"Soliton" solutions in a field theory of microemulsion

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We discuss a field theory of microemulsion that has been previously studied by a number of techniques. We examine the localized solutions of this theory, with a view to understanding the kinetics of phase growth. However, it is also suggested that, in the region of what was formerly considered to be an isotropic Lifshitz point of the phase diagram, there may be a phase of microscopic multilamellar spherical objects. This new phase may displace the swollen lyotropic lamellar phase.

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I. INTRODUCTION

There have been a number of studies of quite simple field theory models of self-assembly, containing oil, water, and amphiphile [1]. These models are distinguished from the Ising-like ϕ^4 model by having a Laplacian squared term with opposite sign to the normal Laplacian contribution. In fact this sort of field theory may be extracted from a frustrated Ising lattice model and the frustration in the lattice couplings is reflected in the opposing signs of these two types of gradient terms. One useful way of thinking about this field theory is that the Laplacian term, having negative coefficient, implies a negative coarse-grained surface-tension term, and there is then a Laplacian squared term required for stability [1]. There result many phases containing numerous planar domain walls. Here the positive- and negative-valued fields correspond to oil and water rich regions and the boundary between them corresponds to amphiphile. However, as the magnitude of the Laplacian coefficient diminishes, it seems natural that there should be fewer such domain walls, and this is reflected in the mean-field theory prediction that the planar domain walls move apart to the limit of infinite spacing as this coefficient vanishes. Indeed, at first sight this is all quite satisfactory as a model of self-assembly since the coefficient of the Laplacian term may be related to the concentration of amphiphile in the phase, the lamellar phase considered to be a lamellar liquid-crystalline phase, and it is indeed to be expected that the mean interlamellar spacing becomes large as the concentration of this component becomes small.

However, there is a fundamental problem in this interpretation based, as it is, on mean-field arguments. First, of course, fluctuations in the lamellar phase result in the well known quasi-long-ranged order. Examination of the low-temperature "tensionless" lamellar phase indicates that $d_L = 3$ away from the large swelling limit, and this may be accepted as an accurate estimate. More significantly, as the coefficient of the Laplacian term vanishes, the field theory itself appears to acquire the naive upper and lower critical dimensions $d_U = 8$, $d_L = 4$, respectively. Clearly, there is a strong possibility that in the vicinity of this point in parameter space, there might be some quite interesting phenomena. We shall argue that, in fact, the highly swollen lamellar phase is not stable with respect to fluctuations and that this may be reflected in the presence of a finite swelling limit in the liquid-crystalline phase. Beyond this limit, the swollen liquid crystal becomes unstable, and we propose that a new phase may result. We are tending to a situation where this phase must have no long-ranged or quasi-long-ranged order and there is every expectation that it would consist of a fluid of the localized solutions of the underlying field theory [2]. The reasons are quite straightforward. If large coherent solutions of the field theory are unstable with respect to fluctuations, then, if there are stable minima or long-lifetime saddle points of the field theory corresponding to localized solutions, we may imagine that they will form a fluid in which the entropy favors a dispersion composed of those localized objects, providing that interactions between them cause no significant destabilization. We may note with interest, however, that the stable localized solutions in the region of the phase diagram under discussion are quite different from micellar objects, these becoming favorable only when the gradient and squared-gradient interactions no longer compete. In the present case one has localized solutions corresponding, roughly, to concentric spheres of surfactant separated by solvent spheres.

Therefore, the steps in establishing the presence of such a phase are as follows: First, one must establish the existence and a stability of localized solutions of the field theory. Second, one must compare the approximate free energy of a phase composed of such objects to the competing phases. This is in principle a difficult calculation, and we shall here merely be able to make an estimate.

In summation, there are two reasons for which we may be interested in such solutions. First, they must be characterized before one can consider study of the phase-transition kinetics of the theory. Second, we believe there is a possibility of a new equilibrium phase structure in the model.

Since the concepts that we discuss owe much to field theory, the solutions we discuss are often called solitons,

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even though they are, technically, merely localized solutions. The remainder of this paper is a description of our attempts to carry out this program of research.

II. SOME PROPERTIES OF LOCALIZED SOLUTIONS

The effective Landau-Ginzburg-Wilson Hamiltonian that we consider is [3,4]

$$H[\tilde{\phi}]=\tfrac{1}{2}\int d\mathbf{q}|\tilde{\phi}(\mathbf{q})|^2(\mathbf{q}^4+b\mathbf{q}^2+c)+\frac{\lambda_0}{4!}\int d\mathbf{q}\,\tilde{\phi}(\mathbf{q}_1)\tilde{\phi}(\mathbf{q}_2)\tilde{\phi}(\mathbf{q}_3)\tilde{\phi}(\mathbf{q}_4)\times\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4), \quad (1)$$

where the coefficients b, c, and λ are connected with the parameters j and m of the original frustrated ising lattice model [5] by the equations [4]

$$b=\frac{-20(j+12m)}{j+12m}, \quad (2)$$

$$c=\frac{120(j+5m)-20}{j+12m}, \quad (3)$$

$$\lambda_0=\frac{800}{(j+12m)^2}. \quad (4)$$

The parameters j and m are, in turn, related to the microemulsion parameters by the equations [5]

$$j=\frac{5}{2}\frac{K}{\theta}-\ln\left[\frac{z_A}{\sqrt{A_0 z_W}}\right]^{1/2}, \quad m=-\frac{1}{4}\frac{K}{\theta}, \quad (5)$$

where z_A, z_O and z_W are the activities of amphiphile, oil, and water respectively; K is the amphiphile-amphiphile interaction energy; and θ is the temperature (times the Boltzmann's constant). Note that the particular case $z_O=z_W$ is considered here, and it is implicitly assumed that the energy of bending of the surfactant film is independent of the direction of the bend (the theory is symmetric in oil and water).

By transforming back to the fields

$$\phi(\mathbf{r})=\frac{1}{(2\pi)^3}\int d\mathbf{r}\,\tilde{\phi}(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{r})$$

in the real space, we find

$$H[\phi]=4\pi^3\int d\mathbf{r}\left[(\Delta\phi)^2+b(\nabla\phi)^2+c\phi^2+\frac{\lambda}{2}\phi^4\right], \quad (6)$$

where, as we commented earlier, there is a Laplacian and Laplacian squared term, and $\lambda\equiv(32\pi^6/3)\lambda_0$. It is known from various mean-field calculations that, in the vicinity of $b=0$, $c=0$, there exist three phases: paramagnetic (disordered), ferromagnetic, and lamellar. These are the appropriate global minima of the Landau-Ginzburg-Wilson Hamiltonian, and within the mean-field approximation, they are also the stable macroscopic phases [6]. The predicted mean-field phase diagram is sketched in Fig. 1.

However, as outlined in the Introduction, we believe that such phases are not stable with respect to fluctuations in the limit $b=0$ and we therefore seek localized solutions of the Hamiltonian (6), with the prospect of constructing a macroscopic fluid of these objects. Such a phase would acquire stability in the vicinity of the mean-field lamellar-ferromagnetic phase boundary.

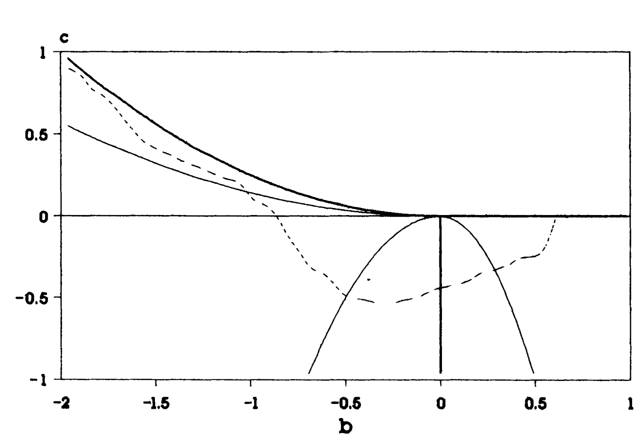

FIG. 1. Mean-field phase diagram. Lamellar (bottom right), ferromagnetic (bottom left), and disordered phases are divided by two bold lines and the bold parabola $c=-b^2/4$, $b<0$. The thin parabolas represent typical families of parameters, which are considered in Sec. III. The dashed curve indicates merely the likely region of stability for the "soliton" phase.

In the present context, a localized solution $\phi_0(\mathbf{r})$ has the property $\phi_0(\mathbf{r})\to 0$ as $|\mathbf{r}|\to\infty$, and, among others, must satisfy the following conditions:

$$\partial_\alpha H[\phi^*]=0, \quad (7)$$

$$\partial_\beta H[\phi^*]=0, \quad (8)$$

as well as

$$\partial^2_{\alpha\alpha}H[\phi^*]\geq 0, \quad (9)$$

$$\partial^2_{\beta\beta}H[\phi^*]\geq 0, \quad (10)$$

where $\phi^*(\mathbf{r})\equiv\alpha\phi_0(\beta\mathbf{r})$. If we define $h_1=\int d\mathbf{r}(\Delta\phi_0)^2$, $h_2=b\int d\mathbf{r}(\nabla\phi_0)^2$, $h_3=c\int d\mathbf{r}\phi_0^2$, and $h_4=(\lambda/2)\int d\mathbf{r}\,\phi_0^4$, we find that Eqs. (7)–(10) imply the conditions

$$h_1+h_2+h_3+2h_4=0, \quad (11)$$

$$h_1-h_2-3(h_3+h_4)=0, \quad (12)$$

$$h_1+h_2+h_3+6h_4\geq 0, \quad (13)$$

$$h_2+6(h_3+h_4)\geq 0. \quad (14)$$

We note that Eq. (11) implies that the inequality (13) is satisfied for $\lambda>0$. Equations (11), (12), and (14) represent only necessary conditions on the solution space, but they are of considerable help in numerical studies of the problem. In particular, they exclude regions of the phase diagram from consideration in seeking localized solutions. For example, from (11) we find that $b<0$ or $c<0$ is the only area in which solutions may be found. Still, the expressions (6)–(14) may not be applied to all choices of solution. The detailed analysis of the asymptotic form of a solution for large distance from its center is necessary since, under certain circumstances, specific terms in these equations may diverge. This analysis may be carried out for a spherical solution of the type we seek to study.

A necessary condition to minimize the energy is $0=(\delta H/\delta\phi(\mathbf{r}))$, which, for the Hamiltonian (6), becomes

$$\Delta^2\phi - b\Delta\phi + c\phi + \lambda\phi^3 = 0 \ . \tag{15}$$

If we consider only spherical solutions, we find that

$$\psi^{(4)} - b\psi^{(2)} + c\psi + \lambda\frac{\psi^3}{r^2} = 0 \ , \tag{16}$$

where $\psi(r) = r\phi(\mathbf{r})$, $r=|\mathbf{r}|$. We suppose

$$\left|\lambda\frac{\psi^3}{r^2}\right| \ll |\psi^{(4)}|, |b\psi^{(2)}|, |c\psi|$$

as $r\to\infty$. Thus,

(1) For $c<0$,

$$\phi\to\phi_{as}, \ \ \phi_{as}(\mathbf{r}) = A\frac{\sin(kr+\chi)}{r} \ , \tag{17}$$

where

$$k = \left[\frac{-b+\sqrt{b^2-4c}}{2}\right]^{1/2} . \tag{18}$$

(2) For $0<c<b^2/4$ with $b<0$,

$$\phi_{as}(\mathbf{r}) = A_1\frac{\sin(k_1r+\chi_1)}{r} + A_2\frac{\sin(k_2r+\chi_2)}{r} \ , \tag{19}$$

$$k_1 = \left[\frac{-b+\sqrt{b^2-4c}}{2}\right]^{1/2} , \quad k_2 = \left[\frac{-b+\sqrt{b^2-4c}}{2}\right]^{1/2} . \tag{20}$$

(3) For $c>b^2/4$ with $b<0$,

$$\phi_{as}(\mathbf{r}) = A_3\frac{\sin(k_3r+\chi_3)}{r}\exp(-k_r4) \ , \tag{21}$$

$$k_3 = \left[\frac{\sqrt{c}-b/2}{2}\right]^{1/2} , \quad k_4 = \left[\frac{\sqrt{c}+b/2}{2}\right]^{1/2} . \tag{22}$$

We may note that the form (6) of the Hamiltonian is not well defined for cases (1) and (2) [Eqs. (17) and (19)] because of the long-ranged nature of the solutions. The alternative form

$$H[\phi] = 4\pi^3\int d\mathbf{r}\left[\phi(\Delta^2 - b\Delta + c)\phi + \frac{\lambda}{2}\phi^4\right] \tag{23}$$

is well defined, being actually the original form of the Hamiltonian, as it is obtained from a frustrated Ising lattice model [7]. The mathematical check on the validity of a numerical solution for cases 1 and 2 may be accomplished using the form (23), and with $h_1 = \int d\mathbf{r}\,\phi\Delta^2\phi$, $h_2 = -b\int d\mathbf{r}\,\phi\Delta\phi$, and h_3 and h_4 given as before, we find that Eq. (11) becomes

$$H[\phi_0] = -4\pi^3 h_4 \ . \tag{24}$$

Equation (15) implies an underlying one-parameter problem. Thus, if a localized solution $\phi_{b,c,\lambda}(\mathbf{r})$ of Eq. (15) is found for the parameters b, c, and λ, then the function

$$\phi_{\beta b,\beta^2 c,(\beta^2/\alpha)\lambda}(\mathbf{r}) = \sqrt{\alpha}\,\phi_{b,c,\lambda}(\sqrt{\beta}\mathbf{r}), \quad \alpha>0, \ \beta>0 \tag{25}$$

is a solution of the same equation with the implied new parameters. This means that there are families of solutions such that

$$(b,c,\lambda)\to(\tilde{b},\tilde{c},\tilde{\lambda}) = \left[\beta b, \beta^2 c, \frac{\beta^2}{\alpha}\lambda\right] , \tag{26}$$

$$\phi(\mathbf{r})\to\tilde{\phi}(\mathbf{r}) = \sqrt{\alpha}\,\phi(\sqrt{\beta}\mathbf{r}) \ , \tag{27}$$

$$H[\phi]\to\tilde{H}[\tilde{\phi}] = \alpha\sqrt{\beta}H[\phi] \ . \tag{28}$$

One important and quite remarkable aspect of these relations is that if a single localized solution is obtained for a given λ, a solution may be obtained for any λ. Thus, without losing generality, the λ can be fixed and kept constant by the condition $\alpha=\beta^2$. Then, if a solution is obtained for a given (b_0,c_0), a solution may be obtained along the curves defined by

$$b=\beta b_0, \quad c=\beta^2 c_0 \tag{29}$$

(see Fig. 1), so that

$$\phi(\mathbf{r}) = \beta\phi_0(\sqrt{\beta}\mathbf{r}), \quad H[\phi] = \beta^{5/2}H_0[\phi_0] \ , \tag{30}$$

where H_0 and $\phi_0(\mathbf{r})$ are the Hamiltonian and the soliton at (b_0,c_0).

Numerical calculations, along with the arguments given in this section, lead us to suppose that long-ranged localized solutions exist throughout the area marked lamellar phase in Fig. 1. In Fig. 2 we present three numerical solutions corresponding to $\lambda=1$ and $(b,c)=(-2.3,1.2)$, curve 1; $(-0.5,-0.5)$, curve 2; and $(0.1,-0.5)$, curve 3. Curve 1 has the asymptotic form of (19), while curves 2 and 3 have the asymptotics of Eq. (17).

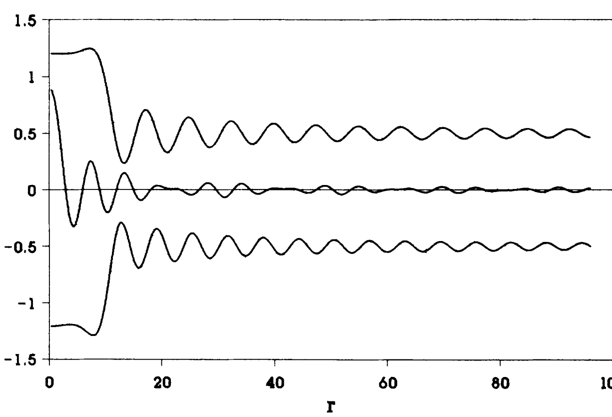

FIG. 2. Examples of localized solutions ($\lambda=1$) ϕ as a function of r that have been determined numerically. From top to bottom they correspond to $(b,c)=(0.1,-0.5)$ with a constant shift of amplitude of $+0.5$, $(b,c)=(-2.3,1.2)$, and $(b,c)=(-0.5,-0.5)$ with a shift of amplitude of -0.5. These shifts have been made to permit all three solutions to be shown on the same plot.

We should emphasize that solutions of such type are microscopic solutions, consisting physically, in most of the phase diagram, of only a few layers. There also exists another spherically symmetric solution of macroscopic extent. Presumably, the latter corresponds to vesiclelike solutions that are sometimes found as metastable variants of the swollen lamellar phase [8]. The microscopic localized solutions potentially represent a more interesting choice, since, in favorable circumstances, these may be so numerous that they actually dominate the phase structure.

The existence of these solutions had been established numerically, and verified by several changes and extensions of the **r** scale. Another check is provided by virial relations. Since the relation (24) is rather trivial and easy to satisfy numerically, we used the following procedure to derive another convergent relation: Once a solution ψ of Eq. (16) is found, the parameters of the asymptotic form ψ_{as} are easy to isolate. Then an equation for $\xi \equiv \psi - \psi_{as}$ that is analogous to (16) can be written, and it is easy to establish a functional the extremum of which provides this equation. This functional leads to a virial equation that is analogous to (12), but convergent.

III. THE POSSIBILITY OF A STABLE DISPERSION OF THE LOCALIZED SOLUTIONS

To investigate the question of stability of a localized solution $\phi_0(\mathbf{r})$ with respect to fluctuations (such stability might lead to at least metastability of the dispersed phase), we must consider eigenvalues ρ_j of the operator $(\delta^2 H)/[\delta\phi(\mathbf{r})\delta\phi(\mathbf{r}')]$. These eigenvalues are given by the equation

$$[\Delta^2 = b\Delta + c + 3\lambda\phi_0^2(\mathbf{r})]\eta_j(\mathbf{r}) = \rho_j \eta_j(\mathbf{r}) \ . \qquad (31)$$

Here $\eta_j(\mathbf{r})$ are the eigenfunctions of the operator. Consider the stability question along the curves defined by Eqs. (29). The equation

$$[\Delta^2 - \tilde{b}\Delta + \tilde{c} + 3\lambda\tilde{\phi}_0^2(\mathbf{r})]\tilde{\eta}_j(\mathbf{r}) = \tilde{\rho}_j \tilde{\eta}_j(\mathbf{r}) \ , \qquad (32)$$

[compare with (31)] where $\tilde{b} = \beta b$, $\tilde{c} = \beta^2 c$, and $\tilde{\phi}_0(\mathbf{r}) = \beta\phi_0(\sqrt{\beta}\mathbf{r})$, possesses eigenfunctions $\tilde{\eta}_j(\mathbf{r}) = \beta^{3/2}\eta_j(\sqrt{\beta}\mathbf{r})$ and eigenvalues $\tilde{\rho}_j = \beta^2\rho_j$. In the vicinity of the origin the negative eigenvalues $\tilde{\rho}_j$ become close to zero and they ultimately acquire stability.

We may discuss the possibility of the macroscopic phases dominated by such objects. It should be noted, of course, that the correct way to proceed at this stage is to carry out a full one-loop calculation of the free energy based on the intersoliton potential obtained from the interaction energy of localized solutions. The interactions may thereby be constructed for various relevant regions of the phase diagram. A full calculation is a major undertaking, and even more elementary models in physics have not been treated in this manner as yet [9]. Our purpose here is, however, merely to indicate the possibility of global stability of such a "soliton" phase. We therefore want to *compare* the free energies of such a phase and the lamellar phase, being interested in the region near the origin of the phase diagram.

First, we may estimate the leading term in the mean-field free energy for the lamellar phase in the vicinity of the order-disorder transition $(c = b^2/4)$. In this region of the phase diagram the lamellar phase may be described by the single harmonic [6]

$$\phi_L(\mathbf{r}) = A\sin(k_L x + \chi_L), \quad \mathbf{r} = (x,y,z) \ . \qquad (33)$$

Here $k_L = \sqrt{-b/2}$. The closer (b,c) are to the curve $c = b^2/4$, the more exact Eq. (33) is. The Hamiltonian (23) becomes

$$H[\phi_L] = \left[\frac{1}{2}\left(c - \frac{b^2}{4}\right) A^2 + \frac{3}{16}\lambda A^4 \right] V \ , \qquad (34)$$

and, using the condition $\partial_A[(H[\phi_L])]/V = 0$ to obtain A, we find

$$\frac{H[\phi_L]}{V} = -\frac{1}{3\lambda}\left(c - \frac{b^2}{4}\right)^2 \ . \qquad (35)$$

So, within this approximation, the free energy of the lamellar phase goes to zero as the parameters (b,c) tend to the mean-field transition curve.

The energy H_{int} of interaction of localized solution $\phi(\mathbf{r})$ and $Q\phi(\mathbf{r}+\mathbf{R})$ (where $Q = \pm 1$) is [10]

$$H_{\text{int}}(R) = H[\phi(\mathbf{r}) + Q\phi(\mathbf{r}+\mathbf{R})] - H[\phi] - H[Q\phi] \ , \qquad (36)$$

where Q may be viewed as a charge emerging from the symmetry of the solution space. If the distance R between the solutions is large enough, we may estimate the energy using the asymptotic form of the soliton ϕ. For the area $0 < c < b^2/4$ with $b < 0$ [see Eq. (19)], the energy is

$$H_{\text{int}}(R) \sim \tilde{A}_1 \frac{\sin(k_1 R + \chi_1)}{R} + \tilde{A}_2 \frac{\sin(k_2 R + \chi_2)}{R} \ . \qquad (37)$$

In the area $c < 0$ {see Eq. (17)], one would have

$$H_{\text{int}}(R) \sim \tilde{A} \frac{\sin(kR + \chi)}{R} \ . \qquad (38)$$

In this latter, the simplest, case, we have found that, in the Debye-Huckel approximation [11], the free energy density of correlation between localized solutions is approximately equal to

$$-2\pi \frac{\tilde{A}^4 \sin\chi}{T^2 k} n^2$$

for

$$n \ll \frac{k^2 T}{8\pi \sin\chi \tilde{A}^2} \ ,$$

where n is the density of the gas of localized solutions and T is the temperature. We know that the free energy to create one isolated localized solution is also negative, and the ideal gas term for the free energy is negative as well. thus, the free energy of a very dilute dispersion (if it *is* diluted) of these "onions" should be negative. It seems likely that addition of short-range interactions provides only overall phase stability and does not affect significantly the comparison between the dispersion and the lamellar phase.

This means that the localized solution phase may be more stable than the lamellar phase at least in a region which is indicated in a topological fashion in Fig. 1.

IV. CONCLUSIONS

We have shown that nontrivial localized solutions exist in part of the mean-field phase diagram. Arguments are forwarded that a dispersion of these objects may even be stable in the large swelling lamellar region of the phase diagram. The latter arguments would require considerable strengthening before the matter can be realistically settled.

However, the implications for experiments are potentially interesting. That is, in the large swelling limit one would expect to find a metastable mesoscopic ($\approx 1\,\mu$m) vesicle or "onion" phase. In addition, there may be a stable phase, such as the one we have discussed, that consists of much smaller onionlike objects in a background of fluctuating layered structures. Such objects may be only a few solvent layers in extent and may be difficult to find. Nevertheless it would be worth attempting careful freeze-fracture studies in the large swelling limit to probe for such a phase.

ACKNOWLEDGMENTS

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[1] See K. A. Dawson, in *Structure and Dynamics of Strongly Interacting Colloids and supramolecular Aggregates in Solution,* edited by S.-H. Chen *et al.* (Kluwer Academic, Netherlands, 1992), and references therein made to other models.

[2] Simulations are of limited value in this regime. However, even the early Monte Carlo studies [see K. A. Dawson, B. L. Walker, and A. Berera, Physica A **165**, 320 (1990)] indicated that the much swollen lamellar phase may be unstable in the vicinity of the putative Lifshitz point.

[3] Y. Levin and K. A. Dawson, Phys. Rev. A **42**, 1976 (1990).

[4] Y. Levin, C. J. Mundy, and K. A. Dawson, Phys. Rev. A **45**, 7309 (1992).

[5] B. Widom, J. Chem. Phys. **84**, 6943 (1986).

[6] K. A. Dawson, Phys. Rev. A **36**, 3383 (1987).

[7] K. A. Dawson, M. D. Lipkin, and B. Widom, J. Chem. Phys. **88**, 5149 (1988).

[8] It is not entirely clear if such a phase is merely metastable. Dr. M. Cates of the Cavendish Laboratory has argued that various mechanisms are available to make such a phase globally stable (private communication).

[9] A. M. Polyakov, *Gauge Fields and Strings* (Harwood Academic, Chur, Switzerland, 1987).

[10] It is of some interest to determine how many localized solutions exist for fixed (b,c). We do not know the answer, and so cannot completely trust an interaction built from only the solutions that have been studied. Still, we here make an estimate based on the solution we have found.

[11] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1993), Chap. 7.