Boundary conditions for the field theory of dynamic critical behavior in semi-infinite systems with conserved order parameter

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The problem of constructing a field theory that describes the dynamic critical behavior of semi-infinite systems whose dynamic bulk critical behavior is represented by model B and whose order parameter is conserved both in the bulk and at the surface is reconsidered. Particular attention is paid to the derivation of the boundary conditions satisfied by the order-parameter field $\phi(\mathbf{x},t)$ and the associated response field $\tilde{\phi}(\mathbf{x},t)$. It is shown that the extremely complicated boundary conditions for ϕ obtained recently by Binder and Frisch [Z. Phys. B **84**, 403(1991)] simplify considerably if all irrelevant surface contributions to the action are discarded. In particular, the boundary conditions for both ϕ and $\tilde{\phi}$ do not involve time derivatives. Although power counting alone admits surface terms other than those anticipated in the paper by Dietrich and Diehl [Z. Phys. B **51**, 343 (1983)], the requirements of detailed balance imply that these extra terms are either absent or redundant. As an application and test, the relaxation of the order-parameter profile from a spatially homogeneous initial nonequilibrium state into thermal equilibrium is investigated, using a zero-loop approximation. The results are in conformity with those of Binder and Frisch.

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I. INTRODUCTION

In a recent paper [1] Binder and Frisch (BF) investigated the dynamics of surface enrichment in binary mixtures that are in contact with an impenetrable wall favoring one of two components. To this end they considered a semi-infinite lattice-gas model with Kawasaki dynamics [2] and investigated it using a layerwise molecular-field approximation. Upon making a continuum approximation, they derived an equation of motion for the (coarse-grained) order-parameter field $\phi(\mathbf{x},t)$ (denoted ψ by BF). Since the dynamics of the model conserves the order parameter, its dynamic bulk critical behavior should be described by the familiar model B of Halperin, Hohenberg, and Ma [3]. Not surprisingly, therefore, the equation of motion found by BF, for points away from the surface, agreed precisely with the one that model B yields if a time-dependent Ginzburg-Landau (TDGL) approximation is used.

This equation of motion is a partial differential equation involving spatial derivatives up to fourth order. Hence, for a system with boundaries, the question arises as to which boundary conditions can, and should, be required to make the solution well defined. BF examined this question in some detail for the semi-infinite geometry considered, namely, the d-dimensional half-space $\mathbb{R}^d_+ = \{\mathbf{x} = (\mathbf{x}_\parallel, z) \mid \mathbf{x} \in \mathbb{R}^{d-1}, z \geq 0\}$ bounded by the $z = 0$ plane, with periodic boundary conditions applied along the $\mathbf{x}_\parallel$ directions. As boundary conditions for $\phi(\mathbf{x},t)$ at the wall ∂V (the $z = 0$ plane) they obtained two formidable expressions, which are too long to be repeated here. Both of these boundary conditions not only involved spatial derivatives but also time derivatives, with the second one even containing time derivatives of spatial derivatives.

The physical problem BF addressed was how the dynamical process of surface enrichment takes place near bulk criticality if one starts from a spatially homogeneous nonequilibrium order-parameter profile $\phi(\mathbf{x},t = 0) = \phi^{(0)}$. As pointed out by BF, there exist no previous studies of this problem for the case of a *conserved* order parameter; earlier studies of critical dynamics in semi-infinite systems have focused almost exclusively on the case of a *nonconserved* order parameter. Specifically, in the field-theoretic analysis of dynamic critical behavior in semi-infinite systems presented by Dietrich and Diehl [4], an explicit two-loop calculation was performed only for a semi-infinite model A. On the other hand, the structure of the ultraviolet singularities, the resulting renormalization-group (RG) equations, and their consequences for the dynamic surface critical behavior near the ordinary and special (surface) transition [5, 6] were also discussed for a semi-infinite version of model B. In addition, explicit results for the free response propagator of semi-infinite model B in various representations were presented in Appendix A of Ref. [5]. In that work, the question of boundary conditions of the *dynamic* theory was bypassed inasmuch as the eigenfunctions that diagonalize the free propagator of the *static* theory were assumed to carry over to the dynamic theory. Since the static action involves only squares of spatial derivatives, only a *single* (and well-known [7–10, 5]) boundary condition at ∂V is needed in the static case. In Ref. [4], this static — and hence *time-independent* — boundary condition was implicitly used, and no second boundary condition was given for $\phi(\mathbf{x},t)$ in the case of model B. In view of BF's findings mentioned above the question arises as to whether the RG analysis of Ref. [4] really applies to model B or whether it needs to be modified. (In the case of model A, the dynamic action involves only squares of spatial derivatives, so that again no boundary condition for ϕ other than the static one is required. Furthermore, the boundary condition used for $\tilde{\phi}$ in Ref. [4] is correct, too. Thus the entire model-A analysis of Ref. [4] is based on a proper choice of boundary conditions. The above-mentioned problem arises only in the case of model B.)

In the present paper we will present a detailed investigation into the question of which boundary conditions should be required for a proper semi-infinite model B. Rather than trying to derive these boundary conditions by means of a coarse-graining procedure from a microscopic theory, we prefer to construct the continuum field theory directly, utilizing general principles such as the locality of the action in space and time, relevance arguments, detailed balance, and the consequences of the conservation law for the order parameter. The advantage of this procedure is that it enables us to relate the boundary conditions to the general properties of a class of dynamic models rather than to the special properties of a particular microscopic model.

The remainder of this paper is organized as follows. In the following section we reformulate the problem in the language of the functional-integral representation of stochastic dynamic models [11–15] and discuss the general constraints that the dynamic action should satisfy. Choosing the most general $\mathcal{J}$ compatible with these constraints, we then derive the boundary conditions for ϕ and $\tilde{\phi}$ and discuss their significance. Our result for the surface terms of $\mathcal{J}$ — and hence the boundary conditions — can be obtained directly from the general form of $\mathcal{J}$ derived in Ref. [11]. This can be done in a controlled fashion by replacing the contact form [$\propto \delta(z)$ and its derivatives] of the surface terms in the static Hamiltonian through a sequence of smooth functions of z that approach the contact form. In Sec. III we apply the theory to the problem of surface enrichment, using the TDGL (zero-loop) approximation. This serves to check that the universal properties of the large-distance and long-time behavior found by BF are correctly reproduced within our much simpler theory with time-independent boundary conditions. Our conclusions are summarized in Sec. IV.

II. CONSTRUCTION OF THE MODEL

A. Constraints on the dynamic action

A convenient framework for our reasoning is the Lagrangian functional-integral formulation of stochastic dynamic models [11–13]. Since we are concerned with model B, we assume that no slow variables other than ϕ are present. Under these circumstances the model can be specified by a functional probability density of the form [16] $\exp(-\mathcal{J}\{\phi,\tilde{\phi}\})\,d\{\phi,\tilde{\phi}\}$, where $\tilde{\phi}$ is the response field associated with ϕ. Restrictions on $\mathcal{J}$ can be obtained by exploiting the following general properties $P1,\ldots,P7$, which the model we wish to define should have.

(P1) Locality of the action $\mathcal{J}$ in space and time. We presume the interactions as well as their perturbation caused by the surface to be of short range (i.e., to decay sufficiently fast as distances increase). Accordingly the functional $\mathcal{J}$ may be assumed to be local in space. Owing to the absence of other slow variables it may be taken to be local in time, too (which is tantamount to the assumption that the dynamics can be described by a Markovian process). Hence $\mathcal{J}$ may be chosen in the form

$$\mathcal{J}_{t_0}^{t_f}\{\tilde{\phi},\phi\} = \int_{t_0}^{t_f} dt \left(\int_V \mathcal{L}_b(\mathbf{x},t)\, d^d x + \int_{\partial V} \mathcal{L}_1(\mathbf{x}_\parallel,t)\, d^{d-1}x_\parallel \right) , \qquad (1)$$

where $\mathcal{L}_b$ and $\mathcal{L}_1$ are functions of ϕ and its space and time derivatives, taken at points $\mathbf{x} \in V$ and $(\mathbf{x}_\parallel, 0) \in \partial V$, respectively. At this stage, the initial time t_0 and the final time t_f may be assumed to be finite; the limits $t_0 \to -\infty$ and $t_f \to +\infty$ will eventually be taken at the end of the calculation.

With a view to our subsequent analysis, let us also make the following remarks. As is well known (see, e.g., Ref. [12]), the functional $\mathcal{J}$ in general should also contain a contribution depending on the way time is discretized. We shall omit this (measure) term $\propto \theta(0)$, choosing a prepoint discretization corresponding to the definition $\theta(0) \equiv 0$. At certain points we applied the standard rules of differential calculus to $\mathcal{J}$. This should be interpreted in the sense that the time discretization at the beginning of the calculation was changed into a midpoint discretization [corresponding to the choice $\theta(0) = 1/2$] and at its end was changed back to the original prepoint discretization.

(P2) Consistency with bulk model B. The bulk dynamics of the model should be the same as that of the standard bulk model B. Taken together with the locality property $P1$, this means that for points off the surface ($\mathbf{x} \notin \partial V$) the model should be equivalent to the Langevin equation

$$\partial_t \phi(\mathbf{x},t) = \lambda_0\, \Delta \mathcal{H}_\phi(\mathbf{x},t) + \zeta(\mathbf{x},t) , \qquad (2a)$$

in which

$$\mathcal{H}_\phi(\mathbf{x},t) = -\Delta\phi(\mathbf{x},t) + \mathcal{U}_b'(\phi(\mathbf{x},t)), \qquad (2b)$$

with

$$\mathcal{U}_b(\phi) = \tfrac{1}{2}\tau_0\, \phi^2 + \tfrac{1}{4!}u_0\, \phi^4 , \qquad (2c)$$

while $\zeta(\mathbf{x},t)$ means a Gaussian random force with mean $\langle\zeta\rangle = 0$ and variance

$$\langle \zeta(\mathbf{x},t)\,\zeta(\mathbf{x}',t')\rangle = -2\lambda_0\, \Delta\, \delta(\mathbf{x}-\mathbf{x}')\, \delta(t-t') \qquad (2d)$$

for points $\mathbf{x}$ and $\mathbf{x}'$ off the surface. In the language of our functional-integral approach this corresponds to a bulk density

$$\mathcal{L}_b = \tilde{\phi}\partial_t\phi - \lambda_0[(\nabla\tilde{\phi})^2 - (\Delta\tilde{\phi})\Delta\phi - (\nabla\tilde{\phi})\cdot\nabla\mathcal{U}_b'(\phi)] \,. \tag{3}$$

Note that we have distributed the spatial derivatives in the quadratic part of $\mathcal{L}_b$ in a symmetric fashion; had we distributed them in a less symmetric fashion, the result $\int_V d^dx\mathcal{L}_b$ would differ from the one implied by Eq. (3) through surface terms.

(P3) Absence of irrelevant and redundant operators. We require that the model be minimal in the sense that only operators are included in $\mathcal{J}$ that are relevant or marginal for d equal to, or slightly less than, the upper critical dimension $d^* = 4$. Since the bulk density $\mathcal{L}_b$ is already known, consider a contribution to $\mathcal{L}_1$ of the symbolic form

$$\lambda_0^{1-a}\,\mu^{d_1(a,b;m,n;\epsilon)}\,g_1(a,b;m,n)\,\partial_t^a\,\partial^b\,\tilde{\phi}^m\,\phi^n \,. \tag{4}$$

Here μ is an arbitrary momentum scale, ∂^b means a spatial partial derivative $\partial^b/(\partial x_{i_1}\cdots\partial x_{i_b})$, and $g_1(a,b;m,n)$ denotes a dimensionless surface coupling constant. Counting dimensions shows that for $d = 4-\epsilon$ the momentum dimension d_1 is given by

$$d_1(a,b;m,n;\epsilon) = 7 - 3m - n - 4a - b + \frac{m+n-2}{2}\,\epsilon \,. \tag{5}$$

We will omit all contributions with

$$d_1(a,b;m,n;0) < 0 \,. \tag{6}$$

This is justified, provided no dangerous irrelevant operator is among these dropped contributions. Whether this premise holds, remains to be seen. Note that condition (6) rules out, in particular, a contribution to $\mathcal{L}_1$ of the form $\tilde{\phi}\,\partial_t\phi$ since $d_1(1,0;1,1;0) = -1$. The irrelevance of such a surface term (in the RG sense) is the ultimate reason why the boundary conditions we are going to find will not involve time derivatives.

(P4) Conservation of the order parameter. We require that ϕ be a conserved density both at the surface and away from it. Thus

$$M_V \equiv \int_V \langle\phi(\mathbf{x},t)\rangle\, d^dx \tag{7}$$

should be a constant of motion in the following strong sense. In a mathematically satisfactory definition of semi-infinite systems of the kind we are interested in one would have to consider the thermodynamic limit of an appropriate finite system of hypercylindrical shape with cross-sectional area $A = L_\|^{d-1}$, height $L_\perp$, and volume $|V| = AL_\perp$ (i.e., with $V = [0,L_\|]^{d-1}\times[0,L_\perp]$). Even for this finite V the time derivative $\dot{M}_V$ of M_V should vanish. An immediate consequence of this requirement is that both the bulk order parameter

$$m_b \equiv \lim_{L_\|,\,L_\perp\to\infty}\frac{1}{|V|}\int_V\langle\phi(\mathbf{x},t)\rangle\,d^dx$$
$$= \langle\phi(\mathbf{x},t)\rangle \tag{8}$$

as well as the excess order parameter

$$m_s \equiv \lim_{L_\|,\,L_\perp\to\infty}\frac{1}{A}\int_V[\langle\phi(\mathbf{x},t)\rangle - m_b]\,d^dx$$
$$= \int_0^\infty[\langle\phi(\mathbf{x}_\|,z,t)\rangle - m_b]dz \tag{9}$$

are constants of motion, where the averages in the second lines of Eqs. (8) and (9) refer to the semi-infinite system. The above requirement

$$\dot{M}_V = 0 \tag{10}$$

is fulfilled if all monomials appearing in $\mathcal{J}$ other than the $\tilde{\phi}\,\partial_t\phi$ term of $\mathcal{L}_b$ are invariant under a shift $\tilde{\phi}(\mathbf{x},t)\to\tilde{\phi}(\mathbf{x},t)+\tilde{\Phi}(t)$ with an arbitrary $\mathbf{x}$ independent $\tilde{\Phi}(t)$. To see this, note that this shift invariance can be exploited in a standard manner to conclude that $\langle\delta\mathcal{J}\rangle$, the expectation value of the implied change

$$\delta\mathcal{J} = -\int dt\,\tilde{\Phi}(t)\,\frac{d}{dt}\int_V\phi(\mathbf{x},t) \tag{11}$$

of $\mathcal{J}$, must vanish. Owing to the arbitrariness of $\tilde{\Phi}(t)$, Eq. (10) holds, indeed.

(P5) Causality. Introducing bulk sources $\tilde{J}(\mathbf{x},t)$ and $J(\mathbf{x},t)$ as well as surface sources $\tilde{J}_1(\mathbf{x}_\|,t)$ and $J_1(\mathbf{x}_\|,t)$, we define the functionals

$$\mathcal{Z}\{\tilde{J},J;\tilde{J}_1,J_1\} = e^{\mathcal{W}\{\tilde{J},J;\tilde{J}_1,J_1\}}$$
$$= \left\langle e^{(\tilde{J},\tilde{\phi})+(J,\phi)+(\tilde{J}_1,\tilde{\phi}_s)+(J_1,\phi_s)}\right\rangle \,. \tag{12}$$

Here the notation $\tilde{\phi}_s$ is used for the field $\tilde{\phi}$ on the surface, by analogy with ϕ_s. Furthermore, the abbreviations

$$(\tilde{J},\tilde{\phi}) \equiv \int dt\int_V \tilde{J}(\mathbf{x},t)\,\tilde{\phi}(\mathbf{x},t) \tag{13}$$

and

$$(J_1,\phi_s) \equiv \int dt\int_{\partial V} J_1(\mathbf{x}_\|,t)\,\phi_s(\mathbf{x}_\|,t) \tag{14}$$

were introduced. In Eqs. (13) and (14), the volume element d^dx and the surface element $d^{d-1}x_\|$ have been suppressed for conciseness. The same will frequently be done below.

Causality means that if the sources J and J_1 vanish for $t \geq t_{\max}$, then the functionals $\mathcal{Z}$ and $\mathcal{W}$ must be independent of the sources $\tilde{J}(\mathbf{x},\tilde{t})$ and $\tilde{J}_1(\mathbf{x}_\|,\tilde{t})$ with $\tilde{t} \geq t_{\max}$. Specifically, the cumulants

$$\mathcal{W}^{(\tilde{N},N;\tilde{M},M)}(\tilde{\mathbf{x}}_1,\tilde{t}_1;\ldots;\mathbf{r}_M,t_{N+M}) \equiv \prod_{j=1}^{\tilde{N}}\frac{\delta}{\delta\tilde{J}(\tilde{\mathbf{x}}_j,\tilde{t}_j)}\prod_{k=1}^{N}\frac{\delta}{\delta J(\mathbf{x}_k,t_k)}\prod_{\ell=1}^{\tilde{M}}\frac{\delta}{\delta\tilde{J}_1(\tilde{\mathbf{r}}_\ell,\tilde{t}_{\tilde{N}+\ell})}\prod_{m=1}^{M}\frac{\delta}{\delta J_1(\mathbf{r}_j,t_{N+k})}\,\mathcal{W}\,|_{\tilde{J}=J=\tilde{J}_1=J_1=0} \tag{15}$$

must vanish whenever $\tilde{t}_j > \max_{1\leq k\leq N+M}(t_k)$ for at least one $\tilde{t}_j$, $j = 1, \ldots, \tilde{N}+\tilde{M}$. This rules out surface terms of the form specified in Eq. (4) with $m = 0$; i.e., the surface coupling constants $g_1(a, b; 0, n)$ must vanish.

For later use, let us also recall from Refs. [11] and [13] the form of the dynamic action one obtains for a general Gauss-Markov process on a discretized time lattice in the continuous time limit. It reads

$$\mathcal{J}_{t_0}^{t_f}\{\tilde{\phi},\phi\} = \int_{t_0}^{t_f} dt \int_V [\tilde{\phi}\,(\dot{\phi} - F) - \tilde{\phi}\, D\, \tilde{\phi}] \,. \tag{16}$$

For the *bulk* model B defined by the Langevin equation (2a), the noise correlation (2d), and the replacement $V \to I\!R^d$, the quantities F and D are given by $F = \lambda_0\, \Delta \mathcal{H}_\phi$ and $D = -\lambda_0\, \Delta$. In the semi-infinite case that we are concerned with, the interpretation of Eq. (16) remains to be clarified: according to our considerations above one expects boundary contributions to F [i.e., contributions $\propto \delta(z)$], whose precise form must still be determined. Likewise, we must find out which surface terms are produced by the term involving D and which boundary conditions should be required for this operator. We will return to these questions below. For the moment it suffices to note that the form (16) of the dynamic action ensures causality. (See, e.g., Ref. [12].)

(P6) Detailed balance and relaxation to thermal equilibrium. As a standard property known from bulk critical dynamics [3], we have the condition that the system relax from (almost) any initial configuration $\phi(\mathbf{x}, t_0) \equiv \phi^{(0)}(\mathbf{x})$ to a thermal equilibrium state characterized by a Boltzmann factor $\exp(-\mathcal{H})$. The Hamiltonian $\mathcal{H}$ in our case has the form

$$\mathcal{H} = \int_V [\tfrac{1}{2}(\nabla\phi)^2 + \mathcal{U}_b(\phi)] d^d x + \int_{\partial V} \mathcal{U}_1(\phi)\, d^{d-1}x_\parallel \,. \tag{17}$$

Its bulk density is dictated by the requirement that the operator $\mathcal{H}_\phi$ in Eq. (2b) coincide with the functional derivative $\delta\mathcal{H}/\delta\phi$ up to surface terms. Just as we did not include a bulk magnetic field in $\mathcal{H}$, we will ignore for the time being all contributions to the surface density $\mathcal{U}_1$ that break the symmetry $\phi \to -\phi$. The appropriate choice then is [5]

$$\mathcal{U}_1(\phi) = \tfrac{1}{2} c_0\, \phi^2 \,. \tag{18}$$

Of course, the inclusion of symmetry-breaking surface terms would be absolutely indispensable for a proper investigation of surface enrichment. Our rationale here is that we must first understand the symmetric case; once this has been achieved, the addition of symmetry-breaking terms will turn out to be a relatively straightforward matter.

In order to discuss the consequences of detailed balance for the action $\mathcal{J}$, let $\mathcal{T}$ denote time reversal. For the time-reversed field we have

$$\mathcal{T}\phi(\mathbf{x}, t) = \epsilon_\phi\, \phi(\mathbf{x}, -t), \tag{19}$$

with $\epsilon_\phi = \pm 1$. Since we are dealing with a purely relaxational model, both choices of the time parity ϵ_ϕ are possible. (Depending on whether ϕ is imagined as a particle density or spin density, one would choose $\epsilon_\phi = +1$ and -1, respectively.) We introduce the conditional functional probability density

$$\mathcal{P}(\{\phi^{(2)}\}, t_2 \mid \{\phi^{(1)}\}, t_1) \propto \int_{\phi^{(1)}}^{\phi^{(2)}} d\{\phi\} \int d\{\tilde{\phi}\}\, e^{-\mathcal{J}_{t_1}^{t_2}} \,, \tag{20}$$

where the integration over ϕ is over all fields $\phi(\mathbf{x}, t)$, $t_1 \leq t \leq t_2$, with $\phi(\mathbf{x}, t_1) = \phi^{(1)}(\mathbf{x})$ and $\phi(\mathbf{x}, t_2) = \phi^{(2)}(\mathbf{x})$. Detailed balance means that

$$\mathcal{P}(\{\phi^{(2)}\}, t_2 \mid \{\phi^{(1)}\}, t_1)\, e^{-\mathcal{H}\{\phi^{(1)}\}} = \mathcal{P}(\{\epsilon_\phi\, \phi^{(1)}\}, -t_1 \mid \{\epsilon_\phi\, \phi^{(2)}\}, -t_2)\, e^{-\mathcal{H}\{\epsilon_\phi\, \phi^{(2)}\}}. \tag{21}$$

As discussed elswhere [17], this relation can be used in conjunction with ergodicity to prove the limiting behavior

$$\lim_{t_2 - t_1 \to \infty} \mathcal{P}(\{\phi^{(2)}\}, t_2 \mid \{\phi^{(1)}\}, t_1) = \frac{\exp\left(-\mathcal{H}\{\phi^{(2)}\}\right)}{\mathcal{Z}[\mathcal{H}]} \,, \tag{22}$$

where $\mathcal{Z}[\mathcal{H}]$ denotes the partition function pertaining to $\mathcal{H}$. Since the Hamiltonian is time-reversal symmetric, $\mathcal{H}\{\phi\} = \mathcal{H}\{\epsilon_\phi\, \phi\}$, Eq. (21) yields

$$\mathcal{J}_{t_0}^{t_f}\{\tilde{\phi},\phi\} + \mathcal{H}\{\phi(t_0)\} = \mathcal{J}_{-t_f}^{-t_0}\{\mathcal{T}\tilde{\phi}, \mathcal{T}\phi\} + \mathcal{H}\{\mathcal{T}\phi(-t_f)\} \,. \tag{23}$$

The difference of the Hamiltonians can be written as

$$\mathcal{H}\{\mathcal{T}\phi(-t_f)\} - \mathcal{H}\{\phi(t_0)\} = \int_{t_0}^{t_f} dt \left(\int_V (\dot{\phi}\mathcal{H}_\phi) + \int_{\partial V} (\dot{\phi}\mathcal{H}_{\phi_s}) \right) \,, \tag{24}$$

where we have introduced the surface operator

$$\mathcal{H}_{\phi_s} \equiv \mathcal{U}_1'(\phi_s) - \partial_n \phi \,. \tag{25}$$

Here $\phi_s(\mathbf{x}_\parallel) \equiv \phi(\mathbf{x}_\parallel, z = 0)$, while ∂_n denotes the normal derivative $\partial_z \mid_{z=0}$. Substituting Eq. (24) into Eq. (23) and comparing the terms $\propto \dot{\phi}$ in the integrals $\int_V$ and $\int_{\partial V}$ with those on the right side, we recover the usual bulk equation

$$\mathcal{T}\tilde{\phi}(\mathbf{x}, t) = -\epsilon_\phi [\tilde{\phi}(\mathbf{x}, -t) - \mathcal{H}_\phi(\mathbf{x}, -t)] \,, \quad \mathbf{x} \notin \partial V \tag{26}$$

and obtain the boundary condition

$$\partial_n \phi(\mathbf{x}_s, t) = \mathcal{U}_1'(\phi(\mathbf{x}_s, t)) \,, \quad \mathbf{x}_s \in \partial V \,. \tag{27}$$

In the derivation of Eq. (27) we have presumed, in accordance with $P3$, that $\mathcal{L}_1$ does not contain terms $\propto \dot{\phi}$. The boundary condition (27) is precisely the one known from the static theory. Thus $P3$ and detailed balance are sufficient to ensure that the static boundary condition (27) carries over to the dynamic theory.

These conclusions do not yet exhaust the consequences of detailed balance. As shown in Ref. [11], detailed balance implies that the quantities F and D in Eq. (16) both can be written in terms of a reaction matrix R, so that $\mathcal{J}$ takes the form

$$\mathcal{J}_{t_0}^{t_f}\{\tilde{\phi},\phi\} = \int_{t_0}^{t_f} dt \int_V \left\{ \tilde{\phi}\left[\dot{\phi} - \frac{\delta R}{\delta\phi} + R\left(\frac{\delta\mathcal{H}}{\delta\phi} - \tilde{\phi}\right)\right]\right\} . \tag{28}$$

If we discretized position space, R would be a symmetric matrix in position space. This suggests to write the reaction matrix of our model in the symmetric fashion

$$R = \overleftarrow{\nabla}\lambda_0\nabla , \tag{29}$$

where $\overleftarrow{\nabla}$ acts to the left, while ∇ acts as usual to the right. Whether Eq. (28) with this choice of R yields meaningful results in our case is not yet clear at this stage. Two issues need to be clarified. On the one hand, we must understand which boundary conditions should be required for the reaction operator R. On the other hand, we must convince ourselves that the action of R on the boundary contribution $\delta(z)\mathcal{H}_{\phi_s}$ to $\delta\mathcal{H}/\delta\phi$ can be interpreted in a meaningful fashion. That this is indeed the case will be shown in Sec. II A where both issues will be settled.

(P7) Euclidean invariance and internal symmetries. The bulk density $\mathcal{L}_b$ given in Eq. (3) is compatible with the invariance of the bulk theory under the Euclidean group $E(d)$ of translations and rotations in $\mathbb{R}^d$ (as it should). The presence of the surface causes a breakdown of the $E(d)$ invariance. However, the boundary terms of $\mathcal{J}$ (i.e., $\mathcal{L}_1$) should still be invariant under the group $E(d-1)$ of rotations and translations in $\mathbf{x}_\parallel$ space.

Since we have not included any symmetry-breaking fields in $\mathcal{H}$, the required internal symmetry of $\mathcal{J}$ simply becomes

$$\mathcal{J}_{t_0}^{t_f}\{-\tilde{\phi},-\phi\} = \mathcal{J}_{t_0}^{t_f}\{\tilde{\phi},\phi\} . \tag{30}$$

B. Boundary conditions and field equations

The restrictions implied by $P1, \ldots, P5$ and $P7$ yield a surface density of the form

$$\begin{aligned}\mathcal{L}_1 = {} & b\,\phi\,\partial_n\tilde{\phi} + a_1\,(\partial_n\tilde{\phi})\,\partial_n\phi + a_2\,(\nabla_\parallel\tilde{\phi})\,\nabla_\parallel\phi \\ & + a_3\,\phi\,\partial_n^2\tilde{\phi} + g_1\,\phi\,\partial_n^3\tilde{\phi} + g_2\,(\partial_n\tilde{\phi})\,\partial_n^2\phi \\ & + g_3\,(\partial_n^2\tilde{\phi})\,\partial_n\phi + g_4\,(\nabla_\parallel\partial_n\tilde{\phi})\,\nabla_\parallel\phi + v\,\phi^3\partial_n\tilde{\phi} .\end{aligned} \tag{31}$$

Using this form of $\mathcal{L}_1$ with arbitrary values of the surface coupling constants, we would not recover the static boundary condition (27). Detailed balance ($P5$) imposes strong additional requirements. By analogy with the situation for bulk terms, one expects these to fix the values of all dynamic surface coupling constants introduced in Eq. (31) in terms of the static surface coupling constant c_0 and λ_0 (except those of eventual redundant surface operators). Before we show this by giving a formal derivation of $\mathcal{L}_1$ based on Eq. (28), we first present a more physical derivation of the desired boundary conditions.

In Ref. [4] two boundary conditions were explicitly given: one is the static boundary condition (27) for ϕ; the second one reads

$$[\partial_n - \mathcal{U}_1''(\phi)]\Delta\tilde{\phi}(\mathbf{x}_s,t) = 0 , \quad \mathbf{x}_s \in \partial V . \tag{32}$$

As mentioned there, this boundary condition is necessary in order to ensure consistency with the fluctuation-dissipation theorem. The missing second boundary condition for ϕ follows from the physical requirement that there be no current through the surface; that is, we must require

$$j_n = 0 \tag{33}$$

for the normal component of the current operator

$$\mathbf{j} = -\lambda_0\nabla\mathcal{H}_\phi . \tag{34}$$

Just as for the other boundary conditions, Eq. (33) is meant to hold inside of the correlation functions. (Since we are dealing with a field theory, j_n is a fluctuating quantity.) Using Eqs. (34) and (2b), Eq. (33) can be rewritten as

$$\partial_n[\Delta\phi - \mathcal{U}_b'(\phi)](\mathbf{x}_s,t) = 0 , \quad \mathbf{x}_s \in \partial V . \tag{35}$$

In order to obtain the missing second boundary condition for $\tilde{\phi}$, we use the equation of motion that follows from the invariance of the generating functional $\mathcal{Z}\{\tilde{J},J;\tilde{J}_1,J_1\}$ under a change of the integration variable $\tilde{\phi}$, namely,

$$\left\langle 2\lambda_0\,\Delta\tilde{\phi} + \dot{\phi} + \nabla\cdot\mathbf{j} - \tilde{J}(\mathbf{x},t)\right\rangle_{\{\tilde{J},J;\tilde{J}_1,J_1\}} = 0 , \quad \mathbf{x} \notin \partial V \tag{36}$$

where $\langle\,\rangle_{\{\tilde{J},J;\tilde{J}_1,J_1\}}$ denotes an average in the presence of the sources $\tilde{J}, \ldots, J_1$. We wish to integrate this equation over a film that is bounded in the perpendicular direction by the planes $z = +\delta$ and $-\delta$ but unbounded in the parallel direction, and then let $\delta \to 0+$. In doing this, we must pay attention to possible contributions $\propto \delta(z)$ [which we dropped in Eq. (36), setting $z > 0$]. One such term follows from the source term $\propto \tilde{J}_1$; to avoid it, we set $\tilde{J}_1 = 0$. Since ϕ is a locally conserved density even at the surface, the coefficient of an eventual delta-function contribution to the term $\dot{\phi} + \nabla\cdot\mathbf{j}$ in Eq. (36) should vanish. Finally, no δ-function contributions linear in $\tilde{\phi}$ occur other than the boundary term $\propto \partial_n\tilde{\phi}$ arising from the necessary integration by parts of $(\delta/\delta\tilde{\phi})\int dt \int_V (\nabla\tilde{\phi})^2$, because no monomials quadratic in $\tilde{\phi}$ are contained in $\mathcal{L}_1$. Combining these considerations, we conclude that we must have

$$\partial_n\tilde{\phi} = 0 . \tag{37}$$

The two boundary conditions, Eq. (35) and Eq. (37), not explicitly given in Ref. [4], have an obvious mathematical significance: they make the reaction operator (29) self-adjoint for fields of type $\tilde{\phi}$ and $\lambda_0\,\Delta\mathcal{H}_\phi$.

We now return to Eq. (28), the general form of $\mathcal{J}$ for a Gauss-Markov process with detailed balance. Into this we must insert

$$\frac{\delta \mathcal{H}}{\delta \phi} = \mathcal{H}_\phi(\mathbf{x},t) + \delta(z)\,\mathcal{H}_{\phi_s} \qquad (38)$$

and the reaction operator (29). In order to avoid divergences, we represent the δ function in Eq. (38) by a sequence of smooth functions, such as

$$\delta_\Lambda(z) = \Lambda\, e^{-\Lambda z}\ , \quad \Lambda \to \infty\,. \qquad (39)$$

Upon making appropriate integrations by parts, the resulting action $\mathcal{J}$ can be brought in the form (1) so that the bulk density $\mathcal{L}_b$ is given by Eq. (3). The surface density is found to be

$$\mathcal{L}_1 = \lambda_0\,(\partial_n\tilde\phi)\,\Delta\phi - \lambda_0\,(\Lambda\,\partial_n\tilde\phi + \Delta\tilde\phi)[\mathcal{U}_1'(\phi) - \partial_n\phi] \qquad (40)$$

up to terms of order $o(\Lambda)$. The result is in conformity with Eq. (31). The coupling constants g_1 and v vanish, so the associated surface operators $\phi\,\partial_n^3\tilde\phi$ and $\phi^3\partial_n\tilde\phi$ are missing. Owing to the boundary condition (37), the latter obviously is a redundant operator. Similarly, Eq. (32) shows that the former corresponds to a redundant operator up to operators included in Eq. (40). All other surface operators included in Eq. (31) also occur in Eq. (40).

We proceed by deriving the boundary conditions corresponding to the result (40). As usual [10], these must follow from the contributions $\propto \delta(z)$ to the field equations ("equations of motion") resulting from the invariance of the generating functional $\mathcal{Z}\{\tilde J, J; \tilde J_1, J_1\}$ under a change of the integration variables $\tilde\phi$ and ϕ. Choosing changes $\delta\tilde\phi$ and $\delta\phi$ that vanish for $t = t_0$ and t_f, we can write the implied change of $\mathcal{J}$ as

$$\delta\mathcal{J}_{t_0}^{t_f} = \int dt\Bigg(\int_V(\mathcal{J}_{\tilde\phi}\,\delta\tilde\phi + \mathcal{J}_\phi\,\delta\phi) + \int_{\partial V}(\mathcal{J}_{\tilde\phi_s}\,\delta\tilde\phi + \mathcal{J}_{\tilde\phi_s'}\,\partial_n\delta\tilde\phi + \mathcal{J}_{\Delta\tilde\phi_s}\,\Delta\delta\tilde\phi + \mathcal{J}_{\phi_s}\,\delta\phi + \mathcal{J}_{\phi_s'}\,\partial_n\delta\phi + \mathcal{J}_{\Delta\phi_s}\,\Delta\delta\phi)\Bigg) \qquad (41)$$

with

$$\mathcal{J}_{\tilde\phi} = \dot\phi + \lambda_0\,\Delta[\Delta\phi - \mathcal{U}_b'(\phi) + 2\tilde\phi]\ , \qquad (42a)$$

$$\mathcal{J}_\phi = -\dot{\tilde\phi} + \lambda_0[\Delta - \mathcal{U}_b''(\phi)]\Delta\tilde\phi\ , \qquad (42b)$$

$$\mathcal{J}_{\tilde\phi_s} = \lambda_0\,\partial_n[\Delta\phi - \mathcal{U}_b'(\phi) + 2\tilde\phi]\ , \qquad (42c)$$

$$\mathcal{J}_{\phi_s} = \lambda_0\{\,[\partial_n - \mathcal{U}_1''(\phi)]\,\Delta\tilde\phi - [\Lambda\,\mathcal{U}_1''(\phi) + \mathcal{U}_b''(\phi)]\,\partial_n\tilde\phi\}_s\ , \qquad (42d)$$

$$\mathcal{J}_{\tilde\phi_s'} = \lambda_0\,\Lambda\,[\partial_n\phi - \mathcal{U}_1'(\phi_s)]\ , \qquad (42e)$$

$$\mathcal{J}_{\phi_s'} = \lambda_0\,\Lambda\,\partial_n\tilde\phi\ , \qquad (42f)$$

$$\mathcal{J}_{\Delta\tilde\phi_s} = \lambda_0\,[\partial_n\phi - \mathcal{U}_1'(\phi_s)]\ , \qquad (42g)$$

and

$$\mathcal{J}_{\Delta\phi_s} = \lambda_0\,\partial_n\tilde\phi\,. \qquad (42h)$$

Upon addition of the contributions from the source terms, use of this in the functional integral for $\mathcal{Z}\{\tilde J, J; \tilde J_1, J_1\}$ yields the field equations

$$\langle \mathcal{J}_A - J_A\rangle_{\{\tilde J,J;\tilde J_1,J_1\}} = 0\ , \quad A = \tilde\phi, \ldots, \Delta\phi_s\ , \qquad (43)$$

where J_A means the respective bulk or surface source $\tilde J, \ldots, J_1$, or 0 that couples to the operator A.

For $A = \tilde\phi$, Eq. (43) is precisely the (bulk) equation of motion (36). Likewise, Eq. (43) with $A = \phi$ is well-known from the bulk case. The remaining field equations give us the boundary conditions. Choosing $A = \tilde\phi_s'$ or $A = \Delta\tilde\phi_s$ in Eq. (43), we recover the static boundary condition (27) in the form

$$\langle \partial_n\phi - \mathcal{U}_1'(\phi_s)\rangle_{\{\tilde J,J;\tilde J_1,J_1\}} = 0\,. \qquad (44a)$$

Similiarly, the choice $A = \phi_s'$ or $A = \Delta\phi_s$ yields

$$\langle \partial_n\tilde\phi\rangle_{\{\tilde J,J;\tilde J_1,J_1\}} = 0\ , \qquad (44b)$$

which is Eq. (37). If we substitute this boundary condition (44b) into the field equations (43) for $A = \tilde\phi_s$ and $A = \phi_s$, these become

$$\langle \partial_n[\Delta\phi - \mathcal{U}_b'(\phi)] - \tilde J_1/\lambda_0\rangle_{\{\tilde J,J;\tilde J_1,J_1\}} = 0\ , \qquad (44c)$$

and

$$\langle \{[\partial_n - \mathcal{U}_1''(\phi)]\Delta\tilde\phi\}_s - J_1/\lambda_0\rangle_{\{\tilde J,J;\tilde J_1,J_1\}} = 0\ , \qquad (44d)$$

in precise agreement with our previous findings, Eqs. (35) and (32).

Equations (44a)–(44d) are a central result of this paper. They hold for the regularized interacting theory — i.e., beyond mean-field theory. Since in their derivation no use was made of the specific form of the potentials $\mathcal{U}_b$ and $\mathcal{U}_1$, they must also be valid for more general choices of $\mathcal{U}_b$ and $\mathcal{U}_1$. In particular, they hold if we include magnetic bulk and surface field terms, making the replacements

$$\mathcal{U}_b \to \mathcal{U}_b - h_0\,\phi \qquad (45a)$$

and

$$\mathcal{U}_1 \to \mathcal{U}_1 - h_{1,0}\,\phi\,. \qquad (45b)$$

[Following Refs. [10] and [18], one might even want to incorporate a cubic term $(w_0/3!)\,\phi^3$ in $\mathcal{U}_1$.] Note that the surface magnetic field $h_{1,0}$ might equivalently be introduced via the source term

$$\lambda_0\,h_{1,0}\int_{\partial V}(\Lambda\,\partial_n\tilde\phi + \Delta\tilde\phi)\,. \qquad (46)$$

This is in conformity with the above expressions (42e) and (42g) for $\mathcal{J}_{\tilde\phi_s'}$ and $\mathcal{J}_{\Delta\tilde\phi_s}$, respectively, and the corresponding field equations (43).

C. The free response and correlation propagators

Our final result for the action $\mathcal{J}$ is given by Eqs. (1), (3), and (40). This may be compared with the action used in Ref. [4]. An integration by parts shows that the former agrees with the model-B result given in Eq. (II.5) of Ref. [4] up to terms proportional to the redundant surface operator $\partial_n \tilde{\phi}$. While the model-B analysis of Ref. [4] is based on a correct expression for the action, the boundary conditions derived in the previous section have not properly been implemented. As a consequence, some of the results of Ref. [4] for the free response propagator $G = \langle \phi\, \tilde{\phi} \rangle_0$ and the free correlation propagator $C = \langle \phi\, \phi \rangle_0$ are incorrect, as we will show now.

The response propagator G may be determined as the solution to the equation

$$[\partial_t - \lambda_0 \Delta\,(\tau_0 - \Delta)]\, G(\mathbf{x}, t; \tilde{\mathbf{x}}, \tilde{t}) = \delta(\mathbf{x} - \tilde{\mathbf{x}})\, \delta(t - \tilde{t}) \quad (47)$$

that satisfies the boundary conditions

$$(\partial_n - c_0) G(\mathbf{x}_s, t; \tilde{\mathbf{x}}, \tilde{t}) = 0\,, \quad (48a)$$

$$(\Delta - \tau_0)\partial_n\, G(\mathbf{x}_s, t; \tilde{\mathbf{x}}, \tilde{t}) = 0\,, \quad (48b)$$

$$\tilde{\partial}_n G(\mathbf{x}, t; \tilde{\mathbf{x}}_s, \tilde{t}) = 0\,, \quad (48c)$$

$$(\tilde{\partial}_n - c_0)\, \tilde{\Delta}\, G(\mathbf{x}, t; \tilde{\mathbf{x}}_s, \tilde{t}) = 0 \quad (48d)$$

for $\mathbf{x}_s$, $\tilde{\mathbf{x}}_s \in \partial V$ and $\mathbf{x}$, $\tilde{\mathbf{x}} \notin \partial V$. Upon taking Fourier transforms,

$$G(\mathbf{x}, t; \tilde{\mathbf{x}}, \tilde{t}) = \int_{\omega, \mathbf{p}} \hat{G}(\mathbf{p}; z, \tilde{z}; \omega)\, e^{-i\omega(t-\tilde{t}) + i\mathbf{p}\cdot(\mathbf{x}-\tilde{\mathbf{x}})_{\parallel}} \quad (49)$$

with $\int_\omega \equiv \int_{-\infty}^{\infty} d(\omega/2\pi)$ and $\int_{\mathbf{p}} \equiv \int d^{d-1}(p/2\pi)$, Eq. (47) becomes an ordinary differential equation for $\hat{G}$, which can be solved by standard means. At $z = \tilde{z}$, $\hat{G}$ and its first two derivatives with respect to z must be continuous; its third derivative must have a jump discontinuity $-\lambda_0^{-1}\, \theta(z - \tilde{z})$ in order that the term $\propto \partial_z^4 \hat{G}$ on the left-hand side of Eq. (47) produces the δ-function singularity on the right-hand side. Using these conditions together with the fact that $\hat{G}$ must decay as $z \to \infty$ at fixed $\tilde{z}$ (or as $\tilde{z} \to \infty$ at fixed z), one finds that $\hat{G}$ can be written in the form

$$\hat{G}(z, \tilde{z}) = \frac{1}{\lambda_0\, (\kappa_+^2 - \kappa_-^2)} \left(A_+(\tilde{z})\, e^{-\kappa_+ z} - A_-(\tilde{z})\, e^{-\kappa_- z} + \frac{1}{2\kappa_-}\, e^{-\kappa_- |z - \tilde{z}|} - \frac{1}{2\kappa_+}\, e^{-\kappa_+ |z - \tilde{z}|} \right)\,, \quad (50)$$

where the variables $\mathbf{p}$ and ω have been suppressed. The complex momenta $\kappa_\pm$ are the roots with real part $\mathrm{Re}\kappa_\pm > 0$ of

$$\kappa_\pm^2 = \mathbf{p}^2 + (\tau_0/2) \pm [(\tau_0/2)^2 + i(\omega/\lambda_0)]^{1/2}\,. \quad (51)$$

The contributions from the last two terms of Eq. (50) are the usual bulk response propagator $\hat{G}_b(\mathbf{p}; z - \tilde{z})$ (cf. Ref. [4]).

Upon inserting Eq. (50) into the boundary conditions (48a) and (48b), we can determine the functions $A_\pm$. The result is

$$A_\pm(z) = \frac{1}{2\kappa_\pm} (f_\pm\, e^{-\kappa_\pm z} + g_\pm\, e^{-\kappa_\mp z}) \quad (52)$$

with

$$f_\pm \equiv f(\kappa_\pm, \kappa_\mp; c_0, \kappa) = \frac{\kappa_\pm \kappa_\mp (\kappa_\pm^2 - \kappa_\mp^2) - c_0[\kappa_\pm(\kappa^2 - \kappa_\pm^2) + \kappa_\mp(\kappa^2 - \kappa_\mp^2)]}{\kappa_\pm(\kappa^2 - \kappa_\pm^2)(c_0 + \kappa_\mp) - \kappa_\mp(\kappa^2 - \kappa_\mp^2)(c_0 + \kappa_\pm)} \quad (53a)$$

and

$$g_\pm \equiv g(\kappa_\pm, \kappa_\mp; c_0, \kappa) = \frac{2c_0 \kappa_\pm (\kappa^2 - \kappa_\mp^2)}{\kappa_\pm(\kappa^2 - \kappa_\pm^2)(c_0 + \kappa_\mp) - \kappa_\mp(\kappa^2 - \kappa_\mp^2)(c_0 + \kappa_\pm)}\,, \quad (53b)$$

where

$$\kappa = +\sqrt{\mathbf{p}^2 + \tau_0}\,. \quad (54)$$

Our result for $\hat{G}$ thus becomes

$$\hat{G}(\mathbf{p}; z, \tilde{z}; \omega) = \tfrac{1}{2\lambda_0} \left(\frac{\tau_0^2}{4} + i\frac{\omega}{\lambda_0} \right)^{-1/2} \left(\frac{1}{2\kappa_-}(e^{-\kappa_-|z-\tilde{z}|} - f_-\, e^{-\kappa_-(z+\tilde{z})} - g_-\, e^{-(\kappa_- z + \kappa_+ \tilde{z})}) - \frac{1}{2\kappa_+}(e^{-\kappa_+|z-\tilde{z}|} - f_+\, e^{-\kappa_+(z+\tilde{z})} - g_+\, e^{-(\kappa_+ z + \kappa_- \tilde{z})}) \right)\,. \quad (55)$$

The result given in Appendix B of Ref. [4] differs from ours through the replacements $f_\pm \to (c_0 - \kappa_\pm)/(c_0 + \kappa_\pm)$ and $g_\pm \to 0$. In the special case $c_0 = 0$ (corresponding to the special transition), both results agree since

$$f(\kappa_+, \kappa_-; 0, \kappa) = -1 \quad (56a)$$

and

$$g(\kappa_+, \kappa_-; 0, \kappa) = 0\,. \quad (56b)$$

But for general values of c_0, they differ.

The free correlation propagator may be expressed in terms of the free response propagator; in the $\mathbf{p}z\omega$ representation one has

$$\hat{C}(\mathbf{p};z,z';\omega) = 2\lambda_0 \int_0^\infty d\tilde{z}\, \hat{G}(\mathbf{p};z,\tilde{z};\omega) \times (\mathbf{p}^2 - \partial_{\tilde{z}}^2)\hat{G}(-\mathbf{p};z',\tilde{z};-\omega)\,. \tag{57}$$

Since the boundary conditions obeyed by the free propagators G and C are different, except in the special case $c_0 = 0$, their representation in terms of eigenfunctions that satisfy these boundary conditions seems to be of limited practical use in perturbative renormalization-group calculations. Rather it seems preferable to work in a $\mathbf{p}zt$ or $\mathbf{p}z\omega$ representation.

III. DYNAMICS OF SURFACE ENRICHMENT

In this section we shall investigate, within the framework of our model, the problem studied by BF: the relaxation of the order-parameter profile $m(z,t) = \langle\phi(\mathbf{x}_\|, z, t)\rangle$ from a homogeneous nonequilibrium profile

$$m(z,0) \equiv m_b \tag{58}$$

into thermal equilibrium, where m_b is the equilibrium value of the bulk order parameter. For simplicity, we will content ourselves with a zero-loop analysis. Since in such an approach a distinction of bare and renormalized quantities is unnecessary, the subscript 0 will be dropped on bare quantities such as τ_0, c_0, etc. Our model is defined by Eqs. (1), (3), and (40), where bulk and surface magnetic fields h and h_1 have been included in the potentials $\mathcal{U}_b$ and $\mathcal{U}_1$ given in Eqs. (2c) and (18), as indicated in Eqs. (45a) and (45b).

The equation of motion that governs the time evolution of the profile is given by Eq. (2a), with the identification $\phi \leftrightarrow m$ and the noise term ζ set to zero. Solutions must be sought which satisfy the boundary conditions (27) and (35). We write

$$m(z,t) = m_b + \sigma(z,t) \tag{59}$$

and expand $\mathcal{U}_b'$ and $\mathcal{U}_1'$ about m_b, the minimum of $\mathcal{U}_b$. This gives

$$\mathcal{U}_b'(m) = r\,\sigma + O(\sigma^2) \tag{60a}$$

and

$$\mathcal{U}_1'(m) = -l + c\,\sigma + O(\sigma^2)\,, \tag{60b}$$

with

$$l = h_1 - c\,m_b\,. \tag{61}$$

In terms of these quantities the equation to be solved becomes

$$\lambda^{-1}\partial_t\sigma(z,t) = -\partial_z^4\sigma(z,t) + r\,\partial_z^2\sigma(z,t) \tag{62a}$$

with the boundary conditions

$$\partial_z(\partial_z^2\sigma - r\sigma)\,|_{z=0} = 0 \tag{62b}$$

and

$$(\partial_z\sigma + l - c\,\sigma)\,|_{z=0} = 0\,. \tag{62c}$$

In the sequel we will assume that $c > 0$, restricting ourselves to the case of subcritical surface enhancement.

The equilibrium profile $m_\infty \equiv m(z,\infty)$ to which the profile relaxes corresponds to a deviation σ of the form

$$\sigma_\infty = \tfrac{l}{c+\kappa}\, e^{-\kappa z}\,, \tag{63}$$

where

$$\kappa \equiv \sqrt{r} = 1/\xi \tag{64}$$

is the reciprocal of the bulk correlation length ξ. [Note that this definition of κ is consistent with our previous one in that Eq. (54) for $\mathbf{p} = \mathbf{0}$ yields the same value of κ as Eq. (64) for $\tau > 0$ and $h = 0$. Hence no confusion should arise from the fact that we use the same symbol.] Upon making a Laplace transformation,

$$\bar{\sigma}(z,s) = \int_0^\infty ds\, e^{-st}\,\sigma(z,t)\,, \tag{65}$$

we find

$$\bar{\sigma}(z,s) = \frac{l/s}{(\kappa_+ - \kappa_-)(c + \kappa_+ + \kappa_-)} \times \left(\kappa_+\, e^{-\kappa_+ z} - \kappa_-\, e^{-\kappa_- z}\right)\,. \tag{66}$$

Here $\kappa_\pm$ are the roots

$$\kappa_\pm = \{(r/2) \pm [r^2/4 - (s/\lambda)]^{1/2}\}^{1/2} \tag{67}$$

with positive real part. [Just as in the above-mentioned case of κ, this definition of $\kappa_\pm$ agrees with the previous one given in Eq. (51) if $\mathbf{p} = \mathbf{0}$, $\tau > 0$, and $h = 0$.]

One can easily verify that the singularities resulting from the branch points of the roots at $s = \lambda(r/2)^2$ cancel in $\bar{\sigma}$. Hence $\bar{\sigma}$ is analytic in the complex s plane except for a branch cut from 0 to $-\infty$ along the negative real axis (see Fig. 1). It follows that the standard integration path $\mathcal{C}$ for Laplace inversion may be deformed in the manner illustrated in Fig. 1 into the path $\mathcal{C}_{-+}$ around the negative real s axis. Thus

$$\sigma(z,t) = \frac{1}{2\pi i}\int_{\mathcal{C}_{-+}} ds\,\bar{\sigma}(z,s)\,e^{st}\,. \tag{68}$$

The path $\mathcal{C}_{-+}$ is composed of a path $\mathcal{C}_-$ with $s = \omega - i0$, $-\infty < \omega < 0^-$, a circular piece around the origin, and a path $\mathcal{C}_+$ with $s = \omega + i0$, $0^- > \omega > -\infty$. Let $\chi(z,t)$ be the response function describing the response of $m(z,t)$ to the surface field l. Then we have in Laplace space

$$\bar{\sigma}(z,s) = \bar{\chi}(z,s)\,\frac{l}{s}\,. \tag{69}$$

From the integration over the circular piece we recover the static contribution (63) in the form

$$\sigma_\infty(z) = \bar{\chi}(z,0)\,l\,, \tag{70}$$

where

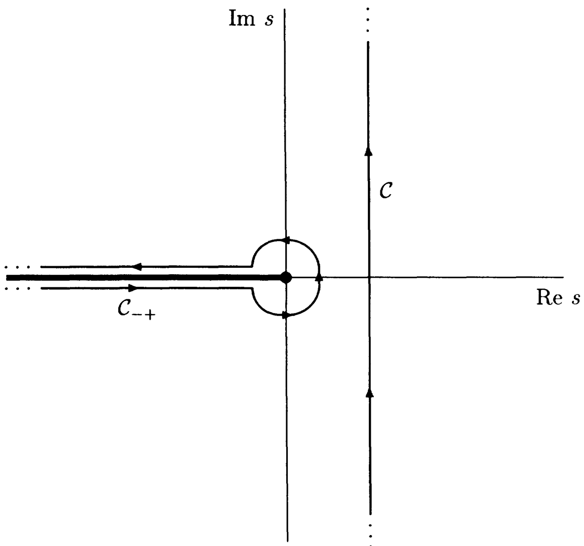

FIG. 1. Deformation of the integration path $\mathcal{C}$ for Laplace inversion into the path $\mathcal{C}_{-+}$ around the branch cut (solid line).

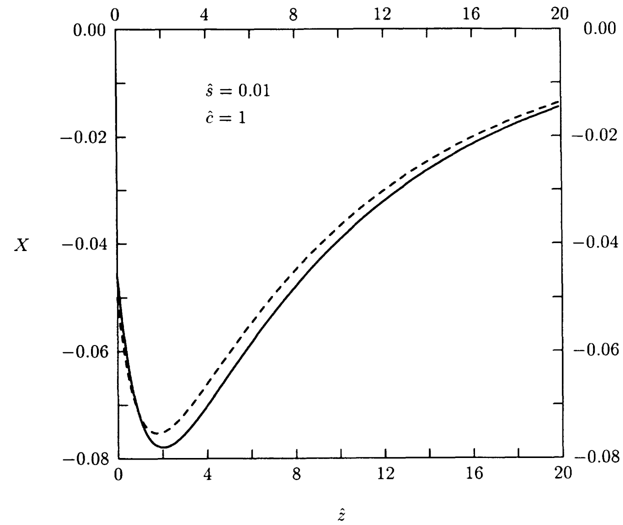

FIG. 2. Scaling function $X(\hat{z}, \hat{s}, \hat{c})$ for $\hat{s} = 0.01$ and $\hat{c} = 1$. The solid curve is the exact zero-loop result; the dashed curve is the asymptotic form given in Eq. (78).

$$\bar{\chi}(z, 0) = \chi_\infty(z) = \frac{1}{c + \kappa} e^{-\kappa z} \tag{71}$$

is the static response function. Noting further that $\bar{\sigma}(z, s)^* = \bar{\sigma}(z, s^*)$ under complex conjugation, and introducing the imaginary part

$$\bar{\chi}''(z, \omega) \equiv \mathrm{Im}\bar{\chi}(z, \omega + i0) \ , \tag{72}$$

one finally concludes that the Laplace inversion may be written as

$$\sigma(z, t) = \sigma_\infty(z) + \frac{l}{\pi} \int_{0+}^{\infty} \frac{d\omega}{\omega} \bar{\chi}''(z, -\omega) \, e^{-\omega t} \ . \tag{73}$$

Let us first discuss the behavior of $\bar{\chi}$ for $|\, s \,| \ll \lambda r^2$. To this end we write the normalized deviation of $\bar{\chi}$ from its equilibrium value in the scaling form

$$[\bar{\chi}(z, s) - \chi_\infty(z)]/\chi_\infty(0) = X(\kappa z, s\lambda^{-1} r^{-2}, c\kappa^{-1}) \tag{74}$$

and expand $\kappa_\pm$ in powers of the scaled variable

$$\hat{s} \equiv s\,(\lambda r^2)^{-1} \ . \tag{75}$$

This gives

$$\kappa_+ = \kappa[1 - \tfrac{1}{2}\hat{s} + O(\hat{s}^2)] \tag{76a}$$

and

$$\kappa_- = \kappa\,\hat{s}^{1/2}[1 + \tfrac{1}{2}\hat{s} + O(\hat{s}^2)] \ . \tag{76b}$$

The inverse of these momenta are the decay lengths

$$\xi_\mp^{\mathrm{BF}}(s) = 1/\kappa_\pm(s) \tag{77}$$

discussed by BF.

On substituting the above expansions into Eq. (71), one finds that the scaling function $X(\hat{z}, \hat{s}, \hat{c})$ behaves as

$$X(\hat{z}, \hat{s}, \hat{c}) \approx -\sqrt{\hat{s}} \left(e^{-\sqrt{\hat{s}}\hat{z}} - \frac{\hat{c}}{1 + \hat{c}} e^{-\hat{z}} \right) [1 + O(\sqrt{\hat{s}})] \tag{78}$$

in the limit $\hat{s} \to 0$, with $\hat{z} \equiv \kappa z$ and $\hat{c}$ fixed. Directly at the surface, X is negative,

$$X(0, \hat{s}, \hat{c}) \approx -(1 + \hat{c})^{-1}\, \hat{s}^{1/2} + O(\hat{s}) \ . \tag{79}$$

As z increases from $z = 0$, X decreases until it reaches its minimum at

$$\kappa z_{\mathrm{min}} \approx -\ln\left[(1 + \hat{c}^{-1})\hat{s}^{1/2}\right] \ . \tag{80}$$

Finally, on the scale $z \approx \kappa^{-1}\hat{s}^{-1/2}$ we have exponential decay,

$$X\left[z \approx (\lambda r/s)^{1/2}\right] \approx -\hat{s}^{1/2} \exp\left(- \hat{s}^{1/2}\hat{z} \right) \ . \tag{81}$$

These results are illustrated in Fig. 2, in which we have plotted the quantity X as a function of $\hat{z}$ for $\hat{s} = 0.01$ and $\hat{c} = 1$. The behavior of X can be easily understood on physical grounds. Compared to the equilibrium profile, there is originally a deficiency of order near the surface. This deficiency corresponds to the fact that X is negative near the surface. Since the order parameter is conserved, relaxation towards thermal equilibrium requires that order be transported towards the surface. This takes time. The maximum depth from which order can be transported to the surface within time t is roughly given by $z_{\mathrm{max}} \approx 1/\kappa_-(t^{-1}) \approx (r\lambda t)^{1/2}$ for long times. At distances large compared to this depth X must therefore vanish.

Next we turn to the critical case $r = 0$. On the integration path $\mathcal{C}_+$ chosen in Eq. (73) we have

$$\begin{aligned} \kappa_+(s = -\omega + i0, r = 0) &= (\omega/\lambda)^{1/4} \\ &= \kappa_-(-\omega + i0, 0)/i \ . \end{aligned} \tag{82}$$

Inserting this into Eq. (66) and using Eq. (69), we obtain

$$\chi''(z, -\omega) = -\frac{1}{2c} \frac{1}{(1 + w)^2 + w^2} \, \Xi(w, cz) \ , \tag{83a}$$

where the function Ξ and the variable w are defined by

$$\Xi(w,\hat{z}) \equiv \sin w\hat{z} + (1+2w)\cos w\hat{z} - e^{-w\hat{z}} \quad (83b)$$

and

$$w \equiv c^{-1}(\omega/\lambda)^{1/4} , \quad (83c)$$

respectively. Our result for $\sigma(z,t)$ thus becomes

$$\sigma(z,t;r=0,c) = \frac{l}{c} - \frac{l}{c}\int_0^\infty \frac{dw}{\pi w}\,\frac{2\,\Xi(w,cz)}{(1+w)^2+w^2}\,e^{-c^4w^4\lambda t} . \quad (84)$$

The asymptotic long-time behavior can be determined as follows. The integrand in Eq. (84) is exponentially small unless $w < (c^4\lambda t)^{-1/4}$. If we let $t \to \infty$ at fixed c and z, the conditions $\lambda t \gg z^4$ and $\lambda t \gg c^{-4}$ will both be satisfied at late stages. These conditions imply that for those values of w for which the integrand is not exponentially small we have $w \ll 1$ and $wcz \ll 1$. Accordingly the function Ξ and the w-dependent factor multiplying the exponential may be expanded in powers of w and wcz. Upon keeping the leading order and performing the integration, one obtains

$$\sigma(z,t) \approx \frac{l}{c}\left(1 - \frac{\Gamma(1/4)}{\pi c}\,(1+cz)(\lambda t)^{-1/4} + O(\sqrt{\lambda t})\right) . \quad (85)$$

All results given above are in accordance with the scaling behavior one expects on phenomenological grounds, with the critical exponents taking their familar mean-field values.

IV. SUMMARY AND CONCLUSIONS

The present paper had a twofold aim: We wanted to construct a semi-infinite model B that is, first, capable of modeling the dynamical process of surface enrichment near bulk criticality and, second, minimal in the sense that irrelevant and redundant interactions are discarded in order to make the model as simple as possible. The solution to this problem is contained in the dynamic action defined by Eqs. (1), (3), and (40). The second part of our aim was to clarify which boundary conditions should be imposed on the order-parameter field ϕ and the associated response field $\tilde{\phi}$ in such a model with a conserved order parameter, a question that is, of course, intimately connected with the first part of our aim. Our results for the boundary conditions are given in Eqs. (44a)–(44d).

Owing to the requested minimality property, the boundary conditions have no explicit time dependence and are as simple as in the static case. Their physical meaning is clear: One of the boundary conditions for the order-parameter field ϕ is just the usual static boundary condition (27); the second one corresponds to the requirement that the current through the surface must be zero. The response field $\tilde{\phi}$ was found to satisfy Neumann boundary conditions. As a second boundary condition for $\tilde{\phi}$, the one given in Ref. [4] was recovered — namely, the requirement that the field $\lambda_0\Delta\tilde{\phi}$ satisfy the static boundary condition. This may be understood as a direct consequence of the fact that the operator $\lambda_0\Delta\tilde{\phi}(\mathbf{x},t)$ describes the response with respect to a magnetic field $h(\mathbf{x},t)$.

The greater simplicity of our model makes it more accessible to analytic calculations than BF's lattice and continuum models, which should be in the same dynamic (bulk and surface) universality class. In the preceding section we have explicitly verified that the universal properties found in BF's mean-field analysis of the dynamics of surface enrichment are correctly reproduced. Our zero-loop investigation of the behavior near bulk criticality may be improved by a renormalization-group analysis based on the $\epsilon = 4 - d$ expansion. Since the conclusions of Dietrich and Diehl [4] concerning the structure of the ultraviolet singularities remain valid, the required surface counterterms and the resulting renormalization-group equations may be gleaned from there. On the other hand, the computational technique used in the two-loop calculations of Ref. [4] for model A — the expansion of the free response and correlation propagators in terms of static eigenfunctions — requires modifications in the present, model-B, case. The obvious reason is the following. In the case of model A, the fields ϕ and $\tilde{\phi}$ satisfied the same (static) boundary condition. Thus the static eigenfunctions were an appropriate basis for both the free response and the free correlation propagator. In the case of model B, ϕ and $\tilde{\phi}$ satisfy in general distinct boundary conditions. Furthermore, the static eigenfunctions do not in general satisfy the second boundary condition required for ϕ. While eigenfunctions satisfying both boundary conditions for either ϕ or $\tilde{\phi}$ could be determined, the advantage of working in a given eigenfunction basis is lost. Utilizing a $\mathbf{p}z$ representation seems more appropriate.

[1] K. Binder and H. L. Frisch, Z. Phys. B **84**, 403 (1991).
[2] K. Kawasaki, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1972), Vol. II, Chap. 11.
[3] B. I. Halperin, P. C. Hohenberg, and S.-K. Ma, Phys. Rev. Lett. **29**, 1548 (1972); P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
[4] S. Dietrich and H. W. Diehl, Z. Phys. B **51**, 343 (1983).
[5] H. W. Diehl, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1986), Vol. X, p. 75.
[6] For a general review of critical behavior at surfaces and a list of references, see K. Binder, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. VIII, p. 1; Vol. X, Ref. [5].
[7] H. W. Diehl and S. Dietrich, Z. Phys. B **42**, 65 (1981); Phys. Lett. **80A** , 408 (1980).
[8] H. W. Diehl and S. Dietrich, Phys. Rev. B **24**, 2878 (1981); Z. Phys. B **50**, 117 (1983).
[9] For an extensive recent discussion of the static boundary condition, see Ref. [10].

[10] H. W. Diehl and A. Ciach, Phys. Rev. B **44**, 6642 (1991).
[11] H. K. Janssen, Z. Phys. B **377** (1976).
[12] For a detailed exposition of the functional-integral approach to stochastic dynamic models, see H. K. Janssen, in *Dynamical Critical Phenomena and Related Topics*, edited by C. Enz, Springer Lecture Notes in Physics Vol. 104 (Springer-Verlag, Berlin, 1979).
[13] H. K. Janssen, in *From Phase Transitions to Chaos, Topics in Modern Statistical Physics*, edited by G. Györgyi, I. Kondor, L. Sasvári, and T. Tel (World Scientific, Singapore, 1992).
[14] R. Bausch, H. K. Janssen, and H. Wagner, Z. Phys. B **24**, 113 (1976).
[15] C. de Dominicis and L. Peliti, Phys. Rev. B **18**, 353 (1978).
[16] Note that this definition of $\mathcal{J}$ differs from the sign convention for $\mathcal{J}$ used in Refs. [4], [11], and [14] through a minus sign.
[17] See, e.g., R. Graham, in *Quantum Statistics in Optics and Solid-State Physics*, edited by G. Höhler, Springer Tracts in Modern Physics Vol. 66 (Springer-Verlag, Berlin, 1973).
[18] A. Ciach and H. W. Diehl, Europhys. Lett. 12, 635 (1990); **15**, 693(E) (1991).