Definition of Thermodynamic Phases and Phase Transitions

There are various thermodynamic variables one can use to describe matter in thermal equilibrium, some of the common ones being: mass or number density ρ, energy density e, temperature T, pressure P, and chemical potential μ (assuming for simplicity that the material is composed of one pure substance, not a mixture such as brass). By definition the states of a "simple" system can be parameterized by two such (independent) variables, in which case the others can be regarded as functions of these. We will assume we are modelling a simple material. Then a particularly good choice for independent variables is T and μ. It is a fundamental fact of thermodynamics that the pressure P is a convex function of these variables, and, in particular, this convexity embodies certain mechanical and thermal stability properties of the system. Moreover, all thermodynamic properties of the material can be obtained from P as a function of T and μ by differentiation.[1] We give the following definitions.

Definitions: A thermodynamic phase of a simple material is an open, connected region in the space of thermodynamic states parametrized by the variables T and μ, the pressure P being analytic in T and μ. Specifically, P is analytic in T and μ at (T_0, μ_0) if it has a convergent power series expansion in a ball about (T_0, μ_0) that gives its values. Phase transitions occur on crossing a phase boundary. See Figure 1.

The graph of $P = P(T, \mu)$ is not only convex but (for all reasonable physical systems) also has no (flat) facets. We use this in our definition of phase; without this property there would typically be open regions of states representing the coexistence of distinct phases. Figure 2 below illustrates how the choice of independent variables can lead to the appearance of domains representing two or more coexisting phases. Note in particular the isothermal (i.e., constant T) "tie lines" connecting the distinct phases that can coexist at the range of overall intermediate densities spanned at a fixed temperature.

The figures also illustrate an intrinsic difference between vapor and liquid "phases", which can be analytically connected, and between these regions of the fluid phase and the solid phase, which cannot be so connected. Note that in these figures failure of the analyticity of the function P occurs on curves in the (T, μ) and (T, ρ) planes. In the modern literature[2] an important distinction is made between "field" variables and "density" variables, which helps to explain various consequences of the choice of independent and dependent variables.

The foregoing constitutes a "thermodynamic" description of phases and phase transitions. There is a deeper description, that of *statistical mechanics*, deeper in that it allows natural ("molecular") models from which one can in principle compute the pressure as a function of T and μ. Statistical mechanics can be based on either quantum or classical mechanics; we will use the latter here for convenience.

In the statistical mechanical description the thermodynamic states are realized or represented as probability measures on a certain space K, the measures still parameterized by thermodynamic variables as above (two variables for our simple system, say, specifically temperature T and chemical potential μ). The space K

is, in a common model of a simple material, the space of all possible positions x and momenta p of infinitely many point particles. We will use the notation $\mathbf{x} = \{x_1, x_2, \ldots\}$ and $\mathbf{p} = \{p_1, p_2, \ldots\}$ to denote the sets of the position and momentum variables for all the particles.

It is valuable, in particular, to consider a finite system of N particles contained in a reasonably shaped domain, say Ω, of volume V. In this case the probability densities, on the disjoint union $\cup_N S_N$ of the $(\mathbf{x}, \mathbf{p})$ spaces $S_N = \Omega^N \times \mathbb{R}^{3N}$ for N particles, are proportional to the weights

$$f_N(T, \mu; \mathbf{x}, \mathbf{p}) = e^{-\beta E_N(\mathbf{x},\mathbf{p})+\beta\mu N}, \tag{1}$$

while the overall normalization constant (or "partition function") is

$$\Xi_V(T, \mu) = 1 + \sum_{N=1}^{\infty} \int d\mathbf{x} d\mathbf{p} f_N(T, \mu; \mathbf{x}, \mathbf{p}), \tag{2}$$

where $\beta = 1/k_B T$, k_B being Boltzmann's renowned constant.

The structure of the energy E_N is determined only when one settles on the type of "interactions" the constituent particles can undergo; that not only depends on the material being modelled but also on what environment (external forces, etc.) one may want to impose on the system. In the simplest case the particles are assumed to interact only among themselves, through some translation invariant "interaction potential" $\varphi(x_i - x_j)$ which decays to zero sufficiently rapidly as the separation $|x_i - x_j| \to \infty$. The "kinetic energy" of the j^{th} particle is, classically, $p_j^2/2m$, m being the mass of the particle. The total energy is then

$$E_N = \sum_j \frac{p_j^2}{2m} + \frac{1}{2} \sum_{i,j:i\neq j} \varphi(x_i - x_j). \tag{3}$$

And the so-called "grand canonical" pressure of the finite-volume system is given by

$$P_V(T, \mu) = \frac{k_B T \ln[\Xi_V(T, \mu)]}{V}. \tag{4}$$

(Note that the convexity of $P_V(T, \mu)$ is ensured by this formulation.) However, it is not hard to see for reasonable interaction potentials φ that the pressure P_V as a function of T and μ is everywhere analytic. Consequently, in order to model a sharp phase transition it is necessary to consider the thermodynamic limit[3]

$$P(T, \mu) = \lim_{V\to\infty} P_V(T, \mu). \tag{5}$$

Then $P(T, \mu)$ may be identified as the thermodynamic pressure to which our definitions of a phase and a phase transition applies.

Footnotes

1. For this reason the function $P(T, \mu)$ is referred to as a "thermodynamic potential". Alternative potentials (for describing the same physical system) follow by Legendre transforms.
2. R.B. Griffiths and J.C. Wheeler, Phys. Rev. A **2** (1970) 1047-1064.
3. The proof of the existence of the thermodynamic limit requires conditions on the interaction potential $\varphi(x)$ for $|x| \to 0$ and $|x| \to \infty$ and on the sequence of domains Ω_k as $V_k \to \infty$ with $k \to \infty$. See M.E. Fisher, Arch. Ratl. Mech. Anal. **17** (1964) 377-410.

Figures

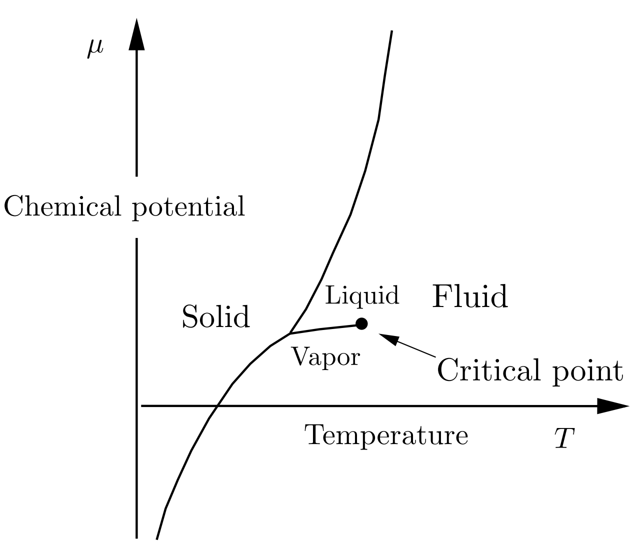

Fig 1. A simple phase diagram in the (μ, T) plane.

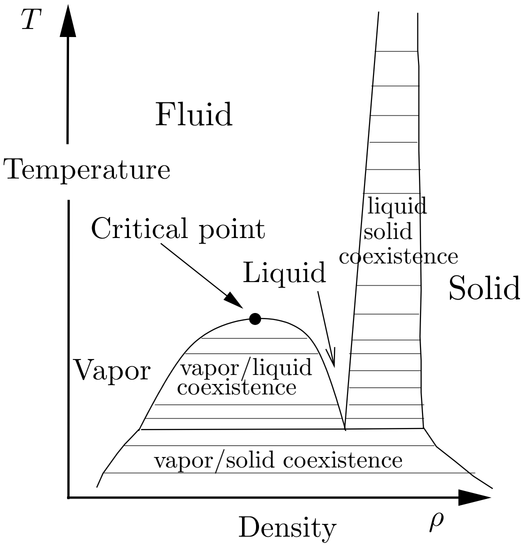

Fig 2. A simple (T, ρ) diagram illustrating coexisting phases.

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