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Liquid-expanded—liquid-condensed phase transition in amphiphilic monolayers: A renormalization-group approach to chiral-symmetry breaking of hydrocarbon-chain defects

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This paper is concerned with the liquid-expanded (LE) —liquid-condensed (LC) transition in monolayers of amphiphilic molecules at the air-water interface. A model, which can be mapped into the Blume-Emery-Griffiths Hamiltonian, has been considered before within the (mean-field) Bragg-Williams approximation and it gave results which could be successfully compared with experiment. The LE-LC transition has been associated with a chiral-symmetry breaking of the hydrocarbon-chain defects. This model is treated here with a Migdal-Kadanoff approximate position-space renormalization group. Renormalization-group flows are consistent with those obtained by previous authors. The connection between experimental and Hamiltonian parameters is easiest for a particular choice of ensemble, which turns out to be rather subtle for this problem. As in the work of Lavis, Southern, and Bell, isotherms in the surface-pressure—molecular-area plane do not show a signature of the LE-LC transition. The better agreement between experiments (showing a compressibility jump at the LE-LC transition) and mean-field theory suggests that in these cases long-range forces depending on the nature of the polar head and on the water substrate *p*H are responsible for the jump.

I. INTRODUCTION

Monolayers of simple amphiphilic molecules (e.g., fatty acids or alcohols) at the air-water interface, exhibit a variety of phase transitions. One of these, at relatively high surface density, is the so-called liquid-expanded (LE) —liquid-condensed (LC) transition. A similar transition also occurs in more complex systems, such as those containing molecules with two hydrophobic chains (phospholipids and lecithins), two polar heads (hydroxyhexadecanoic acids, abbreviated HHA in the literature), or discotics (BH-*n*). In this paper we present a position-space renormalization-group study (PSRG) of the LE-LC transition in the simplest amphiphilic monolayers.

In contrast with the gas-liquid transition in monolayers whose experimental study is extremely difficult, the LE-LC transition offers the advantage of being relatively easy to observe. Since, moreover, the nature of the LE-LC transition is not yet completely clear (in particular the order of the transition is still a subject of controversy), this type of system has been subjected to a large number of theoretical as well as experimental investigations.[1]

Experiments have shown that the LE-LC transition is not an artifact caused by a small spreading pressure and a crossover to a three-dimensional state. However, a piece of perfectly horizontal isotherm in the surface-pressure (Π) —molecular-area (σ) diagram, which is the unmistakable signature of a first-order transition, has never been observed despite very careful experimentation where the return to equilibrium of the system was monitored at each point through relaxation-time measurements.[2] Even the recent experiments of Von Tscharner and McConnel[3] and of Lösche, Sackmann, and Möhwald[4] have not allowed clear conclusions to emerge. Indeed their very clever microscopic observation technique of phopholipid monolayers, which is based on fluorescent probes, has led these groups to contradictory results. The first one does not find anything which can support the hypothesis of a first-order LE-LC transition, while the second group has found evidence for domains, a characteristic of phase coexistence.

Finally, the results of Bois *et al.*,[2] who have systematically studied surface-pressure relaxation times, are quite clearly in favor of a continuous (so-called "second-order") transition: indeed, these times, measured along Π-σ isotherms, become very important near the transition, as one would expect when there is critical slowing down. Moreover, Bois has never obtained a horizontal isotherm segment, even when sufficient time was allowed for return to equilibrium. Note also that the experiment was performed below the spreading pressure and that there was no leak of the surfactant.

The model whose predictions most closely resemble the observations is in our opinion that recently suggested by Firpo, Legré, Bois, and Baret[5] (FLBB). In the present paper we use a more sophisticated method to study their model and we extend their conclusions. Let us then discuss the FLBB model in a bit more detail. Firpo *et al.* use the fact that, close to the LE-LC transitions, kinks in the hydrophobic chains are by far the dominant type of defect. They then propose to keep two molecular states of different helicity, kink (+) and kink (−). In the broken-(chiral-) symmetry phase, one of the moelcular states is more populated and the area per molecule is smaller since molecules in the same state can partially overlap. Lattice-gas sites can be vacant or populated by one of the two species. The model can thus be mapped into a spin-1 problem. FLBB use mean-field theory to draw their conclusions. Despite the important simplifications contained in all of the above hypothesis, the results obtained by Firpo *et al.* are qualitatively very satisfactory. For example, using parameters (interaction energy, intrachain entropy, molecular area, etc.) taken from the literature, they correctly reproduce (see Fig. 1) experimental isotherms obtained with a monolayer of pentadecanoic acid. Moreover, this model can be extended to study the evolution along isotherms of surface-pressure relaxation times: the results obtained there agree as well with experimental data.

In two dimensions when short-range forces only are important, a mean-field solution is usually inadequate. We thus present in this paper an approximate renormalization-group solution of the model of Firpo *et al.*[5] Up to now, PSRG solutions for monolayer models are due to Lavis, Southern, and Bell[6] (LSB) and to two of us[7] (AT). The former group proposed a spin-1 model based on the cooperativity of molecules without defects (transbonds only) where there is no decrease in area or in entropy per molecule when neighboring molecules are in the same state. They use a "majority rule" renormalization-group technique in the tradition of Niemeijer and Van Leeuwen.[8] The latter group on the other hand was looking for a nematic-type transition with a coupled spin-$\frac{1}{2}$-XY model within the Migdal-Kadanoff[9] (MK) approximation. The spin-$\frac{1}{2}$ variable accounts for molecules with and without kinks, the former ones having also an orientational (XY) degree of freedom. Both of the above groups obtain a continuous phase transition without jump or rapid change in the isothermal compressibility. It is legitimate to expect such a jump, or at least a rapid compressibility change, from a Firpo *et al.* type model which introduces area and entropy decreases for neighboring molecules which are in the same state.

In Sec. II we show how our problem is related to the Blume-Emery-Griffiths[10] (BEG) Hamiltonian. PSRG results on that model were obtained by Berker and Wortis[11] (BW) and Adler, Aharony, and Oitmaa[12] using Niemeijer-Van Leeuwen-type techniques, by Kaufman *et al.*[13] who worked with the MK approximation, and by others (see, e.g., Ref. 13 for more references). In Sec. III we discuss the PSRG technique and our results are compared with those of the literature. The choice of ensemble necessary to connect Hamiltonian parameters and experimentally measured quantities turns out to be somewhat subtle in our case. This problem and our results are discussed in Sec. IV. Finally, Sec. V summarizes experimental and theoretical results and draws conclusions. The Appendix presents an alternate discussion of the choice of ensemble.

II. THE FLBB MODEL AND ITS RELATION TO THE BEG MODEL

A. The FLBB model

This three-state model simulates the behavior of simple molecular monolayers in the vicinity of the LE-LC transition. In the range of molecular areas where the transition occurs, the most frequent intrachain defects are kinks. The model thus uses as basic molecular states a plus state whose defect configuration going up the chain is gauche (+) trans-gauche (−) and a minus state with configuration gauche (−) trans-gauche (+). These two configurations have a different helicity and one cannot go from one state of the molecule to the other by a simple rotation (contrary to what the intentionally schematic Fig. 2 might suggest): there is an energy barrier between both configurations. The third state accounts for vacancies.

The above states are represented by eigenvalues of operators S_i associated with each site: $S_i = +1$ for the plus state, $S_i = -1$ for the minus state, and $S_i = 0$ for a

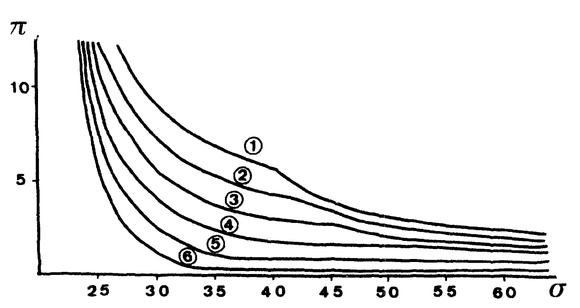

FIG. 1. Surface-pressure (Π in dyn/cm) —molecular-area (σ in Å^2) obtained for the FLBB model within mean-field theory for temperatures (1) 310 K, (2) 303 K, (3) 296 K, (4) 289 K, (5) 282 K, and (6) 275 K.

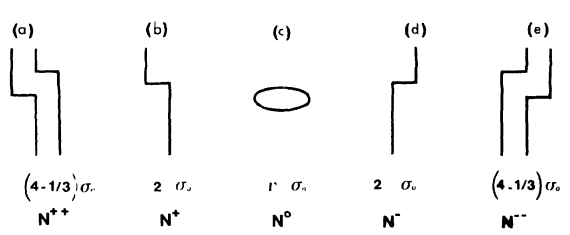

FIG. 2. Schematic representation of various molecular configurations introduced in the FLBB model with their associated area and number operators. Note that (+) and (−) states have a different helicity and cannot be transformed into one another by a simple rotation. (a) A pair of (+) kinks [N_{++} of these pairs, each of which occupies an area $(4-\frac{1}{3})\sigma_0$]. (b) Kink (+) (N_+ of them each of area $2\sigma_0$). (c) Vacancy (N_0 of area $\nu\sigma_0$). (d) Kink (−) (N_- of area $2\sigma_0$). (e) Pair of kink (−) [N_{--} of area $(4-\frac{1}{3})\sigma_0$].

vacancy. This choice of basic molecular states lead FLBB to include the possibility of a decrease in area per molecule when neighboring molecules are in the same state since molecules with the same helicity can overlap more easily than molecules of opposite helicity. Hence, to each site of the lattice corresponds an area which depends on the occupation of the site and of its neighbors. Similarly, the cooperative nesting of two chains limits their configurational phase space and thus a decrease in the intrachain entropy is possible depending on the occupation of a site and of its neighbors.

The energetic and entropic parameters used are $|\omega|$, the attractive interaction energy between arbitrary nearest-neighbor molecules; $|\Delta\omega|$, the additional attractive interaction energy between nested nearest-neighbor molecules in the same state; ΔE, the excitation energy of a molecule in either the $+1$ or -1 state; ΔS, the internal entropy of the $+1$ or -1 states whose defect is free to move along the chain; α, a positive coefficient which describes phenomenologically the entropy loss of a nested pair of molecules in the same state; $2\sigma_0$, the area of an isolated molecule; $v\sigma_0$, the area of a vacancy. The total intrachain entropy ΔS_t may thus be written

$$\Delta S_t = \Delta S[N^+ + N^- - \alpha(N^{++} + N^{--})] , \tag{2.1}$$

where $0 \le \alpha \le \frac{1}{3}$ for a triangular lattice and where N^+ is the number of molecules in the plus state while N^{++} is the number of pairs of molecules which are both in the plus state. The total area A of the monolayer on the other hand is

$$A = \sigma_0[2(N^+ + N^-) + vN^0 - \tfrac{1}{3}(N^{++} + N^{--})] . \tag{2.2}$$

For a temperature T and a surface pressure Π, FLBB thus worked with the following thermodynamic potential:

$$\begin{aligned} H - T\Delta S_t + \Pi A = {} & -|\omega|(N^{++} + N^{+-} + N^{-+} + N^{--}) - |\Delta\omega|(N^{++} + N^{--}) + \Delta E(N^+ + N^-) \\ & - T\Delta S[N^+ + N^- - \alpha(N^{++} + N^{--})] + \Pi\sigma_0[2(N^+ + N^-) + vN^0 - \tfrac{1}{3}(N^{++} + N^{--})] . \end{aligned} \tag{2.3}$$

B. Relation to the BEG model

The following occupation-number operators are defined for each site i: $\frac{1}{2}(S_i^2 + S_i)$ for a plus state, $\frac{1}{2}(S_i^2 - S_i)$ for a minus state, $1 - S_i^2$ for a vacancy. With these operators, one can write the following expressions for the number of molecules and the number of pairs (bracketed indices run over nearest-neighbor pairs):

$$N^{++} = \frac{1}{4}\sum_{\langle ij\rangle}(S_i^2 + S_i)(S_j^2 + S_j) , \tag{2.4a}$$

$$N^{--} = \frac{1}{4}\sum_{\langle ij\rangle}(S_i^2 - S_i)(S_j^2 - S_j) , \tag{2.4b}$$

$$\begin{aligned} N^{+-} + N^{-+} = {} & \frac{1}{4}\sum_{\langle ij\rangle}[(S_i^2 + S_i)(S_j^2 - S_j) \\ & + (S_i^2 - S_i)(S_j^2 + S_j)] , \end{aligned} \tag{2.4c}$$

$$N = \sum_i S_i^2 , \tag{2.4d}$$

$$N^0 = \sum_i 1 - \sum_i S_i^2 . \tag{2.4e}$$

If we set

$$\mathscr{H} = -\frac{H + \Pi A - T\Delta S_t}{k_B T} , \tag{2.5}$$

then with Eqs. (2.3) and (2.4) we find

$$\mathscr{H} = K\sum_{\langle ij\rangle} S_i^2 S_j^2 + J\sum_{\langle ij\rangle} S_i S_j - \Delta\sum_i S_i^2 - M\sum_i 1 , \tag{2.6}$$

where

$$J = \frac{1}{2k_B T}\left[|\Delta\omega| + \frac{\Pi\sigma_0}{3} - \alpha T\Delta S\right] , \tag{2.7a}$$

$$K = J + \frac{|\omega|}{k_B T} , \tag{2.7b}$$

$$\Delta = \frac{1}{k_B T}[\Pi\sigma_0(2 - v) + \Delta E - T\Delta S] , \tag{2.7c}$$

$$M = \Pi\sigma_0 v . \tag{2.7d}$$

Equation (2.6) is the BEG Hamiltonian. Note that Δ is conjugate to the number of molecules and M to the number of sites. To draw isotherms, we want to keep the number of molecules fixed and let the volume vary according to the state of the molecules and to the number of vacancies (or sites). This is a nontrivial problem which we discuss in Sec. IV. In the meantime, we study Eq. (2.6) in the standard way to compare with other PSRG results.

III. RENORMALIZATION-GROUP FLOWS AND FIXED POINTS

We use the Migdal-Kadanoff[9] approximation on a triangular lattice.[14,7] Bonds are moved in the standard way. There are, however, two popular ways of treating single-site terms. In one of them (the Emery-Swendsen procedure), single-site terms are not moved, while in the other procedure, single-site terms are shared equally among bonds and then moved. The first method has the advantage that it is exact for $J = K = 0$. The second method on the other hand has the advantage that the results are insensitive to redefinitions of the S_i which mix single-site and bond parameters.[14]

We have investigated results obtained from both procedures. The fixed-point topology is similar in both cases but exponents are different. We discuss briefly the following recursion relations which were obtained with the Emery-Swendsen procedure:

$$c'^{1/3}=c^{4/3}(1+2z)\ , \tag{3.1a}$$

$$z'=z\left[\frac{1+zw^2(v^2+v^{-2})}{1+2z}\right]^6 , \tag{3.1b}$$

$$v'^2=\frac{1+zw^4(v^4+v^{-4})}{1+2zw^4}\ , \tag{3.1c}$$

$$w'^2=\frac{(1+2zw^4)[1+zw^4(v^4+v^{-4})](1+2z)^2}{[1+zw^2(v^2+v^{-2})]^4}\ , \tag{3.1d}$$

where $c=e^{-E}$, $z=e^{-\Delta}$, $v=e^{J}$, $w=e^{K}$.

Since we are interested mainly in the LE-LC transition, only a small subset of renormalization-group (RG) fixed points are of interest to us. Furthermore, the BEG model has been exhaustively studied in the literature[11–13,6] (see Ref. 13 for further references). Hence we limit ourselves in this section to an outline of the general behavior of the RG flows and to the properties of a few of the fixed points of interest to us, making only a few comparisons with the literature. We follow the notation of Berker and Wortis.[11]

The surfaces appearing on Fig. 3 separate the gas, liquid-expanded (LE), and liquid-condensed (LC) phases corresponding, respectively, to the paramagnetic $(-)$, paramagnetic $(+)$, and ferromagnetic phases of BW. The phase sink fixed points corresponding to each of these phases are $(J^*,K^*,\Delta^*)=(0,0,>0)$ for the gas, $(0,0,<0)$ for LE, and $(\infty,\ln 2-J^*,-\infty)$ for LC. In the first two cases, one can check directly from the recursion relations that the Δ axis is a line of fixed points. We find the positions of the separatrices with a precision of 10^{-2} from diverging renormalization-group flows.

When $\Delta \ll -1$ we recover the two-dimensional Ising model with a critical point at $J=0.305$. The surface indicated by solid lines in Fig. 3 is a surface associated with continuous transitions (critical surface).

The BEG Hamiltonian may be written in the form

$$\mathcal{H}=-\frac{K}{2}\sum_{\langle ij\rangle}(S_i^2-S_j^2)^2-\frac{J}{2}\sum_{\langle ij\rangle}(S_i-S_j)^2 -\left[\Delta-\frac{\gamma}{2}K-\frac{\gamma}{2}J\right]\sum_i S_i^2\ , \tag{3.2}$$

where γ is the lattice coordination number. Here $\gamma=6$, so for $K\gg 1$ and $J\gg 1$ (which imply $S_i=S_j$, $S_i^2=S_j^2$), $\Delta=3J+3K$ appears as a planar domain for discontinuity fixed points. One can indeed verify that $zv^3w^3=1$ is invariant under iteration of Eqs. (3.1) for large values of Δ, K, and J. The line $K=J\gg 1$ is an invariant subset of the above surface.

The plane with long-dash lines which separates the LC and gas phases is part of the $\Delta\sim 3(J+K)\gg 1$ plane. It intersects the critical surface described previously on the T_0P tricritical line. The point T_0 in the Blume-Capel[15]

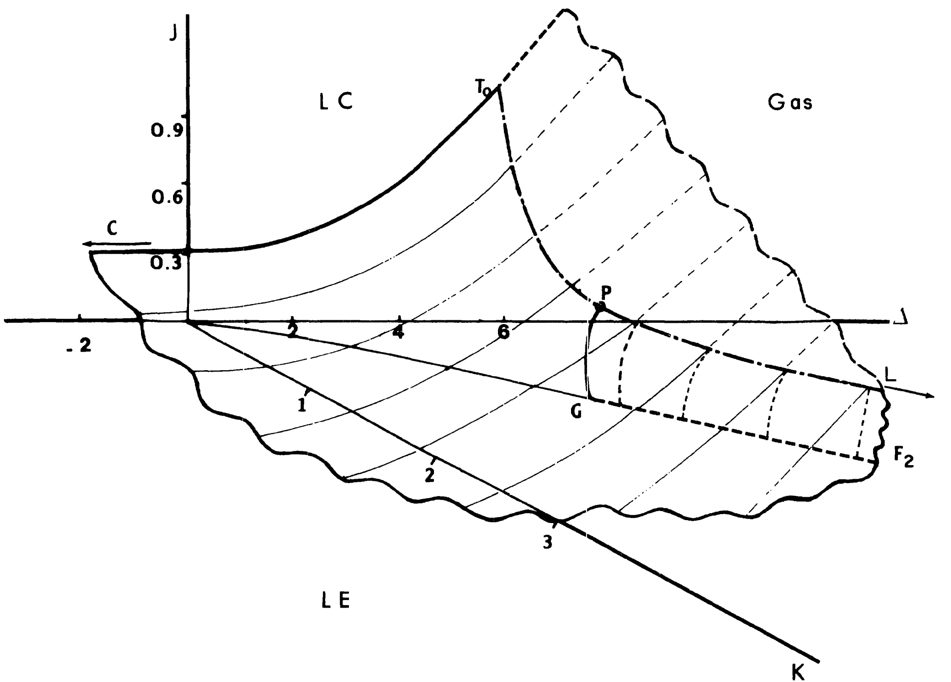

FIG. 3. Overview of renormalization-group flow separatrices in the (J,K,Δ) space. Solid line, surface of continuous transitions between the LE phase (below) and the LC phase (above). Short-dash line, surface of first-order transitions between the LE and gas phases limited below by the first-order Griffiths line (slightly curved here) and limited above by a line of critical end points terminating at P, a special tricritical point such that $J_p=0.47$, $K_p=1.14$, $\Delta_p=5.88$. Long-dash line, surface of first-order transitions LC-gas accompanied by a broken symmetry. [This is the $\Delta\sim 3(J+K)$ plane which terminates for $J<J_P$ on the line of critical end points PL and for $J>J_P$ on the line of tricritical points T_0P. T_0 is the tricritical point of the Blume-Capel model in the $K=0$ plane.] G is the Griffiths-Onsager critical point. For more details, see, for example, Berker and Wortis, Ref. 11.

plane $K=0$ is at $J_T=1.97$, $\Delta_T=6.08$. Under this line, one cannot distinguish the LE and gas phases.

The PGF_2L surface defines a first-order transition between the gas and LE phases. It is limited in the $J=0$ plane by the line GF_2. Griffiths has shown that on that line one recovers the Ising Hamiltonian since after the change of variables $S_i^2=(t_i+1)/2$ one obtains

$$\mathscr{H}_{J=0}=J_i\sum_{\langle ij\rangle}t_it_j+H_L\sum_i t_i \ , \tag{3.3}$$

where

$$J_1=\frac{K}{4},\ H_I=\tfrac{1}{2}(3K-\Delta+\ln 2)\ . \tag{3.4}$$

The ln2 term has an entropic origin. It compensates the decrease in number of configurations when one goes from three to two possible states on each site. Point G can in principle be deduced from Griffiths's symmetry [i.e., from $J_I=0.305$, $H_I=0$ (point C) and from Eq. (3.4)], but that symmetry is not preserved by the MK approximation.[16] Since Griffiths's symmetry is not exactly satisfied, the result $\Delta=3K+\ln 2$ for the intersection of the first-order surface with the $J=0$ plane holds only for $\Delta\gtrsim 5$; deviations from $\Delta=3K+\ln 2$ occur for $\Delta\lesssim 5$. The PL line is a line of critical end points. The coordinates of L are $J_L=0.305$, $K_L=\infty$, $\Delta_L=3K_L+J_L+\ln 2$.

Figure 4 gives more precisely the phase-separation line as a function of K. The intersection between two lines of first-order transitions (dotted lines) and a line of continuous transition (solid line) is a critical end point, while a continuous and first-order line join smoothly at a tricritical point. The latter case occurs for values of K smaller than that corresponding to the point P. Note that the dash-dotted line is the locus of critical end points or tricritical points for various values of K [K is a constant along any other (dotted or solid) line].

The shape of our PSRG flows are qualitatively the same as those of BW[11] and of others.[17] More quantitative comparisons are also possible. For example, on a triangular lattice Adler *et al.*[12] find with a PSRG different from ours that their Ising critical points are at $J=0.365$ while ours are at $J=0.305$. For exponents, a comparison between results obtained on different types of lattices is valid.

Table I compares a few of our exponents (first column) with published results. The second of each pair of exponents quoted under LAFT (this work) are obtained on a triangular lattice by moving bonds as well as single-site terms. It is for this latter case that the agreement with the work of Kaufman *et al.*,[13] for example, is best. These authors have used the MK approximation with moving of single-site terms but they worked on a square lattice. They have also noted differences between the exponents obtained from single-site moving and from the Emery-Swendsen procedure. In our case, the main difference is that the exponent y_6 is irrelevant in the former approach and marginal in the latter one. Our main conclusions are insensitive to this difference. The calculations presented in Sec. IV use the equations (3.1) derived from the Emery-Swendsen procedure.

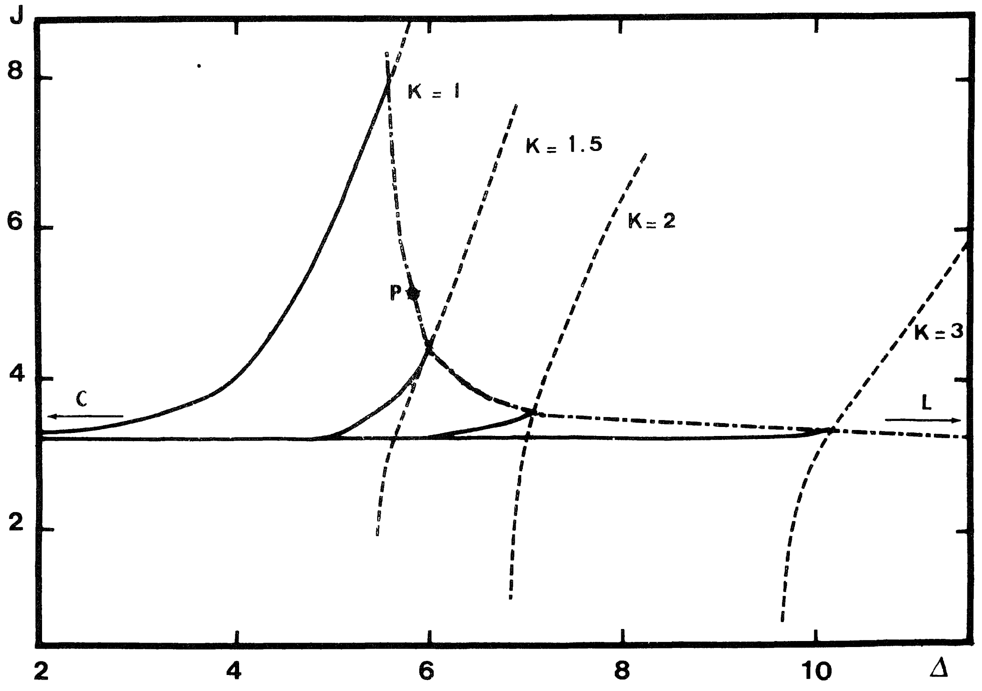

FIG. 4. Evolution of the phase boundaries for various values of the parameter K. Solid lines, continuous transitions. Dashed lines, first-order transitions (between LE and gas below the intersection with the solid lines and between LC and gas above). The dash-dotted line is the locus of intersection points between first-order and continuous transitions. The value of K changes along this line which corresponds to tricritical points above the point P and to critical end points below it.

TABLE I. Exponents for a few fixed points. Comparison of exponents corresponding to a few fixed points, C, L, and G, relevant to this work (LAFT). BW is Ref. 11, LSB is Ref. 6, and KGYF is Ref. 13. Exactly known results are $y_2=1$ at points C and G and $y_4=1.875$ at point G. The second number in the LAFT column was obtained by moving sites to derive the recursion relations. The exponent y_6 in this approach was calculated by using, for example, e^{Δ} at point C as a scaling variable (e.g., see Ref. 11, Table III caption).

	Point C LE-LC				Point L Gas-LE-LC			
	LAFT	BW	LSB	KGYF	LAFT	BW	LSB	KGYF
y_2	0.747 0.747	0.726	0.638	0.747	0.747 0.747	0.727	0.638	0.747
y_4	$-\infty$ $-\infty$	-1.04	<0	$-\infty$	2 2	2	2	2
y_6	0 $-\infty$	$-\infty$	<0	$-\infty$	0 $-\infty$	$-\infty$	<0	$-\infty$

IV. CHOICE OF ENSEMBLE AND CALCULATION OF ISOTHERMS

A. Choice of ensemble and method of calculation

Even though average thermodynamic quantities are independent of the choice of ensemble, the relationship between real physical quantities and Hamiltonian parameters defined on a lattice gas is more natural in a particular ensemble. In the usual lattice-gas approaches to gas-liquid transitions, for example, the volume associated with each lattice site is fixed and the average occupation is controlled by a chemical potential. In other words, the grand canonical ensemble is the most natural choice. If one is confronted with a problem at close packing where the volume occupied by a molecule depends on its internal state, then the isothermal-isobaric ensemble is more convenient.[7] The number of sites is fixed and equal to the number of molecules. Here we are faced with a situation which borrows certain aspects from both of the above problems since we have vacancies which are most easily treated within the grand-canonical ensemble while the volume change associated with a change of molecular state is most easily treated within the isothermal-isobaric ensemble.

Suppose we start from the isothermal-isobaric ensemble. Then one wants to compute (with $\beta=1/k_BT$ and μ the chemical potential)

$$N\mu=-\beta^{-1}\ln[\mathrm{Tr}_N(e^{-\beta(F+\Pi A)})] , \tag{4.1}$$

where $F=H-T\Delta S_t$ with H and ΔS_t defined in Eq. (2.3), while A is the surface operator and Tr_N represents a trace constrained to a fixed number of molecules N. Equation (4.1) may also be written in the form

$$0=\ln[\mathrm{Tr}_N(e^{\beta\mu N}e^{-\beta(F+\Pi A)})] . \tag{4.2}$$

Within our spin model, however, a trace over all spin configurations at fixed number of sites N_s contains configurations with different values of N. Instead, to evaluate Eq. (4.2) we should consider a variable number of sites depending on the spin configuration so that the number of molecules is fixed. This is extremely difficult. Since, in any case, physical quantities depend only on N/N_s, we let the number of molecules vary and fix the number of sites. This means that we can instead consider

$$0=\ln[\mathrm{Tr}_{N_s}(e^{\beta\mu N-\beta(F+\Pi A)})] , \tag{4.3}$$

where we now have a lattice with a fixed number of sites and the trace over spin configurations corresponds to varying numbers of molecules. If any two of the intensive variables, T, Π, μ are given, the other one must be calculated so that Eq. (4.3) is satisifed. In practice, we fix T and Π and determine μ. To draw isotherms, the area per molecule σ is determined numerically from (see also the Appendix)

$$\frac{A}{N}=\sigma=\left[\frac{\partial\mu}{\partial\Pi}\right]_T . \tag{4.4}$$

Note that Eq. (4.3) can also be derived by taking the grand-canonical ensemble as a starting point instead of the isothermal-isobaric ensemble. The Appendix gives an alternate derivation of Eqs. (4.3) and (4.4).

Using Eqs. (2.3) and (2.6), Eq. (4.3) takes the following more explicit form:

$$0=\ln[\mathrm{Tr}_{N_s}\exp(\bar{H})] , \tag{4.5a}$$

where

$$\bar{H}=K\sum_{\langle ij\rangle}S_i^2S_j^2+J\sum_{\langle ij\rangle}S_iS_j-D\sum_i S_i^2-M\sum_i 1 \tag{4.5b}$$

with

$$D=\Delta-\frac{\mu}{k_BT} . \tag{4.5c}$$

If we let a superscript in parenthesis number the iterations performed we have

$$\ln[\mathrm{Tr}_{N_s}\exp(\bar{H})] = \ln\{\mathrm{Tr}_{N_s^{(n)}}\exp[\bar{H}^{(n)}(K^{(n)},J^{(n)},D^{(n)}) + E^{(n)}N_s^{(n)}]\} , \tag{4.6}$$

where $N_s^{(n)} = N_s/b^{nd}$ with $d=2$ the dimension of the system and $b=2$ the length rescaling. When n is large, we are in general in the neighborhood of a phase sink fixed point where $\bar{H}^{(n+1)} \sim \bar{H}^{(n)} \sim \bar{H}^*$. Then (with $b^d = 4$)

$$\frac{\ln[\mathrm{Tr}_{N_s}\exp(\bar{H})]}{N_s} = \frac{E^{(n)}}{b^{nd}} + \frac{\ln[\mathrm{Tr}_{N_s^{(n)}}(\exp\bar{H}^*)]}{N_s} . \tag{4.7}$$

In the limit where the number of iterations is large $N_s^{(n)} \ll N_s$ and since $\bar{H}^*$ is not singular, the last term is completely negligible. Since $\bar{H}$ has the same form as $\mathcal{H}$ in Eq. (2.6), the recursion relations also have the same form. In particular, from Eq. (3.1a) we deduce that

$$E^{(n+1)} = 4E^{(n)} - 3\ln(1+2z^{(n)}) . \tag{4.8}$$

Iterating and combining with Eq. (4.7), we find, with $E^{(0)} = 0$,

$$\frac{1}{N_s}\ln[\mathrm{Tr}(\exp\bar{H})] = \lim_{n\to\infty}\left[-3\sum_{i=0}^{n-1}\frac{1}{4^{i+1}}\ln(1+2z^{(i)})\right] . \tag{4.9}$$

The value of μ which makes this expression vanish is equal to the chemical potential corresponding to Π and T.

B. Results for isotherms

The method described above does allow us to obtain physically sensible isotherms, as pictured in Fig. 5. But, contrary to the results obtained within the mean-field approximation for the same model, there is no break point and hence no compressibility jump at the LE-LC transition.

Let us briefly describe the renormalization-group flows as we increase the pressure along an isotherm.

(i) At low pressures one iterates towards fixed points along the Δ axis with finite values of Δ. Using energetic and entropic parameters (Table II) which are considered as realistic (the same as those of FLBB), we go continuously from $\Delta > 0$ to $\Delta < 0$. There is thus no first-order transition along the isotherm. Within this PSRG treatment, we also never obtain a gas-LE or gas-LC first-order transition: If we choose points in parameter space where these transitions are possible ($J < 0.3$, $K > 2$ for gas-LE) the chemical potential seems to evolve in such a way that Δ never takes a value large enough to reach the gaseous phase. Our lattice-gas model is in fact an inaccurate description of the very dilute phase.

(ii) At higher pressures the parameters converge towards the LC phase sink fixed point $(J^*, K^*, \Delta^*) = (+\infty, -\infty, -\infty)$. We thus obtain the LE-LC transition, but as can be seen from Fig. 5, there is nothing which can be interpreted as a rapid change in compressibility at the transition. Such a change, if any, would have to come from the nonsingular part of the free energy. A theoretical discussion on this absence of signature at the transition on the isotherms is given by LSB.[6] We present additional remarks on this subject in Sec. V.

TABLE II. Hamiltonian parameters. Numerical values of the parameters entering the Hamiltonian Eqs. (2.3), (2.6) and (2.7). The first four parameters are in units where $k_B = 1$, σ_0 is in Å^2, and ν and α are dimensionless.

$\lvert\omega\rvert$	$\lvert\Delta\omega\rvert$	ΔE	ΔS	σ_0	ν	α
216	522	500	3.5	22	2	0.4

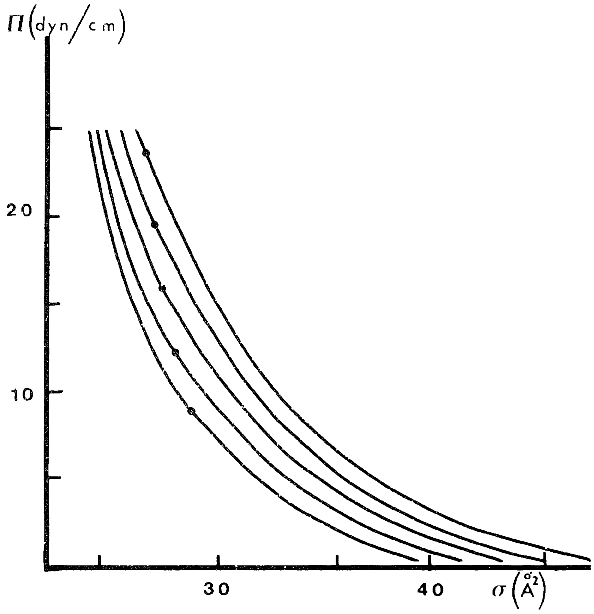

FIG. 5. Surface-pressure—molecular-area isotherms obtained within the PSRG technique for various temperatures as in Fig. 1: (1) 303 K, (2) 296 K, (3) 289 K, (4) 282 K, (5) 275 K. The parameters for the calculation are the same as those used for Fig. 1 and are given in Table II. The dots are critical points. There is no obvious change in the compressibility near the transition. This is discussed in the text.

V. ANALYSIS OF THE RESULTS AND COMPARISON WITH EXPERIMENT

A. Theoretical results

By using the renormalization group to study a simple model we have implicitly assumed the validity of the universality hypothesis for this problem. It is thus not surprising to find that our results, close to a transition, are almost identical to those of LSB.[6] Indeed, whatever the details of the model, the critical exponents which govern the behavior of the isothermal compressibility on either side of the transition should be the same when the dimensionality of the system and order-parameter symmetries of the Hamiltonians are identical. Note, however, that we have not identified physical observables in the same way as LSB, but our definitions are presumably not different enough to lead to effective exponents which markedly differ from those of LSB. In particular, the exponent inequality which they use to explain their results must also be satisfied in our case. More specifically, they point out that a simple extension of the Nienhuis-Nauenberg argument for order-parameter discontinuities at phase transitions shows when one can expect a diverging, jumping, or smoothly behaving compressibility at the transition. The result is that if y is the leading exponent to which the pressure field is coupled, then the necessary condition for each of the above behaviors is, respectively, $y > d/2$, $y = d/2$, and $y < d/2$. One must account for the fact that within our model Eq. (A8) is used to compute the isotherms but since $\partial\mu_s/\partial\mu$ is not singular at the transition, the above argument is still valid. (μ_s is a "site" chemical potential. See Appendix.)

In our case, one can check from Eqs. (2.7) that the pressure field couples to all eigenvectors. Hence, the smooth behavior which we find at the transition is explained by the fact that the LE-LC transition is in the Ising universality class represented by the fixed point C which (Table II) has its largest exponent smaller than $d/2$. It is conceivable, however, that a more accurate treatment of our model would yield results in better agreement with experiment. That could come about in two ways:

(i) The exact relevant exponent for the Ising transition we are interested in is the Onsager result $y = 1 = d/2$. Hence a jump in the compressibility *could* occur ($y = 1$ is not a sufficient condition).

(ii) Far from the transition, results are nonuniversal and can mimic on a coarse scale the appropriate change in monolayer compressibility. To obtain such background nonuniversal terms, however, series expansions are more accurate. A more detailed model may also be required far from the transition.

The following discussion of experimental findings and the very good results[5] of mean-field theory suggest another conclusion.

B. Comparison with experiment

(i) LE-LC transitions in the historical sense of the term, i.e., a break point on the isotherms, occur in simple amphiphilic molecules. For that type of molecule sizable relaxation phenomena of the surface pressure occur near the transition and disappear far from it, as was shown recently by Bois *et al.*[2] for fatty acids. That kind of phenomenon is probably responsible for the hysteresis observed by Tabak, Notter, Ultman, and Dinh[18] on dipalmitoyls lecithins. Increased relaxation times close to a transition can show up as hysteresis, even though the transition is not first order.[5]

One must also account for the fact that to limit the desorption of molecules in the bulk of the water support, experimentalists must work with low-pH substrates. As long as unshielded molecular dipoles are not perpendicular to the surface, they have a nonzero component in the interface plane. This parallel component is partly responsible for the attractive part of the interaction. Indeed, if one assumes a hexagonal array of ferroelectrically ordered dipoles, one finds that the attractive part of the dipolar interaction dominates when the angle between the dipoles and the interface is less than 35.3 deg.[19]

Note also that for $1/r^3$ attractive interactions, the marginal dimension for which Landau theory applies is two.[20] (For short range forces such as interchain Van der Waals coupling, the marginal dimension is four.) Hence when dipolar forces dominate, it is not surprising that mean-field theory predicts isotherms which are in agreement with experiment.[5] Indeed, long-range attractive forces increase the cooperativity of the transition, leading probably to a break point, or at least to a relatively rapid change, in the isotherms at the transition. This effect is well simulated by the Bragg-Williams approximation. So, for molecules whose polar groups, unshielded by a low-pH substrate, are sufficiently tilted towards the interface, the mean-field approximation is perhaps more realistic than simple PSRG.

(ii) Simple PSRG techniques of the kind discussed here should be appropriate for experimental systems with short-range forces. There exist experimental cases where there is no compressibility jump. Early experiments, such as those of Glazer and Alexander[21] on long-chain ureas showed that an increase in the pH of the water leads to a disappearance of the "classical" LE-LC transition. More recently, Bouloussa[22] found that on certain dipeptide monolayers *n*-Palm—L-Ala—Gly and *n*-Palm—Gly—L-Ala (*n*-Palm, palmitic acid, or *n*-hexadecanoic; Ala, alanine; Gly, glycine), the simple permutation of two polar groups leads to the appearance or disappearance of the compressibility jump (see Fig. 6).

The above results may be interpreted as follows: In the case of urea molecules, with a very-high-pH substrate, the dissociation rate of polar heads becomes very important. Dissociated hydrophilic groups behave like negative charges among the groups which keep their dipolar moments. There is a disappearance of long-range attractive interactions and of the compressibility jump. In the case of dipeptide molecules, the permutation of two radicals leads to a modification of either the global dipolar moment of the hydrophilic group or of its tilt angle with respect to the interface. If the dipolar component in the interface plane is too weak for molecular areas above the LE-LC transition, this becomes even more so as the pressure increases and the classical LE-LC transition cannot occur. The increase in the vertical component of the dipolar moment with pressure has been demonstrated in the experiments of Welles *et al.*[23] on palmitic acid. In both of the above experiments the conditions for existence of long-range attractive forces have been suppressed and the compressibility jump has disappeared.

Suppose that the present PSRG approach gives the correct qualitative behavior of the isotherms for certain molecules. It would be possible to experimentally verify this hypothesis: If the transition continues to exist without obvious signature on the isotherms, it must be experimentally uncovered by studies of surface-pressure relaxation. Such experiments would be difficult because the transition will be unobservable if it occurs at a pressure larger than the spreading pressure in the experimentally accessible temperature range. Moreover, it would be

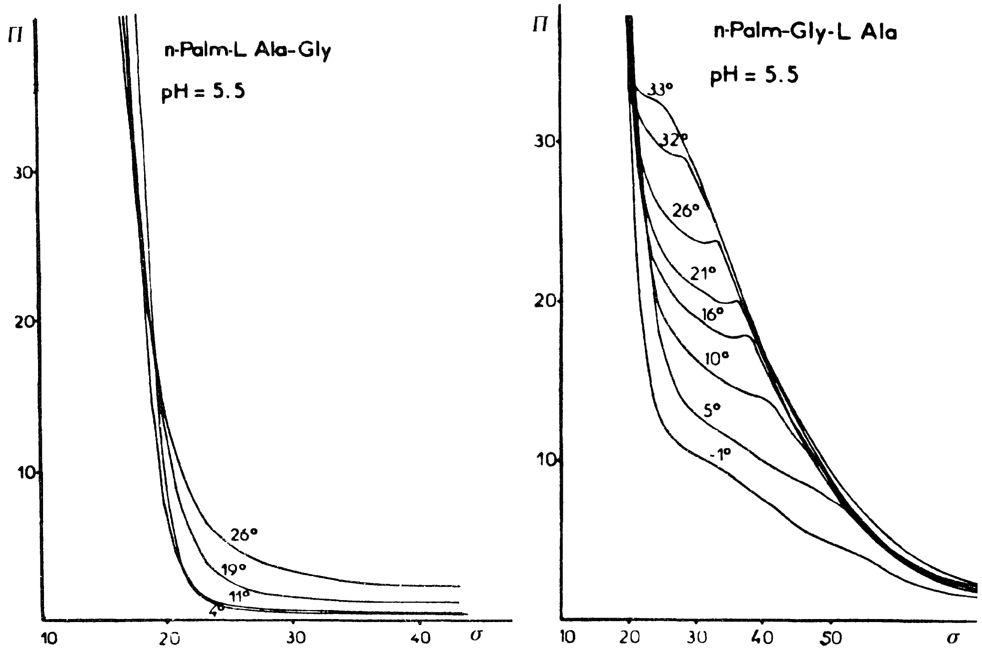

FIG. 6. Surface-pressure (Π in dyn/cm) —molecular-area (σ in Å^2) obtained by Bouloussa (Ref. 22) with two isomers which differ only in the position of the Gly (glycine) and L-Ala (alanine) groups in the polar head. One can notice the disappearance of a break in the isotherms obtained with the compound L-Ala—Gly. (*n*-Palm is palmitic acid, or *n*-hexadecanoic.)

necessary to verify that the absence of a compressibility jump is not caused by a strong bulk water desorption. The latter is not likely, however, since it would not then be possible to obtain a very low compressibility in the small molecular-area range.

Our study is not completely conclusive. But if our PSRG calculation has the slightest resemblance to the true solution of the model, and if this model is realistic, then the above arguments suggest that dipolar forces may play a dominant role in the LE-LC transition and that even in cases where no transition is observed, relaxation experiments may reveal some interesting results.

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APPENDIX: ON THE APPROPRIATE CHOICE OF ENSEMBLE

The situation which most closely mimics the experiment is one in which the number of molecules is fixed while the volume varies either because of a change in the number of vacancies (or equivalently number of sites) or because of a change in the molecular configuration. In practice, it is easier to keep a fixed number of sites and to trace over the spin states, i.e., to let volume and number of molecules change. (In the grand-canonical ensemble, fixing the number of sites fixes the volume, but not here.) In other words, it is easiest to compute at fixed number of sites N_s,

$$R=\sum_{j,N,A} e^{-\beta(E_j+\Pi A-\mu N)}=\mathrm{Tr}_{N_s}(\exp H)\,, \tag{A1}$$

where N is the number of molecules, A the area, and E_j the energy in state j for a system of size A with N particles. Π is the surface pressure and μ the chemical potential for the molecules. The thermodynamic meaning of the partition function Eq. (A1) and of its Lagrange multipliers is found from the usual statistical and thermodynamic considerations.[24] In particular, one finds that

$$N_s\mu_s=-k_BT\ln R\,, \tag{A2}$$

where μ_s is the thermodynamic-potential conjugate to the number of sites. (The reader will find the analogy to a system with two kinds of chemical species useful.)

Since the number of sites is not really constrained but adjusts itself to the number of molecules and the imposed values of Π and $k_BT=\beta^{-1}$, one expects that we must require $\mu_s=0$. To show that, note that considerations of extensivity (Gibbs-Duhem) give

$$N\,d\mu=-S\,dT-N_s d\mu_s+A\,d\Pi\,, \tag{A3}$$

where S is the entropy. This means, in particular, that we may write μ as a function of μ_s, T, and Π. A Legendre transform gives us a thermodynamic potential which depends on T, Π, and N_s/N:

$$dI \equiv d\left[\mu+\frac{N_s}{N}\mu_s\right] = -\frac{S}{N}dT+\frac{A}{N}d\Pi+\mu_s\, d\left[\frac{N_s}{N}\right], \tag{A4}$$

where

$$\frac{N_s}{N} = -\left[\frac{\partial\mu(\mu_s,T,\Pi)}{\partial\mu_s}\right]_{T,\Pi}. \tag{A5}$$

Equation (A5) allows one to find μ_s as a function of T, Π, and N_s/N. Since N_s/N is not constrained from the outside, it means that its conjugate thermodynamic force μ_s vanishes, or alternatively that I is an extremum with respect to N_s/N, a condition which also implies that $\mu_s=0$. Since $\mu_s=0$ for all values of T and Π, we also find from Eq. (A4) that

$$\sigma=\frac{A}{N}=\left[\frac{\partial I}{\partial \Pi}\right]_T=\left[\frac{\partial \mu}{\partial \Pi}\right]_T, \tag{A6}$$

where for each value of T and Π, μ is such that $\mu_s=0$ as stated in Eq. (4.4).

Two more remarks. First note that

$$d\mu_s=\left[\frac{\partial\mu_s}{\partial\mu}\right]_{T,\Pi}d\mu+\left[\frac{\partial\mu_s}{\partial T}\right]_{\mu,\Pi}dT+\left[\frac{\partial\mu_s}{\partial\Pi}\right]_{\mu,T}d\Pi \tag{A7}$$

which implies that when μ_s vanishes identically,

$$\sigma=\frac{A}{N}=\left[\frac{\partial\mu}{\partial\Pi}\right]_{T,\mu_s=0}=-\frac{\left[\dfrac{\partial\mu_s}{\partial\Pi}\right]_{\mu,T}}{\left[\dfrac{\partial\mu_s}{\partial\mu}\right]_{T,\Pi}}, \tag{A8}$$

where T and Π are given, μ_s is computed from Eq. (A2), and the value of μ is chosen such that $\mu_s=0$. Finally, note that if we had chosen $\mu=0$ in Eq. (A1), arguments similar to those leading to Eq. (A6) show that $(\partial\mu_s/\partial\Pi)_{T,\mu=0}=A/N_s$ which is not the physically relevant quantity.

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