General Criteria for the Stability of Uniaxially Ordered States of Incommensurate-Commensurate Systems

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Reconsidering the variational procedure for uniaxial systems modeled by continuous free energy functionals, we derive new general conditions for thermodynamic extrema. The utility of these conditions is briefly illustrated on the models for the classes I and II of incommensurate-commensurate systems. [S0031-9007(97)04969-7]

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Numerous materials which are under intense investigations in the contemporary condensed matter physics are thermodynamically one dimensional. The well-known examples are various uniaxial materials with incommensurate and commensurate orderings [1] and quasi-one-dimensional conductors with charge or spin density wave instabilities [2]. Order parameters for such systems are generally multicomponent, $\mathbf{u} = (u_1, u_2, \dots, u_N)$, and depend on a single spatial variable x. The principal task is then to find thermodynamically stable configurations $\mathbf{u}_c(x)$, those which minimize the free energy functional $\mathcal{F}$. Since the latter is the one-dimensional integral, it is tempting to treat this variational problem as an equivalent to the standard classical mechanical one [3], with the roles of time variable, vectors in the N-dimensional mechanical configuration space, action functional, and Lagrangian attributed to $x, \mathbf{u}, \mathcal{F}$, and f, respectively, the latter being the free energy density.

In the present Letter we do not follow this widely accepted attitude, but start from two obvious, yet substantial, differences between these two variational schemes. The first one is present in the very extremalization procedure. In contrast to the classical mechanical trajectories, the realizable solutions of the Euler-Lagrange (EL) equations for thermodynamic problems follow after an additional extremalization with respect to the initial (or boundary) conditions. The second difference concerns the content of the free energy densities. In the most interesting models for incommensurate-commensurate (IC) systems, including the basic ones, they contain either terms linear in the first derivatives $\mathbf{u}' = (u_1', u_2', \dots, u_N')$, or terms with higher derivatives $\mathbf{u}^{(j)} \equiv \frac{\partial^j \mathbf{u}}{\partial x^j}$ ($j > 1$) (or both), in contrast to the standard mechanical Lagrangians which do not contain analogs of such terms.

Starting from the first observation, we reformulate the procedure of thermodynamic extremalization, and derive, under assumptions specified below, the following necessary conditions for any thermodynamic extremum $\mathbf{u}_c$.

Condition A:

$$\frac{1}{L} \int_0^L \left[\sum_{\alpha=1}^{N} \sum_{j=1}^{n} j\, u_{c,\alpha}^{(j)} \frac{\partial f}{\partial u_{c,\alpha}^{(j)}} - x \frac{\partial f}{\partial x} \right] dx = 0\,, \tag{1}$$

where n is the order of highest derivative of $\mathbf{u}$ present in the free energy functional, and L is the length of the system taken in the thermodynamic limit $L \to \infty$. In particular, for free energy densities which do not depend explicitly on x the condition (1) reduces to the simple equality

$$F_c + H = 0\,, \tag{2}$$

where F_c is the averaged value of free energy and H is the integral constant which has the meaning of Hamiltonian in the equivalent classical mechanical problem (but does not have a direct physical meaning in the thermodynamic counterpart).

Conditions B:

$$\frac{1}{L} \int_0^L \sum_{j=0}^{n} u_{c,\alpha}^{(j)} \frac{\partial f}{\partial u_{c,\alpha}^{(j)}}\, dx = 0\,, \tag{3}$$

where $\alpha = 1, \dots, N$.

The ensuing discussion will show that in the case of thermodynamic functionals of the standard "mechanical" form the conditions (1) and (3) are of almost trivial meaning. They, however, have far-reaching implications just in IC models, for which, as was already pointed out, free energy densities depend in more complex ways on derivatives $\mathbf{u}^{(n)}$. These conditions also appear to be a powerful tool in the numerical determination of phase diagrams, particularly for systems with nonintegrable free energy functionals.

In order to derive the conditions A and B we start from the general expression for the free energy functional

$$\mathcal{F} = \frac{1}{L} \int_0^L f\Big[\mathbf{u}(x), \mathbf{u}'(x), \mathbf{u}''(x), \dots, \mathbf{u}^{(n)}(x); x\Big] dx\,, \tag{4}$$

where f is an analytical function of its arguments, bounded from below. Each thermodynamic extremum $\mathbf{u}_c(x)$ of this functional has to obey the variational condition $\delta\mathcal{F}(\{\mathbf{u}_c\}) = 0$, equivalent to the Hamilton variational principle in classical mechanics. This necessary condition leads to the EL equations

$$\sum_{j=0}^{n}(-1)^j \frac{d^j}{dx^j}\frac{\partial f}{\partial u_\alpha^{(j)}} = 0 \qquad (\alpha = 1,\ldots,N), \tag{5}$$

equivalent to the Lagrange equations in classical mechanics. The solutions of the EL Eqs. (5) form a set $\{\mathbf{u}(x;\mathcal{A})\}$ which generally depends on $2nN$ continuous parameters $(a_1,\ldots,a_{2nN}) \equiv \mathcal{A}$. There is a freedom in the definition of the parameters $\mathcal{A}$, the most usual choices being initial conditions $[\mathbf{u}(x_0), \mathbf{u}'(x_0), \ldots, \mathbf{u}^{(2n-1)}(x_0)]$ where x_0 is an arbitrary initial spatial position, and boundary conditions $[\mathbf{u}(x_1), \mathbf{u}'(x_1), \ldots \mathbf{u}^{(n-1)}(x_1); \mathbf{u}(x_2), \mathbf{u}'(x_2), \ldots \mathbf{u}^{(n-1)}(x_2)]$ where x_1 and x_2 are arbitrary end points. In classical mechanics these two choices correspond to the Newton and the Hamilton (variational) axiomatizations, respectively. Thermodynamic extrema, including thermodynamically stable configurations for which $\delta^2\mathcal{F} \geq 0$, are those members of the set $\{\mathbf{u}(x;\mathcal{A})\}$ which extremalize the free energy $\mathcal{F}(\{\mathbf{u}(x;\mathcal{A})\})$ as a function of the parameters $\mathcal{A}$. This additional property completes, together with the EL Eqs. (5), the sufficient condition for thermodynamic extrema. In particular, a configuration which fulfills the conditions $\delta\mathcal{F} = 0$ and $\delta^2\mathcal{F} \geq 0$ is thermodynamically stable only if it is also a minimum in the set $\{\mathbf{u}(x;\mathcal{A})\}$.

The dependence of $\mathcal{F}(\{\mathbf{u}(x;\mathcal{A})\})$ on the parameters $\mathcal{A}$ is generally intricate. It may be at least partly nonanalytic, as is usually the case for the functionals (4) with nonintegrable EL equations [4], and in particular for those with free energy densities f which are explicitly x dependent. Thus, there is no efficient general way to extract local extrema of $\mathcal{F}$ from the set $\{\mathbf{u}(x;\mathcal{A})\}$. However, we can now conveniently reformulate the above proposition that the thermodynamic extrema follow from the succession of the first order variation (5) and the extremalization with respect to the parameters $\mathcal{A}$, into an equivalent, and again sufficient, requirement that the solutions of the EL equations are thermodynamic extrema if they are local extrema in the set $\{\mathbf{u}(x)\}$ of *all* configurations allowed by the functional (4). By this enlargement of the set within which we are looking for the local extrema $\mathbf{u}_c(x)$, we get a freedom to choose arbitrarily (and suitably) the parameters with respect to which the set $\{\mathbf{u}(x)\}$ is analytic and corresponding extremalizations reduce to simple differentiations. This freedom will be partly exploited here, by making two choices of continuous parameters which will lead to the conditions A and B.

The first continuous parameter is introduced in the following way. Let us take one thermodynamic extremum, $\mathbf{u}_c(x)$, and define a set of functions $\{\mathbf{u}(x;q)\}$ by

$$\mathbf{u}(x;q) \equiv \mathbf{u}_c(qx). \tag{6}$$

The free energy functional (4) for this set becomes a function of q given by

$$\mathcal{F}(\{\mathbf{u}(x;q)\}) \equiv F(q) = \frac{1}{qL}\int_0^{qL} f\Big[\mathbf{u}_c(z), q\mathbf{u}_c'(z), q^2\mathbf{u}_c''(z), \ldots, q^n\mathbf{u}_c^{(n)}(z); q^{-1}z\Big]\,dz, \tag{7}$$

with $z \equiv qx$ and $\mathbf{u}_c^{(j)}(z) \equiv \partial\mathbf{u}_c^j(z)/\partial z^j$. The requirement that $\mathbf{u}_c(x)$ is an extremum in the set $\{\mathbf{u}(x;q)\}$ is expressed by

$$[\partial F(q)/\partial q]_{q=1} = 0, \tag{8}$$

provided $F(q)$ is a smooth function of q for $q \cong 1$. Let us also take the thermodynamic limit $L \to \infty$ and assume that $F(q)$ then does not depend on L [up to the corrections of the order $\mathcal{O}(1/L)$]. Under these assumptions, which will be critically examined later on, $F(q)$ may depend on q through only the density f in Eq. (7). The latter is an analytic function of q since it is analytic with respect to $\mathbf{u}', \ldots, \mathbf{u}^{(n)}$ by assumption. The derivative $\partial F(q)/\partial q$ is then well defined and the requirement (8), applied onto the function (7), gives the condition A, Eq. (1).

The further simplification takes place for the functionals (4) in which the free energy density does not depend explicitly on x. Then, as in classical mechanics, there exists an integral constant (Hamiltonian),

$$H = -f + \sum_{\alpha=1}^{N}\Bigg[\sum_{i=1}^{n} u_\alpha^{(i)}\frac{\partial f}{\partial u_\alpha^{(i)}} - \sum_{i=2}^{n}\sum_{j=0}^{i-2}(-1)^j u_\alpha^{(i-j-1)}\frac{d^{j+1}}{dx^{j+1}}\frac{\partial f}{\partial u_\alpha^{(i)}}\Bigg], \tag{9}$$

for each solution of the EL Eqs. (5). Using the obvious identity $H = \frac{1}{L}\int_0^L H\,dx$, and the identity

$$\frac{1}{L}\int_0^L\left(u^{(k)}\frac{d^l}{dx^l}g\right)dx = \frac{1}{L}\left[\sum_{m=0}^{l-1}(-1)^m u^{(k+m)}\frac{d^{l-m-1}}{dx^{l-m-1}}g\right]_0^L + (-1)^l\frac{1}{L}\int_0^L\left(u^{(k+l)}g\right)dx, \tag{10}$$

which follows after l successive partial integrations of the left-hand side, one reduces the expression (9) to

$$H = -F_c - \frac{1}{L}\sum_{\alpha=1}^{N}\left[\sum_{i=2}^{n}\sum_{j=0}^{i-2}\sum_{k=0}^{j}(-1)^{j+k}u_\alpha^{(i-j+k-1)}\frac{d^{j-k}}{dx^{j-k}}\frac{\partial f}{\partial u_\alpha^{(i)}}\right]_0^L + \frac{1}{L}\int_0^L\sum_{\alpha=1}^{N}\sum_{j=1}^{n} j\,u_\alpha^{(j)}\frac{\partial f}{\partial u_\alpha^{(j)}}\,dx. \tag{11}$$

Here g in Eq. (10) is identified with $\partial f/\partial u_\alpha^{(i)}$ from Eq. (9), and $F_c \equiv \mathcal{F}(\{\mathbf{u}_c\})$. The second term on the right-hand side in Eq. (11) is negligible in the limit $L \to \infty$, provided $\mathbf{u}_c(x)$ and its derivatives are finite. All thermodynamically stable extrema have this property since f is bounded from below. The third term vanishes for each thermodynamic extremum due to the condition (1). The expression (11) thus reduces to the condition A, Eq. (2).

The equality (2) is the consequence of the invariance of the functional (4) with respect to translations in x, and of its noninvariance with respect to the changes of x scale. As in classical mechanics, the former invariance ensures the existence of the integral constant H and the degeneracy of the solutions of EL equations with respect to the choice of "initial position" x_0. The number of parameters on which the set $\{\mathbf{u}(x;\mathcal{A})\}$ explicitly depends is then $2nN - 1$. Note that for all nontrivial functionals (4) one has $N \geq 1$ and $n \geq 1$, so that $2nN - 1 \geq 1$. In the simplest nontrivial case $N = n = 1$ the set $\mathcal{A}$ has one parameter, i.e., just H.

For functionals (4) with an explicit x dependence of f, the insertion of the EL Eqs. (5) into the expression (1) leads to the relation $F_c = -H(L)$, where $H(L)$ is given by the, now x dependent, expression (9) at $x = L$. Since the right-hand side in this relation depends on L, it is inconsistent with at least one of two assumptions on the analyticity of $F(q)$ specified below Eq. (8). We come to the conclusion that whenever the free energy density depends explicitly on x, all thermodynamic extrema are isolated nonanalytical points of the corresponding functional (4) with respect to changes of x scale. This fundamental property is the reason why the condition A does not hold for such functionals.

Our second choice of continuous parameters from the set $\{\mathbf{u}(x)\}$ is defined by the scaling $u_\alpha \to s_\alpha u_\alpha$ for any $1 \leq \alpha \leq N$. The steps equivalent to those specified by Eqs. (6)–(8) can be repeated now for each α for which $F(s_\alpha)$ is a smooth function. The corresponding conditions

$$[\partial F(s_\alpha)/\partial s_\alpha]_{s_\alpha=1} = 0 \qquad (12)$$

then reduce to the conditions B. Performing partial integrations and inserting EL Eqs. (5) into Eq. (3), one finally gets the conditions

$$\frac{1}{L}\left[\sum_{l=0}^{n-1} u_\alpha^{(l)} \sum_{j=0}^{n-l-1} (-1)^j \frac{d^j}{dx^j} \frac{\partial f}{\partial u_\alpha^{(j+1+l)}}\right]_0^L = 0\,, \qquad (13)$$

which are constraints on the boundary values of the thermodynamic extrema. Note that the boundary ("surface") terms are the leading ones here, in contrast to the condition A in which the analogous terms are only negligible $\mathcal{O}(1/L)$ corrections to the finite volume terms of the order $\mathcal{O}(L^0)$. Obviously, any periodic solution of EL equations satisfies the conditions (13). To this end it suffices to take into account corrections of the order $\mathcal{O}(1/L)$ coming from the boundary terms in conditions A and B, in particular a correction which adjusts the period to be a divisor of L with an integer ratio. No analogous adjustment for the quasiperiodic and nonperiodic solutions is apparent. The conditions (13) are therefore expected to represent restrictive constraints on these solutions as possible candidates for thermodynamic configurations.

The extremalization of the thermodynamic functional (4) with respect to the parameter set $\mathcal{A}$, and its noninvariance with respect to the transformations $x \to qx$ and $u_\alpha \to s_\alpha u_\alpha$, in particular, become short of physical justification when transposed to its mechanical counterpart. For free energy densities which have the form of conservative Lagrangians one has $n = 1$, and the derivatives $u_1', u_2', \ldots, u_N'$ enter only through a positive definite quadratic form ("kinetic energy"). The criterion (2) then singles out only equilibrium points (homogeneous configurations) $\mathbf{u} = \mathbf{cte}$ as possible extrema. For such solutions the condition (8) is trivially fulfilled, since $\mathbf{u}_c(qx)$ and the corresponding free energy $F(q)$ does not depend on q. The same is true for the conditions B which reduce to $[u_\alpha u_\alpha']_0^L = 0$.

As was announced in the introduction, the utility of the conditions A and B becomes apparent for the functionals (4) which have richer dependences on the derivatives of $\mathbf{u}$ and allow for the x-dependent stable configurations. For illustrations we take the basic models for the classes I and II of IC systems [1], defined by [5]

$$f = \frac{1}{2}(\phi' - \delta)^2 - V(\phi) \qquad (14)$$

and [6]

$$f = (u'')^2 - (u')^2 + \lambda u^2 + \frac{1}{2}u^4\,, \qquad (15)$$

respectively.

The decisive term in the model (14) is the Lifshitz invariant $\delta\phi'$. ϕ is the phase variable, so that $V(\phi + 2\pi) = V(\phi)$, the simplest choice being the sine-Gordon model with a single umklapp term, $V(\phi) \propto \cos p\phi$, where p is an integer. The problem (4), (14) is entirely solvable [5,7], since the corresponding EL equation is integrable and the set $\mathcal{A}$ has one parameter, e.g., H. Here we show how the condition A enables an elegant derivation and an original interpretation of the solution. The condition A for the functional (4), (14) reduces to

$$\begin{aligned} 2\pi\delta = I_c &\equiv \int_0^{2\pi} \phi_c'(\phi)\,d\phi \\ &= \int_0^{2\pi} \sqrt{2[-F_c + \delta^2/2 - V(\phi)]}\,d\phi\,. \end{aligned} \qquad (16)$$

The determination of the thermodynamic phase diagram, i.e., of the dependence of F_c on the control parameters present in the model (14), is thus reduced to the calculation of the integral I_c. The relation (16) also states that for a thermodynamic extremum the corresponding mechanical action variable is just equal to the Lifshitz parameter δ!

The dependence of the period P of the stable configuration on control parameters follows from the known relation for mechanical systems with one degree of freedom, $P = \partial I_c/\partial H$ [8]. Finally, the corresponding configuration $\phi_c(x)$ follows from the quadrature of the EL equation with an *already determined value of* H. Thus, using the equality (2) we avoid a more tedious procedure used in the analyses of the models (14) [5,7], namely, the entire integration of the EL equation (with free H) followed by the minimization of the free energy $F(H)$ as a function of H.

Since the transformation (6) already exhausts the freedom in the choice of variational parameters $\mathcal{A}$ for the model (14), the condition B which is now given by $[\phi(\phi' - \delta)]_0^L = 0$, cannot be an additional constraint, but may only reproduce some already derived property of the extremum ϕ_c. This condition states that the configuration ϕ_c has a slope $\phi' = \delta$ at the points $x = 0, P, 2P, \ldots, NP$, where P is a period and N is a large (macroscopic) integer. It indeed follows independently from the EL equation and the condition (16).

Various criteria suggest [9] that the model (15) is nonintegrable due to the presence of the second derivative of the real order parameter u. Very probably $H = (u'')^2 - (u')^2 - 2u'u''' - \lambda u^2 - \frac{1}{2}u^4$ is the only integral constant among three parameters in the set $\mathcal{A}$. The condition A now reads

$$\int_0^L [2(u_c'')^2 - (u_c')^2]dx = 0\,. \tag{17}$$

Without using this condition, we have minimized numerically the functional (4), (15) in the Fourier basis and showed that the phase diagram contains an enumerable set of metastable periodic solutions with homogeneous domains connected by sinusoidal segments [9]. The subsequent check [10] verifies that all these solutions satisfy the condition (17). Furthermore, by using it, one significantly facilitates the numerical calculation of (meta)stable configurations for the model (15). Namely, the search for local minima in the Fourier basis gives, as a rule, continuous families of periodic configurations. In order to find the proper thermodynamic configurations within one family it suffices to determine zeros of the diagonal quadratic form of Fourier components to which the left-hand side of Eq. (17) reduces. By this we directly confirm that the obtained configuration satisfies the EL equation and determines its period. The more detailed presentation of this procedure for the model (15) and its various extensions is given elsewhere [10].

Applying the condition B to the model (15) we obtain an additional constraint on the boundary points,

$$[u'u'' - u(u' + u''')]_0^L = 0\,, \tag{18}$$

which, together with the arguments given below Eq. (13), reinforces the expectation based on the independent numerical analysis [9] that all thermodynamic extrema of the problem (15) are very probably periodic. Note that by conditions (17) and (18) we have fixed two out of three parameters from the set $\mathcal{A}$ for the problem (15). Very probably $\mathcal{F}$ is not analytic for any choice of the remaining third variational parameter, in close connection with the nonintegrability of the EL equation and the corresponding chaotic structure of the portrait in the phase space (u, u', u'', u''').

Having these and other [10] examples in mind, we connect the limitations of the present method with the degree of the nonintegrability of a given functional by the following conjecture: larger is the number of missing integral constants (in the classical mechanical sense), smaller is the number of analytic conditions for the thermodynamic extrema (like those given by conditions A and B).

In conclusion, necessary conditions for uniaxial thermodynamic extrema are obtained from the extremalization with respect to space and order parameter scales. This procedure proves to be feasible for the free energy densities which are not explicitly dependent on the space variable. In particular, we show that in this case the sum of the averaged free energy and the integral constant (Hamiltonian) vanishes for each thermodynamic extremum. Besides their general significance, the present results will be certainly of practical use in analytical and numerical analyses of particular models for uniaxial systems.

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