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Citation: Vink, R.L.C. and ARCHER, A.J., 2012. Phase separation in fluids exposed to spatially periodic external fields. Physical Review E, 85 (3), 031505, 11pp.

Additional Information:

- This article was published in the journal, Physical Review E [© American Physical Society].

Metadata Record: https://dspace.lboro.ac.uk/2134/12312

Version: Published

Publisher: © American Physical Society

Please cite the published version.
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Phase separation in fluids exposed to spatially periodic external fields

R. L. C. Vink
Institute of Theoretical Physics, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, D-37077 Göttingen, Germany

A. J. Archer
Department of Mathematical Sciences, Loughborough University, Loughborough, Leicestershire LE11 3TU, United Kingdom

(Received 30 September 2011; published 27 March 2012)

When a fluid is confined within a spatially periodic external field, the liquid-vapor transition is replaced by a different transition called laser-induced condensation (LIC) [Götze et al., Mol. Phys. 101, 1651 (2003)]. In \( d = 3 \) dimensions, the periodic field induces an additional phase, characterized by large density modulations along the field direction. At the triple point, all three phases (modulated, vapor, and liquid) coexist. At temperatures slightly above the triple point and for low (high) values of the chemical potential, two-phase coexistence between the modulated phase and the vapor (liquid) is observed; by increasing the temperature further, both coexistence regions terminate in critical points. In this paper, we reconsider LIC using the Ising model to resolve a number of open issues. To be specific, we (1) determine the universality class of the LIC critical points and elucidate the nature of the correlations along the field direction, (2) present a mean-field analysis to show how the LIC phase diagram changes as a function of the field wavelength and amplitude, (3) develop a simulation method by which the extremely low tension of the interface between modulated and vapor or liquid phase can be measured, (4) present a finite-size scaling analysis to accurately extract the LIC triple point from finite-size simulation data, and (5) consider the fate of LIC in \( d = 2 \) dimensions.

DOI: 10.1103/PhysRevE.85.031505

I. INTRODUCTION

Liquid-vapor-type phase transitions in fluids are profoundly affected by confinement (for a recent review see Ref. [1]). Typical effects are the depression of critical temperatures [2], changes in universality [3], or entirely new phenomena altogether [4,5]. The confinement of a fluid between two parallel surfaces is arguably the simplest example one could envision [2]. Already for this case the corresponding phase behavior is extremely rich, especially if the surfaces have different interactions with the fluid [5,6]. With the advance of microcontact printing [7], vapor deposition, and grafting methods [8], as well as photolithography [9], the possibilities of tuning the surface-fluid interaction are essentially endless. In addition to surfaces, confinement in fluids may also be induced via external fields (for example, optical tweezers can be used to realize one-dimensional diffusion channels for colloidal particles in suspension [10]). Hence, well-characterized geometries of ever increasing complexity can be generated, and the phase behavior of fluids confined within these is expected to become correspondingly richer.

With these developments in mind, this paper considers the fate of the liquid-vapor transition in a fluid confined within a static external field having periodic spatial oscillations in one direction. In \( d = 2 \) dimensions, such a field might be realized using a stripe-patterned surface [11,12], while in \( d = 3 \) dimensions, laser [13] or electric fields [14–16] could possibly be used. The case \( d = 3 \) was first considered theoretically in Ref. [17] for a colloid-polymer mixture. The main finding was a new kind of phase transition, referred to as laser-induced condensation (LIC), which takes place provided the field wavelength is large enough. In the presence of the periodic field, one then observes a new third phase (in addition to the vapor and liquid phases) characterized by (i) an average density between those of the vapor and liquid phases, and (ii) large density modulations along the field direction (because of the latter modulations we refer to this phase as the “zebra” phase in what follows). The presence of the zebra phase dramatically alters the liquid-vapor phase diagram: the critical point of the bulk transition is replaced by two new critical points and a triple point. At temperatures between the triple and critical points, vapor-zebra and liquid-zebra two-phase coexistence is observed (at low and high values of the chemical potential, respectively).

In a subsequent publication [18] the peculiar nature of the critical points was elucidated, and also the tensions \( \gamma_{vz} \) and \( \gamma_{lz} \) of, respectively, the vapor-zebra and liquid-zebra interfaces were calculated. The main observations were a critical behavior corresponding to effectively \( d = 2 \) dimensions (i.e., 1 below the system dimension). Furthermore, the critical behavior was shown to be spatially localized in “slabs.” That is, defining the \( z \) axes to be the direction along which the field propagates, critical behavior is observed only for special values of the \( z \) coordinate \( z = z^* \), where \( z^* \) “repeats” with the same period as the field. For those values of \( z \) where the system is critical, one observes critical correlations in directions perpendicular to the \( z \)-axes. Note that the universality class of the resulting critical behavior could not be determined from the data of Ref. [18], as the complexity of the simulations for the colloid-polymer model prevented this. The second main finding were extremely low interfacial tensions. The latter were found, using density functional theory, to be at most \( \gamma_{vz} \sim \sim \gamma_{lz} \sim 10^{-5}k_B T \) per projected particle area (with \( k_B \) the Boltzmann constant, and \( T \) the temperature). The accompanying simulations confirm that \( \gamma_{vz} \) and \( \gamma_{lz} \) must be extremely low, but no numerical values could be obtained (from the simulation data of Ref. [18], interface tensions of exactly zero cannot be completely ruled out either).
In this paper, we therefore reconsider LIC in order to address these questions. We determine the universality class of the LIC critical points. We also elucidate the fate of the correlations in the field direction. In the thermodynamic limit, the latter are shown to vanish, consistent with the finding of Ref. [18] that LIC criticality is an effectively two-dimensional phenomenon. In finite systems, however, fascinating anticornrelations between critical slabs are revealed: if the density in one of the slabs is high, the other slabs respond by assuming an overall lower density, whereby the density excess of the one slab is divided equally among the others. In this work we also determine the extremely low interfacial tensions via computer simulation, as the simulations of Ref. [18] were inconclusive in this respect. As it turns out, such extremely low tensions are inaccessible using “standard” methods [19,20]. An important additional contribution of this work is the presentation of a simulation method by which such extremely low interface tensions can be measured. We also complement our analysis of LIC with a detailed investigation of finite-size effects near the triple point, which turn out to be well described with a detailed investigation of finite-size effects tensions can be measured. We also complement our analysis of LIC with a detailed investigation of finite-size effects near the triple point, which turn out to be well described in experiments [17]. Since the critical behavior was shown to be of dimension \( d \) in Ref. [21]. Finally, we consider LIC near the triple point, which turn out to be well described of LIC with a detailed investigation of finite-size effects.

We emphasize that the simulations and theoretical calculations of this work are based on the Ising model. Compared to a colloid-polymer mixture, computer simulations of the Ising model allow for better equilibration, such that larger system sizes can be reached. Of course, since the universality class of fluids is the Ising one, generic trends observed in the latter directly apply to fluids as well.

This paper is laid out as follows: In Sec. II we present our (Ising) model system and briefly discuss the Monte Carlo simulation methods used. In Sec. III we present our results for the system in \( d = 3 \). In Sec. III A we present the phase diagram and in Sec. III B we develop a simple mean-field theory that is able to qualitatively describe the phase behavior in \( d = 3 \), so as to determine how the phase diagram varies as the parameters in the model are varied. Section III C contains a discussion of our finite-size-scaling analysis and in Sec. III D we present our method and results for obtaining the extremely low interfacial tensions between the zebra and homogeneous phases. In Sec. III E we discuss the nature of the correlations in the system. In Sec. IV we present our results for the system in \( d = 2 \) dimensions and finally in Sec. V we briefly summarize our results.

II. MODEL AND SIMULATION METHOD

We consider the Ising model on rectangular \( L \times L \times D \) \((d = 3)\) and \( L \times D \) \((d = 2)\) lattices with periodic boundary conditions in all directions. The system is exposed to a periodic external field \( V_{\text{per}}(z) \), with the \( z \) axes parallel to edge \( D \) of the lattice. To each lattice site \( i \), a spin variable \( s_i = \pm 1 \) is attached.

The energy of the system is given by

\[
E = -J \sum_{\langle i,j \rangle} s_is_j + H \sum_i s_i + \sum_i V_{\text{per}}(z_i),
\]

where the first sum is over nearest neighbors and the remaining sums over sites. The first term is the usual Ising pair interaction with coupling constant \( J \) (we consider ferromagnetic interactions \( J > 0 \) only). The second term is the interaction of the spins with a homogeneous external magnetic field of strength \( H \). The last term represents the interaction with the periodic field, where \( z_i \) is the \( z \) coordinate of spin \( i \). For the periodic external field we use a block wave of alternating sign

\[
V_{\text{per}}(z) = \begin{cases} -h, & 0 < z \leq \lambda/2, \\ +h, & \lambda/2 < z \leq \lambda, \end{cases}
\]

with \( h \) the field strength and \( \lambda \) the wavelength. Due to the discretization of the lattice we must choose \( \lambda = 2an_1 \), with \( a \) the lattice constant, and \( n_1 \) an integer. The use of periodic boundary conditions implies that the lattice edge \( D = \lambda n_2 \), with \( n_2 \) also an integer. In what follows, the lattice constant is the unit of length \( a = 1 \). In addition, a factor of \( 1/k_BT \) is assumed to have been absorbed into the coupling constants \( J, H, \) and \( h \) such that these quantities are dimensionless.

Monte Carlo simulations and mean-field theory are used to study the phase behavior of the above model. The key output of the simulations is the distribution \( P(m) \), defined as the probability of observing the system in a state with magnetization \( m = \langle 1/N \rangle \sum_i s_i \), with \( N = DL^{d-1} \) the total number of lattice sites. We emphasize that \( P(m) \) depends on all the model parameters introduced above, including the system size. To obtain \( P(m) \) we use single-spin-flip dynamics [22] combined with successive umbrella sampling [23]; the latter scheme ensures that \( P(m) \) is obtained over the entire range \(-1 \leq m \leq 1 \), including those regions where \( P(m) \) is very small. We also use histogram reweighting [24] to extrapolate data obtained for one set of values of the coupling constants to different (nearby) values.

III. RESULTS IN \( d = 3 \) DIMENSIONS

In this section we present results for the case \( d = 3 \). We begin in Sec. III A with simulation results obtained for an external potential with strength \( h = 0.075 \) and wavelength \( \lambda = 10 \). Following this, in Sec. III B, we present mean-field theory results for how the phase diagram varies as the parameters \( h \) and \( \lambda \) are varied.

A. Laser-induced condensation: Phase diagram

To understand LIC in the Ising model it is best to consider the free energy \( F(m) \) as function of the magnetization \( m \). The latter is related to the magnetization probability distribution, \( F(m) = -k_BT \ln P(m) \), to which we have direct access in our simulations. In Fig. 1(a), we show \( F(m) \) for a high value of the coupling constant \( J \) and \( H = 0 \). The salient features are two global minima, at low and high values of \( m \), reflecting a coexistence between two phases (I and II). We also observe a local minimum at \( m = 0 \), corresponding to a phase III, but it is metastable. In Fig. 1(b), we plot \( F(m) \) for a lower value of

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FIG. 1. (Color online) LIC in the $d = 3$ Ising model; plotted in each of the graphs is the free energy $F(m)$ in units of $k_B T$ (vertical axes) versus the magnetization $m$ (horizontal axes). The free energy curves present actual simulation data obtained for system size $L = 10$ and $D = \lambda$. (a) Free energy for $J > J_t$ and $H = 0$, i.e., above the triple point. A coexistence between two phases, I and II, is observed. (b) Free energy for $J = J_t$ and $H = 0$, i.e., exactly at the triple point; three-phase coexistence is observed. (c) Free energy measured between the triple and critical points, $J_{cr} < J < J_t$, but still using $H = 0$. We now observe two common tangent lines: $l_1$ and $l_2$. By choosing $H = \Delta_1$, where $\Delta_1$ is determined from the slope of $l_1$, coexistence between phases I and III can be induced (d). Similarly, from the slope of $l_2$, we obtain $H = \Delta_2$, at which phases II and III coexist (e).

$J$ and $H = 0$. We now observe three minima at equal height corresponding to a triple point, where all three phases coexist. Next, in Fig. 1(c), we show $F(m)$ for an even lower value of $J$, but still using $H = 0$. There is now only one global minimum at $m = 0$. However, by applying an appropriate homogeneous field $H = \Delta_1$, a coexistence between phases I and III is obtained [Fig. 1(d)]. The value of $\Delta_1$ follows from the slope of the “common tangent” line $l_1$. Similarly, by applying a homogeneous field $H = \Delta_2$ (determined from the slope of line $l_2$), coexistence between phases II and III is obtained [Fig. 1(e)]. Finally, at some critical value $J = J_{cr,1}$ ($J_{cr,2}$), the I-III (II-III) coexistence line terminates, below which there is only one phase.

Figure 1 is the analog of LIC [17] in the Ising model, with phase I playing the role of vapor (v), phase II of the liquid (l), and phase III of the zebra (z) phase. Due to spin reversal symmetry, it holds that $H = 0$ at the triple point $J = J_t$. Below the triple point, symmetry implies that $\Delta_1 = -\Delta_2 \equiv \Delta$ and $J_{cr,1} = J_{cr,2} \equiv J_t$. The resulting phase diagram is a symmetric pitchfork [Fig. 2(a)]. The crucial difference with fluids (which typically lack spin reversal symmetry) is that the phase diagram is asymmetric in that case: $J_{cr,1} \neq J_{cr,2}$ and the fields (chemical potentials) $\Delta_i$ are not trivially related to each other [18].

We emphasize that the free energy curves in Fig. 1 are obtained in simulations using $D = \lambda$. If one instead uses $D = \lambda n_2$ with integer $n_2 > 1$, one finds that $F(m)$ develops additional minima, as discussed in detail in Ref. [18]. These additional minima reflect metastable coexistence states and should not be confused with new phases. Hence, also when $D > \lambda$, the generic mechanism of LIC as shown in Fig. 1 still applies.

B. Stability of the zebra phase: Mean-field calculations

In order to develop a qualitative understanding of how the LIC phase diagram of Fig. 2(a) depends on the external field
wavelength $\lambda$, and amplitude $h$, we use the following simple mean-field (Bragg-Williams) approximation [25,26] for the free energy $F$ of the system with Hamiltonian $E$, given in Eq. (1):

$$F = \sum_k \left[ k_B T \frac{1 + m_i}{2} \ln \left( \frac{1 + m_i}{2} \right) + k_B T \frac{1 - m_i}{2} \ln \left( \frac{1 - m_i}{2} \right) + Hm_i - m_iV_{\text{pery}}(z_i) \right] - J \sum\limits_{\langle i,j \rangle} m_i m_j ,$$

(3)

where $m_i \equiv \langle s_i \rangle$ is the average magnetization at lattice site $i$. For a given external potential $V_{\text{pery}}(z)$, the average magnetization profile corresponds to the set $\{m_1, m_2, \ldots\}$ which minimize the free energy (3), i.e., are the solution to the set of equations $\partial F/\partial m_i = 0$. This yields the following set of simultaneous equations:

$$\frac{k_B T}{2} \ln \left( \frac{1 + m_i}{2} \right) + H - V_{\text{pery}}(z_i) - J \sum\limits_{j} m_i m_j = 0 ,$$

(4)

where $\sum_j$ denotes the sum over the six (in $d = 3$) nearest neighbor lattice sites of site $i$. Because the external potential $V_{\text{pery}}(z)$ in Eq. (2) varies only in the $z$ direction, we have magnetization profiles that vary in only this one direction and so solving Eqs. (4) is straightforward. We do so using a simple (Picard) iterative numerical scheme. In Fig. 3 we show some example magnetization profiles calculated for various different values of $J$ as one crosses the transition line from phase I to the zebra phase III. We see a discontinuous change in the average magnetization in the system as one crosses the phase transition.

In Fig. 4(a) we show phase diagrams for various values of the field wavelength $\lambda$ and fixed field amplitude $h = 0.075$ (the upper and lower horizontal lines correspond to $\pm h$, respectively). Note that for clarity we display only the I-III and II-III coexistence lines and do not display the I-II liquid-vapor coexistence line. For $\lambda = 10$, the zebra critical points are marked $A$ and $B$, while point $C$ indicates the triple point. In the limit $\lambda \rightarrow \infty$, the critical points $A$ and $B$ shift toward $(J_{\text{cr,bulk}}, \pm h)$, respectively, where $J_{\text{cr,bulk}} = 1/6$ in the mean-field theory. As $\lambda \rightarrow \infty$, essentially two infinite systems are obtained: one inside a positive (homogeneous) external field $h$, and one inside a negative field $-h$. The value of $H$ at the respective critical point simply has to “cancel” this field. In the opposite limit $\lambda \rightarrow \lambda_{\text{min}} = 2$, we observe the loss of the zebra phase. In order for the zebra phase to survive, $\lambda/2$ must exceed the bulk correlation length, which is the quantity that determines the distance over which the average density changes from one value to another. Indeed, for $\lambda = 4$ and smaller, the critical points $A$ and $B$ can no longer be identified, and only point $C$ survives (which then no longer is a triple point, but a critical point, marking the end of the I-II coexistence region). When $\lambda = 4$ and $h = 0.075$ the mean-field critical point is at $J \approx 0.177$ and when $\lambda = 2$ it is at $J \approx 0.169$. Recall that the mean-field bulk critical point (i.e., for $h = 0$) is at $J_{\text{cr,bulk}} = 1/6 \approx 0.167$.

In Fig. 4(b) we show phase diagrams for fixed $\lambda = 10$ (chosen above the threshold such that the zebra phase survives) and various values of the field amplitude $h$. In the limit $h \rightarrow 0$, we observe that the points $A$, $B$, and $C$ all approach $(J_{\text{cr,bulk}} = 1/6, H = 0)$, the critical point of the bulk system. When $h$ is very small, it is difficult to locate the transition points numerically. However, a threshold value of $h$ below which the zebra phase vanishes appears to be absent in this case (in contrast to the case as $\lambda$ is increased). The effect of
increasing $h$ is that the I-III and II-III transition lines open up, with the transition points $A$, $B$, and $C$ shifting toward larger values of $J$. Note that the value of $H$ at the critical point is always less in magnitude than the value of $h$. When $h = 0.02$, then the critical value $H_{cr} \approx 0.005$, when $h = 0.2$, then $H_{cr} \approx 0.163$, and when $h = 2$, then $H_{cr} \approx 1.957$. We see from these values that as $h$ becomes large, then $H_{cr} \rightarrow h$.

C. Finite-size-scaling analysis

We now continue with our simulation analysis using $\lambda = 10$ and $h = 0.075$. Finite-size scaling is used to locate the triple and critical points. We measure $P(m)$ for various values of $L$, keeping $D = \lambda$ fixed. We thus assume that correlations in the $z$ direction are “cut off” by the periodic field, and so we do not need to scale in this direction (we return to this point shortly). The distribution $P(m)$ is always measured at $H = 0$ and symmetrized by hand afterward such that $P(m) = P(-m)$, thereby imposing the spin reversal symmetry of the Ising model; subsequent histogram reweighting (in $J$ and $H$) is performed using the symmetrized distribution.

To determine $J_c$, we follow the finite-size-scaling approach of Ref. [21]. In Fig. 5(a), we plot the Binder cumulant

$$U_4 \equiv \langle m^4 \rangle / \langle m^2 \rangle^2, \quad \langle m^k \rangle = \int_{-1}^{+1} m^k P(m) dm,$$

as a function of $J$ for various system sizes $L$. In agreement with Ref. [21], the curves for different $L$ essentially intersect in one point (the scatter in the intersections vanishes proportionally to $1/V^2$, with $V$ the system volume, which is not visible on the scale of the graph) and from the intersection we obtain

$$J_c \approx 0.2811.\text{ Note that this exceeds } J_{c,\text{bulk}} \approx 0.2217 \text{ of the critical point in the bulk (} h = 0 \text{) Ising model [27], consistent with the general observation that confinement lowers transition temperatures. At the triple point, } P(m) \text{ is a superposition of three Gaussian peaks, centered around } m = -m_0, m = 0, \text{ and } m = +m_0, \text{ respectively, with equal area under each peak. For such a distribution, one can show that } U_4,_{\text{triple}} = 2/3, \text{ and inspection of Fig. 5(a) indeed reveals that } U_4 = U_4,_{\text{triple}} \text{ at the intersection point. In Fig. 5(b), we plot the free energy } F(m) \text{ at the triple point for various system sizes. The curves clearly show the three minima of the coexisting phases. Note that the minima are shifted to zero and that the vertical scale is divided by } L. \text{ In this representation, the barrier } \Delta F/L \text{ (vertical arrow) is approximately constant. Hence, at the triple point, we observe a free energy barrier that increases linearly with the system size, } \Delta F \propto L. \text{ This implies that the general shape of } F(m) \text{, i.e., featuring three minima, persists in the thermodynamic limit } L \rightarrow \infty, \text{ and thus reflects a genuine triple point (see also Ref. [28] where these ideas were first applied to first-order phase transitions). For values of } J \text{ between the triple and critical points, coexistence with the zebra phase (phase III) is observed at appropriate values } H = \pm \Delta \text{ of the external magnetic field. To locate } J_c, \text{ we perform the same cumulant analysis as in our previous work [18]. For a given value of } J, \langle m \rangle \text{ and } U_4 \text{ are measured as functions of } H \text{ (due to symmetry, only } H \geq 0 \text{ needs to be considered). One then uses these}
data to construct a graph of $U_4$ versus $\langle m \rangle$ (which thus is parametrized by $H$). The resulting curve reveals a maximum, corresponding to $H = \Delta$, enveloped by two minima [29]. The average value of the cumulant at the minima equals $Q_4$. In Fig. 6(a), we plot $Q_4$ versus $J$ for different $L$; from the intersection point we conclude that $J_{cr} \approx 0.2531$ (the corresponding critical field $\Delta_{cr} \approx 0.017$). The difference $\Delta$ in the magnetizations $\langle m \rangle$ at the minima yields the order parameter. The latter is analyzed in the finite-size-scaling (FSS) approach. Following density functional calculations [18], we discuss how this approach may be generalized to LIC, but it was clear that the main computer power is not sufficient to reach the system sizes required for this method to work. Hence, we propose a different method.

The key observation is that the periodic field $V_{pe}(z)$ suppresses interface fluctuations (capillary waves) in the $z$ direction: even though $\gamma$ is very low, the I-III and II-III interfaces are sharp. This is in contrast to conventional liquid-vapor interfaces which, at low interface tension, are extremely broad [32,33]. The fact that the interfaces remain sharp is the property we exploit to extract $\gamma$. To this end, we consider a simulation box with edge $D = 4a$. In Fig. 7, we show instantaneous magnetization profiles $m(z)$ obtained for two equilibrated samples at fixed overall magnetization $m$. The value of $m$ must be chosen such that half the system is occupied by phase I and the remainder by phase III, which can be obtained from the local maximum in the free energy (point A in Fig. 1(d)).

Since the interfaces are essentially flat, one can easily identify where the phases are located. In Fig. 7(a), we see one large domain of phase I (characterized by a low overall magnetization) coexisting with one large domain of phase III (characterized by large modulations in the magnetization). Hence, two I-III interfaces are present (recall that periodic boundaries are used). In Fig. 7(b), we again observe I-III phase coexistence, but this time the phases are arranged such that four I-III interfaces are present. In equilibrium, arrangement (a) is preferred since it has the smallest interface area: $2L^2$ versus $4L^2$, with $L$ the lateral box size. However, for finite $L$, arrangement (b) is also frequently observed, since $\gamma$ is small. In fact, from the ratio of counts $R$, the interface tension can be determined

$$\ln R = 2\gamma L^2 + \Delta S, \quad R = n_a/n_b,$$  \hspace{1cm} (6)
where \( n_t \) denotes the number of times arrangement \( t = (a,b) \) was seen during a very long simulation run (note that this simulation must be performed at fixed \( m \) chosen to yield equal volumes of both phases). The “offset” \( \Delta S \) reflects the combinatorial and translational entropy difference between the arrangements. The former is zero since there are as many ways to distribute the phases as in (a) as there are for (b). However, there is additional translational entropy for arrangement (a) since the domains are twice as large (we thus expect \( \Delta S = \ln 2 \approx 0.69 \)).

To simulate at fixed \( m \) we use Kawasaki dynamics: two spins of opposite sign are randomly selected and flipped, and the resulting spin configuration is accepted with the Metropolis criterion [22]. To facilitate frequent transitions between arrangements (a) and (b) of Fig. 7, we also use a collective Monte Carlo move. To this end, we introduce the block domain \( B_i \), which contains all spins whose \( z \) coordinate is in the range \( \lambda b_i/2 < z < \lambda (b_i/2 + 1) \), with \( b_i \) an integer (periodic boundary conditions must be applied). In the collective move, two block domains \( B_1 \) and \( B_2 \) are randomly selected with the constraint that \( |b_1 - b_2| > 0 \) and even. The domains are then swapped, and the resulting spin configuration is accepted with the Metropolis criterion (in our simulations, Kawasaki and collective moves are attempted in a ratio 1:0.03, respectively).

To test our approach we consider \( 0.264 < J < 0.278 \), which is between the triple and critical points. We use \( m = -0.426 \) for this is the value where phases I and III were seen to occupy equal volumes. In Fig. 8(a), we plot \( \ln R \) versus \( L \) for \( J = 0.275 \); the data are indeed well described by Eq. (6), and by fitting \( \gamma \) can be estimated. In Fig. 8(b), we plot the corresponding estimates of \( \gamma \) versus \( J \). Despite the admittedly rather large statistical uncertainty, our data confirm that the tension is extremely low, and that it decreases as \( J \) is lowered; both these observations are in qualitative agreement with theoretical predictions [18].

E. Correlations in the field direction

In the finite-size-scaling analysis of Sec. III C we varied \( L \) keeping \( D = \lambda \) fixed. We thus assumed the correlations in the field direction to be short ranged: critical correlations develop only in the lateral \( L \) directions, but not in the direction \( D \) along the field, such that the resulting critical behavior is effectively two dimensional (and belonging to the \( d = 2 \) Ising universality class). To verify this assumption we now consider the critical regime using a larger value \( D = 5\lambda \). We perform simulations at \( J = J_c \) and fixed \( m = -0.426 \) (the latter corresponds to the average magnetization at the critical point). To simulate at fixed \( m \) we use Kawasaki dynamics and collective moves (as in the previous section). However, for the collective moves, the block domain \( B_i \) was taken to be a single lattice layer, containing those spins whose \( z \) coordinate equals \( z_i \) (at criticality, this choice yields a higher accept rate). A pair of layers is chosen randomly and swapped, with the constraint that the sign of \( V_{\text{peg}}(z) \) in the layers is the same, and accepted with the Metropolis criterion.

In Fig. 9(a), we plot the susceptibility profile \( \chi(z) = L^2 [\langle m(z) \rangle^2 - \langle m(z) \rangle^2] \) for various values of \( L \). The susceptibility diverges with \( L \) only at selected values \( z = z_{cr} \), which “repeat” with the same period as the field. The critical behavior is thus spatially confined to those \( L \times L \) slabs for which the corresponding \( z \) coordinate equals one of the \( z_{cr} \). To determine the universality class we compare the average peak heights \( \chi_L \) of the susceptibility profiles to the finite-size-scaling prediction \( \chi_L \propto L^{\gamma/\nu} \), with \( \gamma \) the susceptibility critical exponent. This result is shown in Fig. 9(b), and the \( d = 2 \) Ising value \( \gamma/\nu = 7/4 \) is strikingly confirmed. Hence, the observed universality class does not depend on the value of \( D \) used in the scaling analysis, which \textit{a posteriori} provides the justification for the approach of Sec. III C.

Next, we ask whether correlations exist between critical slabs. To this end, we introduce the pair correlation function

\[
C(z_1, \Delta z) \propto \langle m(z_1) m(z_1 + \Delta z) \rangle - \langle m(z_1) \rangle \langle m(z_1 + \Delta z) \rangle.
\]

(7)

measured between the slabs at \( z = z_1 \) and \( z = z_1 + \Delta z \), respectively. We choose \( z_1 \) to coincide with one of the critical slabs, and we normalize such that \( C(z_1, 0) \equiv 1 \). In Fig. 10, we show the correlation function for a system with \( D = 5\lambda \) (a), and for \( D = 20\lambda \) (b). We find that the slabs at \( \Delta z = n\lambda \) with integer \( n > 0 \) are \textit{anticorrelated} from the (critical) slab at \( n = 0 \). Moreover, the amplitude \( A \) of the anticorrelations is independent of \( \Delta z \), but it decreases with \( D \). In fact, an almost perfect “lever rule” is observed,

\[
A = \lambda/(D - \lambda).
\]  

(8)

That is: if there happens to be an excess magnetization in one of the critical slabs, the remaining critical slabs respond by assuming a lower magnetization, in a manner such that the
excess magnetization is shared equally on average. In the limit $D \to \infty$, the amplitude $A$ of the correlations becomes zero, consistent with our assumption that long-ranged correlations in the field direction are absent. We also point out that the correlations in Fig. 10 are very different from critical correlations; the latter decay as power laws, $\lim_{\Delta \to \infty} C(z, \Delta z) \propto 1/\Delta^\gamma$ with critical exponent $\gamma$, for which we see no evidence in our data. In fact, the anticorrelations of Fig. 10 are also observed in the noncritical regime of the phase diagram (explicit checks were performed for $J = 0.27$ using $m = -0.82$ and $m = -0.04$, corresponding to a pure phase I and phase III, respectively).

**IV. RESULTS IN $d = 2$ DIMENSIONS**

We now consider LIC in $d = 2$ dimensions. The simulations are performed on $L \times D$ periodic lattices, with the field $V_{\text{per}}(z)$ again propagating along edge $D$ of the lattice. In what follows, the field wavelength $\lambda = 8$ with strength $h = 0.1495$.

![Figure 10](image1.png)

**FIG. 9.** (Color online) Investigation of the critical behavior using a simulation box with $D = 5\lambda$; the simulations are performed at fixed magnetization $m = -0.426$ and $J = J_{\text{cr}}$. (a) The susceptibility profiles $\chi(z)$ for $L = 15, 20, 25, 30$ (from bottom to top). The key point to note from this figure is that $\chi(z)$ diverges with $L$ only at special values $z = z_{\text{cr}}$. (b) Finite-size-scaling analysis of the average peak height $\chi_L$ of the susceptibility profiles. We plot $\chi_L$ versus $L$ on double-logarithmic scales. The dashed line corresponds to a power law with exponent $\gamma/\nu = 7/4$ of the $d = 2$ Ising model.

![Figure 11](image2.png)

**FIG. 11.** (Color online) The analog of Fig. 6(a) but for the case $d = 2$. Note the logarithmic vertical scale. The data are obtained using fixed $D = \lambda$. The key observation is that the curves for different $L$ do not intersect in a single point, implying the absence of a critical point. This, in turn, is consistent with $d = 1$ Ising universality.

**A. Phase diagram and scaling analysis**

We first determine whether the LIC critical points occur in $d = 2$ dimensions also. Since the critical behavior was shown to resemble that of a reduced dimension $d - 1$, we now expect the universality class of the $d = 1$ Ising model. As is well

![Figure 12](image3.png)

**FIG. 12.** (Color online) The analog of Fig. 5 but for the case $d = 2$. The main difference is that we now observe a critical point, as opposed to a triple point. (a) The Binder cumulant as a function of $J$ for $H = 0$ and different system sizes $L$. The curves for different $L$ intersect as in Fig. 5, from which one might conclude the presence of a triple point. (b) However, the scaling of the free energy $F(m)$ is not consistent with a triple point. Plotted is $F(m)$ at the cumulant intersection, with $F(m = 0)$ shifted to zero. We see that the depth of the central minimum $\Delta F_2 \to 0$ as $L$ increases, while the depth $\Delta F_1$ of the outer minima appears to be independent of $L$. This type of scaling is consistent with a critical point [28].
known, the latter model does not feature a critical point. In Fig. 11, we repeat the cumulant analysis of Fig. 6(a). In line with the $d = 1$ Ising model, we do not observe an intersection point, confirming the absence of a critical point. While for small $L$ the curves somewhat intersect, the intersections for larger $L$ systematically shift toward larger values of $J$. Hence, in $d = 2$ dimensions, there is no LIC critical behavior.

Next, we investigate the fate of the triple point, using the same analysis as in Fig. 5. We collect data for fixed $H = 0$ and $D = 3$, while $J$ and $L$ are varied. In Fig. 12(a), we plot the Binder cumulant $U_4$ versus $J$ for different system sizes $L$. Consistent with a triple point, we observe a sharp intersection, with the value of the cumulant at the intersection very close to $U_4 = 2/3$ of a triple-peaked distribution. However, the corresponding free energy is not consistent with a triple point; see Fig. 12(b), where $F(m)$ is plotted for three different system sizes; note that we plot $F(m)$ with the central ($m = \frac{L}{2}$) minimum shifted to zero. While $F(m)$ clearly reveals three minima, the central minimum does not survive in the thermodynamic limit. This can be seen from the corresponding “depth,” marked $\Delta F_2$ in the figure, which decreases with $L$. In the limit $L \to \infty$, we have $\Delta F_2 \to 0$, and only the outer minima survive, whose corresponding depths then equal $\Delta F_1$.

The observation in Fig. 12(b) that $\Delta F_1$ is independent of system size is characteristic of a continuous transition [28]. Hence, for LIC in $d = 2$ dimensions, the triple point is destroyed, and replaced by a critical point, in this case at $J_{cr} \approx 0.701$ [as expected, this exceeds $J_{cr, bulk} = \ln(1 + \sqrt{2})/2$ of the bulk $d = 2$ Ising model]. The LIC phase diagram in $d = 2$ dimensions is thus radically different from $d = 3$.

Instead of a pitchfork topology, we now have a single line of first-order phase transitions terminating in a critical point [Fig. 2(b)].

We still find that, for $J > J_{cr}$, the transition is first order. In Fig. 13, we plot the free energy $F(m)$ for $J = 0.8$, $H = 0$ using system sizes $L = 40, 80$ and $D = 2a$. The free energy curves are again shifted such that $F(m = 0) = 0$. While for the smaller system the minimum at $m = 0$ is still visible, it has vanished in the larger system. In addition, the barrier $\Delta F_1$ now increases profoundly with $L$, consistent with a first-order transition [28]. Note also the pronounced flat region in $F(m)$ around $m \sim 0$ for the larger system: this indicates two-phase coexistence with negligible interactions between the interfaces [34]. When a simulation is performed in this regime starting from a random initial spin configuration, the system phase separates to form structures that are strongly affected by the external potential; see Fig. 14(a). However, when the system is fully equilibrated at a “later time,” snapshots show the system containing two coexisting domains of phases I and II; see Fig. 14(b). In a box with periodic boundaries, the domains arrange themselves as two slabs since this minimizes the total interface length.

### B. Rounding effects

Even though the zebra phase (phase III), does not survive in the thermodynamic limit in $d = 2$, we still see remnants of this phase in systems of finite size. If one simulates at $J < J_{cr}$ using an appropriate external field $H$, one finds that in finite systems...
$F(m)$ can still be cast into the forms of Figs. 1(d) and 1(e). Inspection of simulation snapshots then reveals a condensation of droplets onto stripes oriented perpendicular to the field direction [Fig. 14(c)]. However, the droplet size remains finite in this case, owing to the fact that the $d = 1$ Ising model at finite temperature does not support a finite magnetization. Similar finite-size effects occur in colloid-polymer mixtures confined to cylindrical pores, which also belong to the universality class of the $d = 1$ Ising model [35,36].

V. SUMMARY

In this work, we considered the phase behavior of the Ising model exposed to a static periodic field. In $d = 3$ dimensions, we obtain a phase diagram analogous to laser-induced condensation observed in fluids undergoing bulk liquid-vapor-type transitions. That is, a new phase arises (the zebra phase) and the critical point of the bulk model is replaced by two new critical points and a triple point. The main difference compared with fluids is that, due to spin reversal symmetry, the corresponding phase diagram for the Ising model features a symmetry line. The analysis of the present work complements earlier works on laser-induced condensation [17,18] in that (i) a detailed study of finite-size effects at the triple point was presented, (ii) a simple mean-field theory was used to elucidate in a qualitative manner how the $d = 3$ phase transitions depend on the parameters in the external potential, (iii) a method was presented to measure the extremely low tension of interfaces with the zebra phase, and (iv) the nature of correlations along the field direction was further clarified.

We additionally considered the fate of laser-induced condensation in $d = 2$ dimensions. In this case, we find that the zebra phase does not survive in the thermodynamic limit, and the corresponding phase diagram features just a single critical point. This critical point occurs at a temperature below the critical temperature of the pure $d = 2$ Ising model. The universality class of the critical point still needs to be determined. The analysis of the free energy in Fig. 12(b) indicates only a critical transition, since the barrier $\Delta F_1$ is $L$ independent, but no information regarding critical exponents could be obtained. The practical problem here is that, in computer simulations, we are still restricted to system sizes that span only a few field wavelengths. We should also mention that the mean-field theory used in Sec. III B predicts very similar results in $d = 2$ as it does in $d = 3$ and is therefore not reliable when applied in $d = 2$.

Even though our results were obtained for the relatively simple Ising model, the generic features of the observed phase behavior should also apply to real fluids. In particular the experimental realization in $d = 2$ dimensions should be feasible using a stripe-patterned substrate. At moderate temperatures, the condensation of finite-sized droplets should be observable, while at low temperatures a macroscopic demixing should occur (cf. Fig. 14).

ACKNOWLEDGMENTS

R.L.C.V. was supported by the Deutsche Forschungsgemeinschaft (Emmy Noether program, Grant No. VI 483/1-1) and A.J.A. was supported by RCUK.

[1] K. Binder, J. Horbach, R. L. C. Vink, and A. De Virgiliis, Soft Matter 4, 1555 (2008).
[2] M. E. Fisher and H. Nakanishi, J. Chem. Phys. 75, 5857 (1981).
[3] P. G. De Gennes, J. Phys. Chem. 88, 6469 (1984).
[4] A. Valencia, M. Brinkmann, and R. Lipowsky, Langmuir 17, 3390 (2001).
[5] A. O. Parry and R. Evans, Phys. Rev. Lett. 64, 439 (1990).
[6] D. A. Virgiliis, R. L. C. Vink, J. Horbach, and K. Binder, Europhys. Lett. 77, 60002 (2007).
[7] J. Drelich, J. D. Miller, A. Kumar, and G. M. Whitesides, Colloids Surf. A 93, 1 (1994).
[8] S. Minko, in Polymer Surfaces and Interfaces, edited by M. Stamm (Springer, Berlin, 2008), Chap. 11, pp. 215–234.
[9] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Koijima, A. Kitamura, M. Shimohigoshi, and T. Watanabe, Nature (London) 388, 431 (1997).
[10] C. Lutz, M. Kollmann, P. Leiderer, and C. Behringer, J. Phys.: Condens. Matter 16, S4075 (2004).
[11] H. Gau, S. Herminghaus, P. Lenz, and R. Lipowsky, Science 283, 46 (1999).
[12] M. Tröndle, O. Zvyagolskaya, A. Gambassi, D. Vogt, L. Harnau, C. Behringer, and S. Dietrich, Mol. Phys. 109, 1169 (2011).
[13] H. H. Grüninger and J. Baumgartl, Phys. Rev. E 75, 051406 (2007).
[14] Y. Tsori, F. Tournilhac, and L. Leibler, Nature (London) 430, 544 (2004).
[15] Y. Tsori, Macromolecules 40, 1698 (2007).
[16] T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, H. M. Jaeger, P. Mansky, and T. P. Russell, Science 273, 931 (1996).
[17] I. O. Götzke, J. M. Brader, M. Schmidt, and H. Löwen, Mol. Phys. 101, 1651 (2003).
[18] R. L. C. Vink, T. Neuhaus, and H. Löwen, J. Chem. Phys. 134, 204907 (2011).
[19] F. Varnik, J. Baschnagel, and K. Binder, J. Chem. Phys. 113, 4444 (2000).
[20] K. Binder, B. Block, S. K. Das, P. Virnau, and D. Wüster, J. Stat. Phys. 144, 690 (2011).
[21] K. Vollmayr, J. D. Rege, M. Scheucher, and K. Binder, Z. Phys. B 91, 113 (1993).
[22] M. E. J. Newman and G. T. Barkema, Monte Carlo Methods in Statistical Physics (Clarendon Press, Oxford, 1999).
[23] P. Virnau and M. Müller, J. Chem. Phys. 120, 10925 (2004).
[24] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. 61, 2635 (1988).
[25] M. Plischke and B. Berge, Equilibrium Statistical Physics, 3rd ed. (World Scientific, Singapore, 2006).
[26] P. M. Chaikin and T. C. Lubensky, Principles of Condensed Matter Physics (Cambridge University Press, Cambridge, 2000).
[27] G. Orkoulas, A. Z. Panagiotopoulos, and M. E. Fisher, Phys. Rev. E 61, 5930 (2000).
[28] J. Lee and J. M. Kosterlitz, Phys. Rev. B 43, 3265 (1991).
[29] Y. C. Kim and M. E. Fisher, Comput. Phys. Commun. 169, 295 (2005).
[30] K. Binder and D. W. Heermann, Monte Carlo Simulation in Statistical Physics: An Introduction (Springer, Berlin, 2002).
[31] K. Binder, Phys. Rev. A 25, 1699 (1982).
[32] R. L. C. Vink, J. Horbach, and K. Binder, J. Chem. Phys. 122, 134905 (2005).
[33] D. G. Aarts, M. Schmidt, and H. N. Lekkerkerker, Science 304, 847 (2004).
[34] B. Grossmann and M. L. Laursen, Nucl. Phys. B 408, 637 (1993).
[35] D. Wilms, A. Winkler, P. Virnau, and K. Binder, Phys. Rev. Lett. 105, 045701 (2010).
[36] A. Winkler, D. Wilms, P. Virnau, and K. Binder, J. Chem. Phys. 133, 164702 (2010).