.5)

\[ c_w(0) = 1 - c_H(0) - c_T(0) \]
\[ = 0.092. \] (5.5)

\[ c_w(0) = 1 - c_H(0) - c_T(0) \]
\[ = 0.092. \] (5.5)
Parameters remained fixed. The resulting increase in micelle size is substantial. The average numbers of tail units in the cores of each of these are estimated as before to be 53.5, 370.3, 878.5, and 1539.3, respectively.

Experience has shown that below a critical concentration limit, for any choice of interactions, only the trivial solutions (5.6) to the Euler equations can be found. This characteristic is reminiscent of the well-known critical micelle concentration (CMC) phenomenon in amphiphile solutions. However, identification of a true CMC must be based on a study of the partition function for the system as outlined in the next Sec. VI.

The progression presented in Figs. 2-5 shows a "core weakening" phenomenon, i.e., a tendency for \( \delta c_T \) to develop a local minimum at the origin at the larger concentrations. To some extent this may be an indirect result of the strong head-group repulsion which effectively pulls the aggregating molecules radially outward.

The way that concentration affects micelle size can be conveniently dramatized by picking some characteristic length, for instance the smallest radius \( r_0 \) for which

\[
\delta c_T(r_0) = 0, \quad (5.7)
\]

and then plotting those \( r_0 \)'s against \( c \). This has been done in Fig. 6 for the \( J_{HH} = 4, J_{TT} = -2 \) case, some examples of which were illustrated in Figs. 2-5. Similar behavior has been found for other choices of interaction parameters. The smooth-curve fit to the discrete numerical results indicates a vertical tangent at

\[
c_0 \approx 0.0009. \quad (5.8)
\]

This is the critical concentration below which nontrivial solutions appear not to exist. Indeed experience has shown that numerical convergence becomes increasingly slow as this critical point is approached from above, apparently as a result of developing dilatation-contraction instability.

If (as Fig. 6 suggests) the critical concentration (5.8) is a simple branch-point singularity of the function \( r_0(c) \),

\[
r_0(c) = r_0(c_0) + A(c - c_0)^{1/2} + O(c - c_0),
\]

\[
A > 0,
\]

then the curve of stable micelle structures connects to a metastable branch:

\[
r_0(c) = r_0(c_0) - A(c - c_0)^{1/2} + O(c - c_0). \quad (5.10)
\]

This alternative branch has been indicated by a dotted curve in the figure. It seems reasonable to speculate that these metastable aggregates correspond to free energy saddle points (analogous to critical nuclei in nucleation phenomena) over which the system must...
pass in the process of forming stable micelles from dispersed monomers.

On account of the nonlinearity of the determining equations, alternative solutions exist, under proper circumstances, beyond just the trivial [Eq. (5.6)] and the micellar solutions. Figure 7 shows such a case that was discovered inadvertently for the same concentration and interaction choice that applied in the micelle structure Fig. 5. Now the structure is vesicular, with a shell of tail units located around radius \( r = 9.5 \). The compensating head units reside both within the hollow interior and in the exterior regions of this vesicle. Vesicles have been found for other parameter choices as well, thus far only with repulsive head groups \( (J_{HH} > 0) \). It is not yet certain what role the radial truncation at \( r = 20 \) in the numerical analysis has in stabilizing these hollow aggregates.

Figure 8 exhibits yet another type of radially symmetric structure, for \( c = 0.001, J_{HH} = -1.5, J_{TT} = -3 \). The system now has chosen form alternating concentric shells of \( H \) and \( T \) units, with the central core region having predominantly \( H \) character. Although the numerical solution terminates at \( r = 20 \), it is clear that the nonlinear out-of-phase oscillations would go on to arbitrarily large radius if given the chance. With increasing \( r \) these successive shells become locally more and more planar, so that the phase being described is essentially one with parallel lamellae. It would be technically correct to identify this kind of arrangement as a smectic \( A \) phase. On account of the spherical symmetry that has been imposed on the numerical solution, the specific structure shown in Fig. 8 constitutes one of the possible point defects that are possible in that smectic \( A \) phase.

VI. DISCUSSION

The numerical calculations reported here seem to establish that the variational method has some value for investigating aggregation phenomena, at least for nonionic amphiphiles. In most respects the extension to ionic amphiphiles should be straightforward. After eliminating solvent, the independent concentration fields would number three, namely head groups \( (c_H) \), tail groups \( (c_T) \), and counterions \( (c_I) \). Typically the head groups would be reckoned as one per molecule and would bear a true electrostatic charge. The basic free energy functional would include both real Coulombic interactions as well as the pseudo-Coulombic interactions conveyed by the connectivity kernels \( I_\mu \). No doubt the resulting triad of coupled nonlinear Euler equations could be solved by iteration as before. The only feature that might provide some difficulty would be how to handle the nonuniformity of dielectric properties through the region occupied by the aggregate.

In the long run the present variational approach needs to be embedded in a more complete statistical mechanistic formalism. The nature of that formalism is clear. It will be necessary to evaluate partition functions of the form

\[
Q_N(\beta) = \int \delta(c_H, c_T) \exp\left[ -\beta F(c_H, c_T) \right], \tag{6.1}
\]

where the functional integral indicated includes all field variations (with appropriate weighting) subject to the constraints (3.1) that fix the number \( N \) of molecules present. The aggregation structures sought in this paper represent stationary points of the integrand in Eq. (6.1). To effect evaluation of \( Q_N \) it is necessary to account for fluctuations about those extrema. Under some circumstances it may suffice to retain only quadratic fluctuations (second functional derivatives of \( \beta F \) about the extrema). This would lead in turn to calculation of the stabilities, equilibrium constants, and size distributions for aggregates in solution. From this information it would then be possible to identify critical micelle concentrations, and to map out phase diagrams over the entire range of temperature and of solvent—
amphiphile composition variation. The ability to demonstrate how these attributes are controlled by details of amphiphile molecular structure and of the interaction parameters would be a valuable theoretical asset.