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Extension of Landau-Ginzburg free-energy functionals to high-gradient domains

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The Landau-Ginzburg (LG) free-energy-gradient theory is extended to account for domains of intermediate wavelengths. The extension is nonlocal but preserves the universal features of the LG theory, has the same level of complexity, and reduces to it in the small-gradient limit. It also enables one to gain a meaningful insight into the microstructure of a system.

This Rapid Communication extends the Landau-Ginzburg (LG) theory of free-energy functionals[1] to domains of larger gradients than accounted for in the LG theory. These are expected away from the critical point where the divergence of the correlation length arrests the spatial variations. Though it may appear surprising at first, this extension cannot be achieved with higher-order perturbation in gradients, because such an expansion *always* diverges. In what follows, I shall demonstrate that the proper extension has to be a nonlocal one and I will show how to construct it.

To describe the essence of my approach, take ϕ to be a scalar order parameter in one spatial dimension (1D). Let $F(\phi)$ be the functional of free energy and $f(\phi)$ its density

$$F(\phi)=\int f(\phi)dx\,,$$

then the Landau-Ginzburg theory states that

$$f(\phi)=f_0(\phi)+\frac{a}{2}(\phi_x)^2,\quad a>0\,; \tag{1}$$

$f_0(\phi)$ is the energy density of the system in a local homogeneous equilibrium and its inhomogeneity, explicitly assumed to be small, is measured via the gradients. Expression (1) is the essence of the LG theory in its maximal simplicity. My work extends (1) to higher gradients by replacing it with

$$f(\phi)=f_0(\phi)+\frac{a}{2}(\phi_x L_A \phi_x)\,,$$

where L_A is a Lorentzian [see Eqs. (7b) and (11)]. The new expression reduces to the classical one in the small-gradient limit, but for large gradients, as expected on physical grounds, it softens and finally saturates as the gradients grow unbounded. I shall demonstrate that whether the system is a solid lattice or liquidlike, the introduced form interpolates properly between the microscopic and macroscopic descriptions. Stated differently, the LG theory calls explicitly for both the order parameter and its gradient to be small. I shall relax the second constraint, which is to say that while the order parameter is still assumed to be *small,* it may undergo faster spatial change than accounted for in the LG theory. This work was partially motivated by the observed formation of complex patterns and by the appearance of spatiotemporal chaos[2] in the deterministic time-dependent LG equation of motion. Since these phenomena are intimately related to the behavior at the ultraviolet end, this side of the spectrum must be treated even if only approximately. The point which will repeat itself throughout this work is that any extension of the LG theory necessitates taming the growth at the ultraviolet end. Though detailed microscopic information is unknown, the minimal requirement is that of boundedness of the total interaction energy.[3,4] Imposing this condition will suffice to extend the LG theory to higher gradients. It is worth reiterating that it is impossible to achieve a correct extension of a low-k theory to intermediate wavelengths without removing the ultraviolet divergences.

To introduce my extension pertinent to solids, I start with an equally spaced 1D lattice. Its energy of interaction is given by the Hamiltonian

$$H_p=\sum_{n=1}^{N}\frac{d_0}{2}(y_{n+1}-y_n)^2/l^2,\quad d_0=\text{const}\,, \tag{2}$$

where l is the interlattice distance assumed to be large on the atomic scale by very small on the macroscopic scale and $N=[l^{-1}]$, the integer part of l^{-1}. The continuum, final coarse-graining limit, corresponds to setting $l\searrow 0$ ($N\nearrow\infty$), $d_0=al$. Rather than to take this limit, I shall show how the continuum can be gradually approached. To this end I rewrite (2) as

$$H_p=\frac{d_0}{2}\sum_{n=1}^{N}(y_{n+1}^2-2y_ny_{n+1}+y_n^2)/l^2$$
$$=-\frac{d_0}{2}\sum_{n=1}^{N}y_n\Delta_D y_n\,,$$

where

$$\Delta_D y_n\equiv(y_{n+1}-2y_n+y_{n-1})/l^2$$
$$\equiv\frac{2}{l^2}[\cosh(lD)-1]y_n=L_D D^2 y_n\,,$$

where $D\equiv\partial_x$, and

$$L_D\equiv 2\left[\frac{\cosh(lD)-1}{l^2D^2}\right]=\sum_{n=1}^{\infty}\frac{2}{(2n)!}(lD)^{2(n-1)}\,. \tag{3}$$

Thus

$$H_p = -\frac{d_0}{2}\sum_{n=1}^{N} y_n L_D y_{nxx} = \frac{d_0}{2}\sum_{n=1}^{N} y_{nx} L_D y_{nx}\,. \quad (4)$$

Representation (4) is crucial for further development. L_D is a pseudodifferential operator represented in the Fourier space by $(D \leftrightarrow ik)$

$$\hat{L}_D(k) = \frac{4\sin^2(kl/2)}{l^2k^2}\,. \quad (3')$$

The continuum corresponds to taking $\hat{L}_D \equiv 1$. However, meaningful extension of this limit cannot be obtained via truncation of the Taylor expansion at any finite level. For instance, up to a second term, the expansion of $\hat{L}_D \simeq 1 - l^2k^2/12$ and leads to the exploding Hamiltonian

$$H_p \simeq +\frac{d_0}{2}\sum_{n=1}^{N}\left[(y_{nx})^2 - \frac{l^2}{12}(y_{nxx})^2\right]. \quad (5)$$

The third-order approximation, while positive as $k \to \infty$

$$\hat{L}_D \simeq 1 - \frac{l^2}{12}k^2 + \frac{l^4}{360}k^4\,, \quad (6)$$

still has a band of unstable k's. It predicts artificial energetically lower states absent in the discrete predecessor. This situation prevails no matter how accurately we may try to approximate $\hat{L}_D$ with polynomials.

The essence of the difficulty in bridging the gap between the discrete system and the continuum is the inability of polynomial approximants induced by the Taylor expansion to reproduce the global boundedness of $\hat{L}_D$ for all k's. To recover this crucial property instead of (6) we adopt

$$\hat{L}_D = \hat{L}_A + O(l^4)\,, \quad (7a)$$

where

$$\hat{L}_A = \frac{1}{1 + k^2l^2/12}\,, \quad (7b)$$

which closely approximates $\hat{L}_D$ for $k < 1/l$ and preserves its boundedness for all k's. Preservation of boundedness (both from below and above) will appear as a crucial theme in our work. It is achieved by introduction of a *nonlocal* approximant $\hat{L}_A$. [Clearly the choice of $\hat{L}_A$ is nonunique; $\exp(-k^2l^2/12)$ is another possibility; however, both are equivalent up to $O(l^4)$]. In addition to its simplicity, the usefulness of our choice lies in the ease in which the act of $\hat{L}_A$, a Lorentzian, can be reexpressed by local means (see below). In Eq. (4) we thus write

$$H_p = -\tfrac{1}{2}\sum_{n=1}^{N} d_0 y_n L_D y_{nxx} = \sum_{n=1}^{N} h_n l + O(l^4)\,, \quad (8)$$

where $\alpha = d_0/l$ and h_n is the Hamiltonian density, i.e.,

$$h_n = -\tfrac{1}{2}\alpha y_n L_A y_{nxx} = \tfrac{1}{2}\alpha y_{nx} L_A y_{nx}\,. \quad (9)$$

Since l is small on a macroscopic scale, we change $y_n \to y$ and

$$H_p = \sum_{n}^{[l^{-1}]} h_n l \to \int \tfrac{1}{2}\alpha(y_x L_A y_x)dx\,.$$

Away from the infrared limit, we can use the usual interpretation of the link between the free energy and the underlying Hamiltonian and write the extended free-energy functional as

$$F = \int dx[f_0(y) + \tfrac{1}{2}\alpha(y_x L_A y_x)]\,, \quad (10)$$

where, in 1D,

$$L_A y_x \equiv \frac{1}{2\epsilon}\frac{\partial}{\partial x}\int_{-\infty}^{\infty} e^{-|x-\xi|/\epsilon} y(\xi)d\xi, \quad \epsilon^2 = l^2/12\,. \quad (11)$$

Expression (10) contains in its maximum simplification the essence of our extension; a generalized quadratic form replaces the classical one. Its main impact is to soften the high-k content of the free-energy functional. Since L_A contains l, a trace of its microscopic origin, (10) is not a genuine continuum but rather a quasicontinuum. To convert the effect of L_A into local terms, minimize F and hit it with $1 - \epsilon^2\partial_x^2$

$$(1 - \epsilon^2\partial_x^2)\frac{\delta F}{\delta y} = -\frac{\partial^2}{\partial x^2}[\alpha y - \epsilon f_0'(y)] + f_0'(y) = 0\,. \quad (12)$$

The same applies in the dynamic approach to equilibrium via

$$\tau y_t = -(-\partial_x^2)^{\nu}\frac{\delta F}{\delta y}, \quad \tau = \text{const}\,, \quad (13)$$

and $\nu = 0, 1$, depending whether y is $(\nu = 1)$ or is not $(\nu = 0)$ a conserved quantity (model *B* and *A*, respectively, in the terminology of Ref. 5). In a localized form, Eq. (13) reads

$$\tau y_t = \tau\epsilon^2 y_{xxt} + (-\partial_x^2)^{\nu}\{f_0'(y) - [\alpha y - \epsilon^2 f_0'(y)]_{xx}\}\,. \quad (14)$$

Equation (14) is the extended, time-dependent, Landau-Ginzburg equation. The conserved, $\nu = 1$, case in the continuum limit is also known as the (1D) Cahn-Hilliard equation which describes the spinodal decomposition of binary mixture. In the latter case, however, the meaning of ϵ^2 changes as will be explained shortly. The impact of finite ϵ on the linear phase of evolution is given via $[t \to -\lambda, f_0'(y) \to f_{0,0}'y]$

$$-\lambda\tau = \frac{k^{2\nu}[f_{0,0}' + k^2(\alpha - \epsilon^2 f_{0,0}')]}{1 + \epsilon^2k^2} \quad (15)$$

showing that the diffusion of short wavelengths is slowed down. Note that for $f_{0,0}' < 0$ there is a band of unstable wavelengths which leads to formation of spatiotemporal patterns. The time-dependent Landau-Ginzburg equation in its various generalizations is known to exhibit a variety of complex patterns and even a chaotic behavior.[2] Its extended version with its prototype given by (14) will also exhibit a complex behavior. But while the appearance of time-dependent, high-gradient domains contradicts the basic assumptions of the Landau-Ginzburg theory, it is consistent with the presented extension.

Extension to multidimensional lattices is straightforward. For instance, for a 2D rectangular lattice

$$H_p = \sum_{m,n}^{N}[\tfrac{1}{2}(y_{n,m+1} - y_{n,m})^2 + \tfrac{1}{2}(y_{n+1,m} - y_{n,m})^2]l^{-2}\,. \quad (16)$$

We obtain

$$f(y)=f_0(y)+\frac{\alpha}{2}(\nabla_y\cdot\underline{L}_{A_2}\cdot\nabla_y)\,, \tag{17}$$

where now

$$\underline{L}_{A_2}=\begin{pmatrix}a_1 & 0\\ 0 & a_2\end{pmatrix}, \tag{18}$$

$$\hat{L}_{A_x}=a_1=(1+\epsilon^2k_x^2)^{-1}\,,$$

$$\hat{L}_{A_z}=a_2=(1+\epsilon^2k_z^2)^{-1}\,. \tag{19}$$

In a nonrectangular 2D lattice, a_i's take the form

$$a_1^{-1}=1+\beta_0k_x^2+\beta_1k_z^2,\quad a_2^{-1}=1+\gamma_0k_x^2+\gamma_1k_z^2\,, \tag{20}$$

with the specific form of β_i's and γ_i's being dependent on the particular lattice chosen. Note that with $\underline{L}_A\neq\underline{I}$ anisotropy enters explicitly into the system which thus loses its rotational invariance. This is an *essential* anisotropy that cannot be scaled out (as opposed to a nonessential anisotropy introduced into gradients via say $\alpha\phi_x^2+\beta\phi_z^2$).

A related topic is that of strain energy which is often introduced via second-neighbor interactions.[6] In 1D, in addition to the right-hand side of (2), one has

$$\frac{d_1}{2}\sum_{n=1}(y_{n+1}-2y_n+y_{n-1})^2/l^4\,, \tag{21}$$

which in terms of L_A is rewritten as

$$\frac{d_1}{2}\sum_{n=1}^{N}(y_nL_D^2y_{nxxxx})=\frac{d_1}{2}\sum_{n=1}^{N}(y_{nxx}L_D^2y_{nxx})=\int\frac{\beta}{2}(y_{xx}L_A^2y_{xx})dx+O(l^4),\quad \beta=d_1/l\,. \tag{22}$$

The continuum level provides the strain energy (density) $\beta y_{xx}^2/2$ which measures the rigidity (resistance to bending) of a 1D lattice. In higher dimensions care must be taken to ensure that the continuum reduction is invariant under rotation. In 2D we have (β and γ are constants)

$$\tfrac{1}{2}\int[\beta(y_{xx}L_{A_x}^2y_{xx})+2\beta\gamma(L_{A_x}y_{xx})(L_{A_z}y_{zz})+\gamma(y_{zz}L_{A_z}^2y_{zz})]dx\,dz\,.$$

Consider now a hyper-rectangular Bravais lattice $S^{(d)}$ for which we define a set of spin variables $\phi(\mathbf{x})$ ($\mathbf{x}\in S^{(d)}$). If $\phi(\mathbf{x})$ is restricted to the values $\{\pm 1\}$, then the Hamiltonian

$$H=\tfrac{1}{2}\sum_{x,x'}J(\mathbf{x}-\mathbf{x}')\phi(\mathbf{x})\phi(\mathbf{x}')-\sum_{\mathbf{x}}W(\phi(\mathbf{x}))\,, \tag{23}$$

describes an Ising system; W is generally assumed to be an even fourth-order polynomial. More generally, we allow the spin to vary continuously over a real domain. Note that if S_N is a lattice domain and S_N^* its dual, then[7]

$$\sum_{x,x'(\in S_N)}\int J(\mathbf{x}-\mathbf{x}')\phi(\mathbf{x})\phi(\mathbf{x}')=N^{-1}\sum_{\mathbf{k}(\in S_N^*)}\hat{J}(\mathbf{k})\hat{\phi}(\mathbf{k})\hat{\phi}(-\mathbf{k})\,,\qquad N^{-1}\sum_{\mathbf{k}(\in S_N^*)}\hat{\phi}(\mathbf{k})\hat{\phi}(-\mathbf{k})=\sum_{\mathbf{x}(\in S_N)}[\phi(\mathbf{x})]^2\,.$$

Next write the Fourier transform

$$\hat{J}(\mathbf{k})=\sum_{\mathbf{x}(\in S_N)}J(\mathbf{x})e^{-i\mathbf{k}\cdot\mathbf{x}}=\sum_{\mathbf{x}(\in S_N)}J(\mathbf{x})+\sum_{\mathbf{x}(\in S_N)}J(\mathbf{x})[\cos(\mathbf{k}\cdot\mathbf{x})-1]-i\sum_{\mathbf{x}(\in S_N)}J(\mathbf{x})\sin(\mathbf{k}\cdot\mathbf{x})\,.$$

The first term will add to the self-interacting part, the impact of the last term will vanish if J is reflective through an axis [$J(\mathbf{x})=J(\mathbf{x}')$]. The second term in the low-**k** limit yields the Landau-Ginzburg approximation. My regularization yields

$$\hat{J}(\mathbf{k})=\sum_{\mathbf{x}(\in L_N)}J(\mathbf{x})-\tfrac{1}{2}\sum_{\mathbf{x}(\in L_N)}J(\mathbf{x})\hat{L}_{A_d}(\mathbf{k}\cdot\mathbf{x})(k_1^2\mathbf{x}_1^2+\cdots+k_d^2\mathbf{x}_d^2)+O(l^4)\,.$$

In the simplest case of an isotropic nearest-neighbor model $J(\mathbf{x})=J$ if $|\mathbf{x}|=l$ and zero otherwise and we have

$$\tfrac{1}{2}\sum_{\mathbf{x},\mathbf{x}'}J(\mathbf{x}-\mathbf{x}')\phi(\mathbf{x})\phi(\mathbf{x}')=dJ\sum_{\mathbf{x}}[\phi(\mathbf{x})]^2-\frac{l^2J}{2}\sum_{\mathbf{x}}(\nabla_d\phi\cdot\underline{L}_{A_d}\cdot\nabla_d\phi)\,.$$

Incorporating $[\phi(\mathbf{x})]^2$ into $W(\phi(\mathbf{x}))$ we have ($J_*\equiv l^2J$)

$$H=\sum_{\mathbf{x}(\in S_N)}\left[\frac{J_*}{2}(\nabla_d\phi\cdot\underline{L}_{A_d}\cdot\nabla_d\phi)-W(\phi(\mathbf{x}))\right]. \tag{24}$$

Genuine continuum corresponds to $N\nearrow\infty$, $\underline{L}_A\searrow\underline{I}$, and $\sum\rightarrow\int$. In the quasicontinuum extension, we rescale W and J_* by lattices volume, and set $\sum\rightarrow\int d^dx$.

We now turn to the extension of Landau-Ginzburg (and van der Waals) theory to liquids. I consider only the simplest case of binary interactions and as a departing point follow Abraham[8] that takes

$$f(\rho)=f_0(\rho)+\tfrac{1}{2}\rho\int[\rho(\mathbf{r}+\mathbf{r}')-\rho(\mathbf{r})]C(\mathbf{r}',\rho(\mathbf{r}))d\mathbf{r}'\,, \tag{25}$$

here ρ, the fluid density, is the order parameter, C is essentially the binary correlation isotropic function of inhomogeneous fluid, and $\mathbf{r}'$ is the interaction distance, $\mathbf{r}_{12}$. Equation (25) is typical. Similar forms are summarized in Ref. 9. In

Ref. 8 the form (25) was the starting point for numerical studies. In contrast, expanding the integrand and integrating over the solid angle I have

$$\int [\rho(\mathbf{r}+\mathbf{r}')-\rho(\mathbf{r})]C(r',\rho)dr' = \frac{1}{3!}A_1(\rho)\nabla^2\rho + \frac{1}{5!}A_2(\rho)\nabla^4\rho + \cdots , \tag{26}$$

where

$$A_i = -\int |\mathbf{r}'|^{(2i)}C(r',\rho)d\mathbf{r}', \quad i=0,1,2,\ldots, \tag{27}$$

Assume first that C is adequately shielded to ensure the existence of at least the two first moments A_1 and A_2. The classical van der Waals theory results if only A_1 is kept. As before, a direct addition of $A_2\nabla^4\rho$ is disastrous. To restore the boundedness of the integral expression (27), I write

$$\int [\rho(\mathbf{r}+\mathbf{r}')-\rho(\mathbf{r})]C(r',\rho)dr' = \frac{A_1}{3!}\frac{\nabla^2}{1-\beta^2\nabla^2}\rho + \cdots , \tag{28}$$

where $\beta^2 \equiv A_2/A_1$ is the ratio of the fourth to second moments. If β^2 is assumed to be constant (which is the case in the low-density limit), the denominator can be understood operatorically via Fourier space convolution. Thus

$$\underline{L}_A = (1-\beta^2\nabla^2)^{-1}\underline{I}, \quad \hat{\underline{L}}_A(\mathbf{k}) = (1+\beta^2\mathbf{k}^2)^{-1}\underline{I} . \tag{29}$$

In 3D this is a shielded Coulomb potential. Thus

$$f(\rho) = f_0(\rho) + \frac{A_1}{12}(\nabla\rho\cdot\underline{L}_A\cdot\nabla\rho) \tag{30}$$

generalizes in a simple and natural way the van der Waals theory for fluids. In deriving the last result I have assumed the existence of the fourth moment of C which determines A_2. However, if the potential entering into C is unscreened (say the Lennard-Jones potential), the fourth moment diverges and A_2 does not exist. To circumvent this difficulty consider the behavior of the integral for large k. If $\rho(\mathbf{r}) = \rho_k \exp(i\mathbf{k}\cdot\mathbf{r}) + \rho_0$, then

$$\int [\rho(\mathbf{r}+\mathbf{r}')\rho - (\mathbf{r})]Cd\mathbf{r}'$$

$$\Longrightarrow \rho_k \int [\cos(\mathbf{k}\cdot\mathbf{r}')-1]C(\mathbf{r}',\rho_0(r))d\mathbf{r}' \equiv \rho_k(R+A_0) .$$

If C is bounded, then by Riemann's theorem

$$\lim_{k\to\infty} R = \lim_{k\to\infty}\int \cos(\mathbf{k}\cdot\mathbf{r}')C(r',\rho,(r))d\mathbf{r}' = 0 . \tag{31}$$

Thus A_0, which is bounded, is the high-**k** limit. Clearly, the classical gradient theory misses the saturation of the high-**k** content. To achieve the uniform boundedness in **k**, I redefine β in (29) as

$$\beta^2 = A_1/A_0 . \tag{32}$$

Thus, in the leading approximation the low-**k** behavior of the integral has been tied into its exact asymptotic value as $|\mathbf{k}| \nearrow \infty$. Even when A_2 does exist, in the simplest regularization of high gradients, it seems preferable to calculate precisely the high-**k** limit rather than to improve the precision of the intermediate-**k** content via the use of A_2 that comes at the expense of the precise high-**k** limit. In fact, with $\beta^2 = A_2/A_1$ the limit at infinity is A_1^2/A_2 which usually differs from the exact limit A_0.

Last, consider the structure factor $S(k)$. We have

$$S(k) = \frac{V}{\rho_0}\langle|\rho_k|\rangle = \frac{KT}{\rho_0(f''_{0,0}+2A_1k^2\hat{L}_A)} , \tag{33}$$

where V is the volume and ρ_0 is the linearized value of ρ. For $\hat{L}_A \equiv 1$ (i.e., $\beta\equiv 0$) we recover the classical result due to Ornstein-Zernike theory. Note that at the critical point ($f'_{0,0}=0$, $T\to T_c$, $\rho_0\to\rho_{0c}$)

$$S(k) \to \left(\frac{KT_c}{2\rho_{0c}A_1}\right)\frac{1+\beta^2k^2}{k^2} , \tag{34}$$

which diverges classically as $k \searrow 0$ but saturates with k as $k \nearrow \infty$.

In conclusion, we have shown that the LG theory may be extended in a simple way to high-gradient zones, by replacing the gradient-dependent part of the free energy with the quadratic form $(\nabla\phi\cdot\underline{L}_A\cdot\nabla\phi)$ that properly interpolates between the microscopic and the macroscopic descriptions.

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