

Energy Dissipation and Stability of Propagating Surfaces

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Thermodynamic equilibrium states are given by the minimum of a convex free energy function with suitable boundary conditions. Nonconvexity may lead to the coexistence of several phases and the classical Gibbs phase rule allows constructing their equilibrium properties (e.g., density or pressure). Within the framework of nonequilibrium thermodynamics, the maximization of energy dissipation (under suitable boundary conditions) can be used as an extremal principle to find stationary states. We show that stationary states generally exist for convex energy dissipation functions and that nonconvexity leads to metastable and unstable states. A geometric argument, similar in spirit to Gibbs' double-tangent construction, yields the stability limits of stationary states. This argument is applied to study a classical problem of materials science, namely the motion of a grain boundary under the influence of solute drag.

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In analogy to the extremum principles in equilibrium thermodynamics, Onsager proposed in 1931 the principle of maximum energy dissipation [1] for the case of heat conduction. This principle has been exploited successfully, e.g., to describe diffusion-controlled processes by Svoboda *et al.* [2–4] and serves as a convenient tool to find evolution equations for the thermodynamic forces. While the minimum of the free-energy function describes an equilibrium state, the maximum of the energy dissipation describes the evolution of a nonequilibrium system. In both cases, the extremum is unique if the thermodynamic function is convex or concave. A much more complicated situation arises if the function is neither convex nor concave, which we simply call nonconvex. In equilibrium thermodynamics, it is well known that a nonconvex free-energy function may lead to sudden phase transformations or to coexistence of several phases, as described in phase diagrams of materials [5]. In this Letter, we explore the possibility of using the principle of maximum energy dissipation for the case of a nonconvex energy dissipation function.

Nonconvex energy dissipation functions can be found in various fields. A prominent example is the hydraulic jump when water flows down uniformly in an open channel; see, e.g., [6], Ch. 10. The observation is that the water depth h changes abruptly when the average fluid velocity v exceeds a critical value. The energy dissipation per unit length of the channel is $Q = \rho ghbv$, where ρ is the fluid density, b the channel width, s the slope of the channel, and g the gravity constant. The momentum conservation in fluid mechanics yields a relation between h and v in the form $gh^2/2 + hv^2 = C$, where C is a constant. Extracting h from this relation leads to the (clearly nonconvex) dissipation function

$$Q(v) = \rho bs(-v^2 + \sqrt{v^4 + 2gC})v. \quad (1)$$

A second example is the solute drag in grain boundary movement in metal alloys, where a moving interface of finite thickness carries segregated impurity atoms with a concentration profile across the interface. Such a local diffusion process, stationary with respect to the moving interface, reduces the migration velocity v of the interface due to the energy dissipated by the local diffusion process. Prominent approaches by Lücke and Stüwe [7], Cahn [8], and Hillert [9,10] are reported in the literature; for reference, see, e.g., Svoboda *et al.* [11]. For certain values of the velocity v , one observes an instability corresponding to a “jerky” motion of the interface, as already discussed by Cahn in his seminal paper [8] in 1962 and later also by other authors [12–14]. The concept by Svoboda *et al.* [11] describes the phenomenon in terms of dissipation and allows for a difference in the chemical potential of the segregating species at both boundaries of the interface and applies an exact solution for the diffusion equation in the case of an interstitial impurity atom. The second dissipative mechanism is the interface motion itself and is directly related to the velocity v by a mobility coefficient M_0 . The total dissipation can be expressed in this case as [11]

$$Q(v) = \frac{v^2}{M_0} + \frac{Q_0 v^2}{v^2 + Q_0/\alpha}, \quad (2)$$

where Q_0 and α are two positive constants. Again, this dissipation function is clearly nonconvex, which might be related to the observed instability in the interface movement.

In the following, we consider an energy dissipation $Q(v)$ depending on a single variable v and where $Q(0) = 0$ and $Q(v) > 0$, for $v > 0$. For example, v may be the velocity of

a moving interface or the velocity in a channel. Moreover, the free energy G of the system is supposed to change at a rate \dot{G} depending linearly on the variable v :

$$\dot{G} = -Fv, \quad (3)$$

where F is the thermodynamic driving force. One may ask the question under which conditions a planar surface moving at constant velocity would be stable. Calling $d\mathcal{A}$ the area element on the surface \mathcal{A} , the stationary state will be found by maximizing the total energy dissipation $\int_{\mathcal{A}} Q(v)d\mathcal{A}$, where $Q(v)$ is the dissipation of a surface element moving at velocity v , under the constraint of total energy conservation

$$\int_{\mathcal{A}} [Q(v) + \dot{G}]d\mathcal{A} = \int_{\mathcal{A}} [Q(v) - Fv]d\mathcal{A} = 0. \quad (4)$$

Introducing the Lagrange parameter λ , this amounts to maximizing $\int_{\mathcal{A}} [Q(v) - \lambda(Q(v) - Fv)]d\mathcal{A}$ or to minimizing $\int_{\mathcal{A}} P(v)d\mathcal{A}$, with respect to the function $v(\vec{x})$, where \vec{x} is a point on the surface \mathcal{A} , and

$$P(v) = (\lambda - 1)Q(v) - \lambda Fv. \quad (5)$$

A planar surface [with $v(\vec{x}) \equiv \bar{v}$] is a solution of this problem if \bar{v} minimizes $P(v)$ and, according to (4), satisfies

$$Q(\bar{v}) = F\bar{v}. \quad (6)$$

Under these conditions, the Lagrange parameter is

$$\lambda = \frac{Q'(\bar{v})}{Q'(\bar{v}) - F}, \quad (7)$$

where we used the notation $Q' = dQ/dv$. Note that, for the special case of a quadratic energy dissipation ($Q(v) \propto v^2$), the coefficient λ is simply equal to 2 [from (7) and using (6)]. In general, inserting (7) into (5) and using (6),

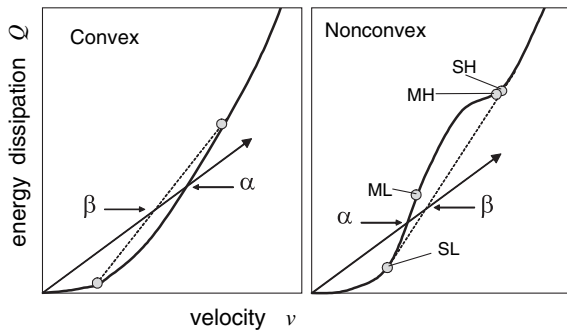


FIG. 1. Schematic plot of the energy dissipation as function of interface velocity. For a convex function (left), the intersection of Fv (arrow) with a chord (broken line) starting at any two positions on $Q(v)$ corresponds to a lower dissipation (β) than the intersection with $Q(v)$ itself (α). This can be reversed for nonconvex functions (right). The convex envelope (broken line) touches the dissipation function at the lower (SL) and higher (SH) limits of stability. ML and MH indicate the lower and the higher limits of metastability.

$$P(v) = -Q(\bar{v})K(v)/K(\bar{v}), \quad (8)$$

where

$$K(v) = Q(v) - vQ'(\bar{v}). \quad (9)$$

This implies that $P(\bar{v}) = -Q(\bar{v})$, $P'(\bar{v}) = 0$, and $P''(\bar{v}) = -Q''(\bar{v})Q(\bar{v})/K(\bar{v})$. If $Q(v)$ is a convex function, then $Q''(\bar{v}) > 0$ and [since $Q(0) = 0$] the convexity also implies that $K(\bar{v}) < 0$. If the function is concave, $Q''(\bar{v}) < 0$ and $K(\bar{v}) > 0$. In both cases, $P''(\bar{v}) > 0$ and \bar{v} minimizes $P(v)$. Hence, for a convex (or concave) energy dissipation function (that is, without an inflection point), a stable state does exist with a constant velocity profile \bar{v} . However, if $Q(v)$ is nonconvex, $P''(\bar{v})$ may take negative values and, as a consequence, the velocity profile may become unstable and split, say, into v_{SL} and v_{SH} . This is illustrated in Fig. 1: if the surface splits into two parts moving at different velocities, the total energy dissipated is given as a linear combination of the contributions by the two parts. This linear combination corresponds to a straight line (shown as broken line) in Fig. 1. The dissipation under a given driving force F can finally be read from the intersection of the broken line with the curve $Q(v) = Fv$ [that is, Eq. (6), shown by long arrows in Fig. 1]. It is obvious from the figure that—in the case of a convex $Q(v)$ —there is always a higher dissipation for the planar surface propagating at constant speed (since $\alpha > \beta$ in the figure), while this is not the case for nonconvex $Q(v)$. This construction shows that stationary states are always located on the convex (or concave) envelope of $Q(v)$, that is, on the straight line being the common tangent which makes Q into a fully convex (or concave) function. Between the lower and the higher limits of stability (SL and SH in Fig. 1, right), a planar surface is not stable and stable propagation is only possible for a surface split into parts moving at speeds v_{SL} and v_{SH} . From the intersection labeled β in Fig. 1, it is possible to calculate the fractions of the surface, λ_{SL} and λ_{SH} , which propagate at velocities v_{SL} and v_{SH} , respectively:

$$\lambda_{SL} = 1 - \lambda_{SH} = \frac{Q_{SH} - Fv_{SH}}{Q_{SH} - Q_{SL} - F(v_{SH} - v_{SL})}. \quad (10)$$

With the stability analysis presented here, we cannot predict how the instability actually develops into the breaking up of the surface into pieces moving at different velocities. It is clear, however, that there is the tendency towards the development of a chaotic (or jerky) motion with different velocities.

This is somewhat analogous to the case of equilibrium thermodynamics [5]: when the free energy $f(c)$ is convex with respect to the thermodynamic variable (for example, the composition c of a solution), then the homogeneous state is stable. If, on the contrary, the free energy is nonconvex (for example, of double-well shape), phase separation (between solutions of different composition) occurs. In such cases, the true equilibrium curve is given by the

convex envelope of the free-energy function. If the starting composition \bar{c} is in an interval of c where the free energy is nonconvex, separation occurs between two phases of composition given by Gibbs' double-tangent construction [15]. The stability of such mixtures has been extensively discussed within the theory of spinodal decomposition proposed by Cahn and Hilliard [16]. According to this analysis, mixtures which are not thermodynamically stable would be clearly unstable if the average composition \bar{c} is such that $f''(\bar{c}) < 0$ and metastable otherwise [15]. It is straightforward to apply the same type of analysis here to the nonequilibrium case, discussing the stability of homogeneous stationary states. The (static) composition variable c has to be replaced by the velocity v , and the free-energy function by the dissipation function.

Indeed, the present theory also predicts metastable states near the stability limits, in analogy to the case of equilibrium mixtures. When looking at Fig. 1 (right), the dissipation function stays locally convex when crossing the point SH from above or SL from below. For the following discussion, we use the notation F_α (with $\alpha = \text{SL, SH, ML, MH}$) to denote the driving force at the lower and higher limits of stability and of metastability, respectively (see Fig. 1). The corresponding velocity v_α is given by the relation (6) $Q(v_\alpha) \equiv Q_\alpha = F_\alpha v_\alpha$. Using these notations, a planar surface separating the two phases and propagating at sufficiently high ($\bar{v} > v_{\text{SH}}$) or low ($\bar{v} < v_{\text{SL}}$) velocity will be stable. When crossing the lower stability limit SL, the flat surface stays metastable, as can be seen from the following analysis. Only large fluctuations are able to drive the planar interface out of its metastable stationary state. Indeed, when there is a small fluctuation of interface velocity $v(\vec{x})$ around the value \bar{v} , then Eq. (8) reduces to

$$P(v(\vec{x})) - P(\bar{v}) \approx P''(\bar{v})(v(\vec{x}) - \bar{v})^2/2, \quad (11)$$

and

$$\int_{\mathcal{A}} [P(v(\vec{x})) - P(\bar{v})] d\mathcal{A} \geq 0 \quad (12)$$

for \bar{v} in the interval between SL and ML, which shows that the planar surface is stable against small fluctuations of velocity.

To discuss the situation in more detail, it is useful to plot the velocity \bar{v} of the stationary state as a function of the externally acting driving force F (see Fig. 2). In this figure the energy dissipation function (Fig. 1) has been replotted using Eq. (6) to show the relation between velocity and driving force. Very similar functions have also been discussed in the context of solute drag in phase boundaries, for example, in [17,18]. Figure 2 shows clearly that—at small driving force—the planar interface is stable. When the driving force reaches the value F_{SL} (which is determined by the double-tangent construction in Fig. 1), the planar interface does not anymore maximize the energy

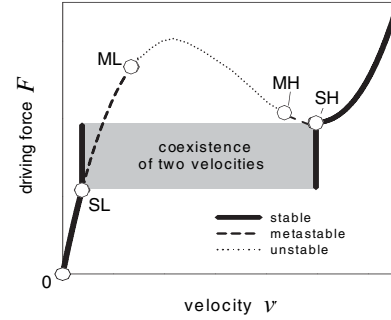


FIG. 2. Relation between driving force and interface velocity for the solute drag problem, based on the energy dissipation function in Fig. 1. Stable, metastable, and unstable branches are shown by full, broken, and dotted lines, respectively. The shaded area indicates the coexistence region of two velocities.

dissipation. As discussed earlier, the stable extremum would be a situation where the interface breaks up into pieces with different velocity, v_{SL} or v_{SH} . This very complex (jerky) motion will, however, only be reached if the planar interface is severely disturbed by a large fluctuation. According to Eq. (8), the planar surface will remain metastable, as long as

$$P''(\bar{v}) = \frac{Q(\bar{v})Q''(\bar{v})}{\bar{v}Q'(\bar{v}) - Q(\bar{v})} \geq 0. \quad (13)$$

For small velocities up to the inflection point ML in Fig. 1, all three quantities, $Q(\bar{v})$, $Q''(\bar{v})$, $\bar{v}Q'(\bar{v}) - Q(\bar{v})$ are positive and the planar interface remains metastable. Metastability is lost at the inflection point because $Q''(\bar{v})$ changes sign. The situation is slightly different when coming from the large velocity side. It is true that after crossing the stability point SH by lowering the speed, the planar surface also remains metastable. However—in the specific example of Fig. 1—metastability is lost because of a change in sign of $\bar{v}Q'(\bar{v}) - Q(\bar{v})$, which occurs before the inflection point is reached. This is why the region of metastability is very small on the large velocity side. In Fig. 2, metastable branches are shown by broken lines. At the large velocity side, the metastable branch is extremely small.

Most earlier theories [8–10,17,18] have studied the solute drag problem in terms of Fig. 2 and discussed the instability based on the fact that, in a certain interval of driving forces, there are two solutions for the velocity. The present treatment, based on an analysis of the dissipation function (Fig. 1), allows an easy calculation of the stability limits (which is very hard from an analysis of Fig. 2 alone) and, in addition, predicts metastable states next to the stability limits.

For comparison, we now also analyze the case of the hydraulic jump, Eq. (1). The shape of the dissipation function is quite different (see Fig. 3). It starts out as a concave function, goes through a maximum at SL, and then has an inflection point at ML. The analysis according to

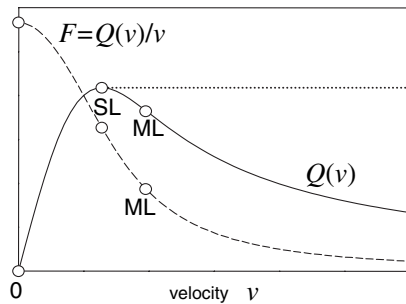


FIG. 3. Schematic plot of Q and F as functions of v according to Eq. (1). The lower stability limit SL corresponds to the maximum of Q and the limit of metastability ML to the inflection point. The convex envelope is shown by a dotted line.

Eq. (8) shows that the flow in the channel corresponds to a stable stationary state at small velocities. The reason is that $Q''(\bar{v}) < 0$ and $K(\bar{v}) > 0$ at small \bar{v} . In fact, $K(\bar{v}) > 0$ for all values of \bar{v} , but $Q''(\bar{v})$ changes sign at the inflection point. As a consequence, the branch $\bar{v} > v_{ML}$ is unstable. The concave envelope of $Q(v)$ is shown by a dotted line in Fig. 3. This line touches the $Q(v)$ curve at the maximum (corresponding to SL) and is horizontal, because the higher limit of stability (SH) is at infinite speed. The maximum position of the curve is given [according to Eq. (1)] as $v_{SL} = (2gC/3)^{1/4}$, and $v_{SH} = \infty$. Inserting this into Eq. (10), it follows that $\lambda_{SL} = 1$ and $\lambda_{SH} = 0$. This means that there is not the coexistence of two stable stationary states in this case, but that stability ends at v_{SL} . For a channel with constant width and slope, one can group all constant quantities into a single one $k = \rho g b s$. Hence, $Q = khv$ and $F = kh$. For large water depths down to $h_{SL} = Q_{SL}/(kv_{SL})$, the flow in the channel is stable. It is metastable for $h_{SL} > h > h_{ML} = Q_{ML}/(kv_{ML})$ and unstable for smaller water depths. The interesting case is the metastable state, where a fluctuation may lead to a sudden increase of the water depth.

In conclusion, we have shown that the principle of maximizing the total energy dissipation can even be applied to complex situations where the dissipation function is non-

convex. In such situations, however, stationary states may become metastable or unstable. Even the coexistence of two stationary states, similarly to the coexistence of two phases in equilibrium thermodynamics, emerges as a possibility. General predictions are difficult as the stability of stationary states depends on the details of the dissipation function and boundary conditions. Here the problem has been solved for two “typical” problems in order to illustrate the procedure.

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