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DYNAMICS OF PHASE TRANSITIONS

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Abstract

Stability of equilibria in first order phase transitions is investigated by Lyapunov's method. If both phases are present then the set of equilibria is strictly asymptotically stable. The 'metastable' states (only one of the phases is present) are unstable states having a peculiar feature.

Keywords: first order phase transition, stability, Lyapunov theory.

1. Introduction

The application of the theory of fluxes and forces to phase transitions has interesting and peculiar features which are worth investigating thoroughly.

First of all let us recall some well known facts. (See e.g., in [1].)

The state of a system consisting of interacting homogeneous bodies is described by a set of extensive variables,

$$x_1, \dots, x_n \,. \tag{1}$$

The fluxes are time rates of the extensive variables,

$$J_k = \dot{x}_k, \qquad k = 1, \dots, n \,. \tag{2}$$

The thermodynamical forces – differences of intensive quantities – are functions of the extensive variables,

$$F_k = \Phi_k(x_1, \dots, x_n) \,. \tag{3}$$

The fluxes are induced by the forces, i.e., they can be given as functions of the forces,

$$J_k = \Theta_k(F_1, \dots, F_n) = \Theta_k(\Phi_1(x_1, \dots, x_n), \dots, \Phi_n(x_1, \dots, x_n)) \tag{4}$$

in such a way that the fluxes are zero if and only if the forces are zero.

Relations (2) and (4) result in a system of differential equations

$$\dot{x}_k = \Gamma(x_1, \dots, x_n) \qquad k = 1, \dots, n \tag{5}$$

which will be written in the following concise form:

$$\dot{x} = \Gamma(x) . \tag{6}$$

Solutions of this dynamical equation are called *processes*. A constant process – i.e., a state – x_* is an equilibrium if and only if the fluxes at x_* are zero, i.e., $\Gamma(x_*) = 0$ (which occurs if and only if the forces are zero at x_*).

The stability properties of equilibria can be examined by Lyapunov's method.

Let us recall that an equilibrium x_* is *stable* if for each neighbourhood N of x_* there is a neighbourhood U of x_* such that for every process r with $r(0) \in U$ we have $r(t) \in N$ for all $t > 0$.

An equilibrium x_* is *asymptotically stable* if it is stable and there is a neighbourhood V of x_* such that for every process r with $r(0) \in V$ we have $\lim_{t\to\infty} r(t) = x_*$.

A set E of equilibria is *strictly asymptotically stable* if

- every equilibrium in E is stable,
- every equilibrium in E has a neighbourhood V such that for every process r with $r(0) \in V$ we have that $\lim_{t\to\infty} r(t)$ is in the closure of E.

Without phase transitions the equilibrium (in a phase) is unique, and

- conditions of intrinsic stability and
- positive entropy production

together imply asymptotic stability which is a mathematical expression for the trend to equilibrium; the present result tells us that every process tends to the unique equilibrium regardless of the initial values ([2], [3] [4]).

It is worth mentioning that the total entropy of the bodies and the environment together is a Lyapunov function for asymptotic stability: the conditions of intrinsic stability ensure that the Lyapunov function has a maximum at the equilibrium and the positive entropy production ensures that the 'total time derivative' of the Lyapunov function has a minimum at the equilibrium.

2. Phase Transitions

The situation is quite different in the case of phase transitions: we shall see that in the investigated system there are different possibilities ([5],[6]):

a) if two phases of the same material are present then the equilibrium is not unique, the set of equilibria is strictly asymptotically stable (which means that processes tend to an equilibrium depending on the initial values),

b) if only one of the phases is present then the equilibrium is unique and is either asymptotically stable or unstable.

Let us consider two bodies in a given environment with constant temperature T_a and pressure P_a; let the two bodies consist of different phases of the same material and suppose that the transition between the phases is of first order.

The state of the system is described by the internal energy, volume and mass of the bodies:

$$(E_1, V_1, M_1, E_2, V_2, M_2)\,. \tag{7}$$

Mass conservation

$$M_1 + M_2 = M_s = \text{const} \tag{8}$$

reduces the number of the independent variables: one of the masses can be disregarded; we shall omit M_2, so we have

$$x = (E_1, V_1, M_1, E_2, V_2)\,. \tag{9}$$

We allow that one of the bodies is 'empty', i.e., has zero mass (and consequently, zero energy and zero volume). Of course, the intensive quantities of such an empty body are not defined, and the force acting on such an empty body is zero. Therefore we assume that the forces have the form

$$\begin{aligned} F \;=\; & \left(\eta(M_1)\left(\frac{1}{T_1} - \frac{1}{T_a}, \frac{P_1}{T_1} - \frac{P_a}{T_a}\right),\quad \eta(M_1 M_2)\left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right),\right. \\ & \left.\eta(M_2)\left(\frac{1}{T_2} - \frac{1}{T_a}, \frac{P_2}{T_2} - \frac{P_a}{T_a}\right)\right), \end{aligned} \tag{10}$$

where

$$\eta(M) = \begin{cases} 1 & \text{if} \quad M \neq 0, \\ 0 & \text{if} \quad M = 0. \end{cases}$$

a) Let us first suppose that $M_1 M_2 \neq 0$. Then (10) implies that equilibrium exists if and only if (T_a, P_a) is on the phase line, i.e.,

$$\mu_1(T_a, P_a) = \mu_2(T_a, P_a) \tag{11}$$

and then the set of equilibria is

$$\{(M_1 e_{1*}, M_1 v_{1*}, M_1, (M_s - M_1)e_{2*}, (M_s - M_1)v_{2*}) \mid 0 < M_1 < M_s\}\;, \tag{12}$$

where the specific internal energies and volumes are uniquely determined by the equations

$$\begin{aligned} T_1(e_{1*}, v_{1*}) &= T_2(e_{2*}, v_{2*}) = T_a\,, \\ P_1(e_{1*}, v_{1*}) &= P_2(e_{2*}, v_{2*}) = P_a\,. \end{aligned} \tag{13}$$

Thus the set of equilibria is a whole line segment; equilibrium is not unique.

Introducing the new notion of strict asymptotic stability of a set of equilibria, we can prove that

- conditions of intrinsic stability and
- positive entropy production

imply the strict asymptotic stability of the set of equilibria in the present case, which means that every process tends to some equilibrium, depending on the initial values.

b) Suppose now that $M_2 = 0$. Then (10) yields that the equilibrium is

$$(M_s e_{1*}, M_s v_{1*}, M_s, 0, 0)\ , \tag{14}$$

where the specific internal energy and volume are uniquely determined by the equations

$$\begin{aligned} T_1(e_{1*}, v_{1*}) &= T_a\ , \\ P_1(e_{1*}, v_{1*}) &= P_a\ . \end{aligned} \tag{15}$$

Again we can prove that

- conditions of intrinsic stability and
- positive entropy production

imply that the equilibrium is asymptotically stable if

$$\mu_1(T_a, P_a) < \mu_2(T_a, P_a) \tag{16}$$

and is unstable if

$$\mu_1(T_a, P_a) > \mu_2(T_a, P_a)\ . \tag{17}$$

Our previous results can be formulated from a different point of view as follows:

If $\mu_1(T_a, P_a) = \mu_2(T_a, P_a)$ then the set of equilibria is the line segment (a connected continuum)

$$\{(M_1 e_{1*}, M_1 v_{1*}, M_1, (M_s - M_1)e_{2*}, (M_s - M_1)v_{2*}) \mid 0 \leq M_1 \leq M_s\} \tag{18}$$

which is strictly asymptotically stable.

If $\mu_1(T_a, P_a) < \mu_2(T_a, P_a)$ then there are two equilibria,

$$(M_s e_{1*}, M_s v_{1*}, M_s, 0, 0) \qquad \text{and} \qquad (0, 0, 0, M_s e_{2*}, M_s v_{2*})\ ; \tag{19}$$

the first is asymptotically stable, the second is unstable.

3. Metastability

States with property (16) are the usual stable states according to classical thermodynamics; states with property (17) are the ones called metastable in classical thermodynamics.

Observe that the notion of metastability is not generally defined in classical thermodynamics and is not introduced in Lyapunov's theory. Now we see that metastable states are unstable in Lyapunov's sense. However, we can find a peculiar feature of this unstability: namely, the hyperplane $M_1 = M_s$ is invariant for the dynamical equation, and restricting the equation to this hyperplane, the state becomes asymptotically stable. This means that if we consider a process in which the other phase is not present, phase transition starts only if a small amount (a 'nucleus') of the other phase appears (by fluctuation).

Thus we can define metastability in general as follows. Suppose the equilibrium is contained in a subset invariant for the dynamical equation. An unstable equilibrium is called metastable with respect to the subset in question, if it becomes a stable equilibrium if we restrict the dynamical equation to that subset.

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