

# Thermodynamics of Phase Transitions I [tsc5]

A pure substance may undergo *abrupt* changes in some state variables when other state variables are varied *gradually*. Phase transitions are associated with singularities in functional relations between state variables.

From a microscopic perspective, phase transitions are the result of a competition between agents of order and agents of disorder:

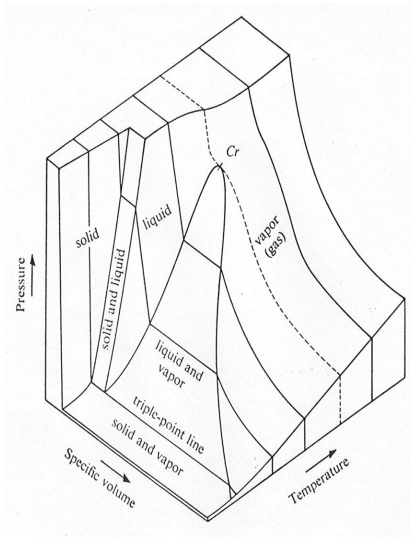
- Agents of order include cohesive forces between atoms and molecules and torques of alignment between electron spins.
- Agents of disorder include thermal fluctuations, structural randomness, and interactions that favor competing ordering tendencies.

Here phase transitions are investigated from a macroscopic perspective. Graphical representations of thermodynamic equations for state of systems with more than one phases are named *phase diagrams*.

## Typical solid-liquid-gas phase diagram:

The function  $p(V, T, n)$  with  $n = \text{const}$  is represented by a surface in  $(p, V, T)$ -space. It consists of

- three single-phase regions: solid, liquid, gas.
- three two-phase coexistence regions: solid/liquid, liquid/gas, solid/gas.
- one three-phase coexistence line: solid/liquid/gas.



At high temperature and not too high pressure, the surface is accurately represented by the classical-ideal-gas equation of state,

$$pV = nRT.$$

At somewhat lower temperatures, the surface is decently described by the van der Waals equation of state,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT.$$

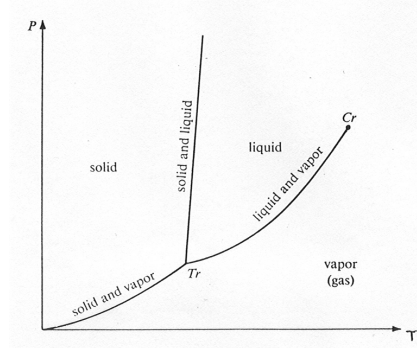
Projection of the phase diagram onto the  $(T, p)$ -plane of intensive variables.

Two-phase coexistence lines:

- vapor-pressure curve (liquid/gas),
- fusion curve (solid/liquid),
- sublimation curve (solid/gas).

Three-phase coexistence point:

- triple point  $(T_t, p_t)$ .



The vapor-pressure curve ends in a critical point  $(T_c, p_c)$ . The fusion curve does not. The difference has to do with symmetry.

- The gas and the liquid are both fully isotropic (rotationally symmetric) and fully homogeneous (translationally symmetric).
- The solid has (by default) a crystallographic structure with lower rotational and translational symmetries.
- Isothermal compression at  $T_t < T < T_c$  produces a high-density fluid (liquid) from a low-density fluid (gas) via condensation.
- Isothermal compression at  $T > T_c$  produces a high-density fluid (liquid) from a low-density fluid (gas) via a gradual increase in density.
- Isobaric heating up at  $p_t < p < p_c$  produces a low-density fluid (gas) from a high-density fluid (liquid) via evaporation.
- Isobaric heating up at  $p > p_c$  produces a low-density fluid (gas) from a high-density fluid (liquid) via a gradual decrease in density.
- There are no gradual paths between phases with different symmetries, i.e. between the solid and the liquid or between the solid and the gas.
- All processes from a crystalline solid phase to a liquid (gas) phase involve melting (sublimation), with both phases coexisting while melting (sublimation) is in process.
- Whereas the fusion curve may not end in a critical point, it may bend over and terminate on  $p$ -axis. The implication would be that the highly compressed substance does no longer have a crystalline structure.
- A gradual change between a liquid, where particles are able to drift, and an amorphous solid, where they are frozen in place, is conceivable. Both structures have the same symmetry.

### Additional and alternative phases:

This list with pointers to illustrations is meant to demonstrate the diversity of phase behavior. Approaches to quantitative analysis follow later.

- Most substances have several solid phases with different crystallographic structures. A prominent example is H<sub>2</sub>O [tsl4].
- Even liquids come with qualitatively different structures. Liquid crystal phases have a variety of orientational and translational order molecules suspended in solution [tsl51].
- Liquid helium offers different possibilities, namely superfluid phases, characterized, among other things, by a vanishing viscosity [tln33].
- Solids in one crystallographic structure may have different electron spin orderings (paramagnetic, ferromagnetic, antiferromagnetic, ferrimagnetic). Magnetic ordering may produce lattice distortions [tsl49].
- Superconductivity is a phase associated with conduction electrons in metals, for example, characterized, among other things, by a vanishing resistivity.
- Many types of ordering in condensed matter are hierarchical in nature. Surfactant molecules, for example, tend to aggregate in various configurations such as spherical or cylindrical micelles, which then have a tendency to order in a manner akin to liquid crystals [tsl50].

### Classification of phase transitions:

The distinction between *discontinuous* (first-order) and *continuous* (second-order) phase transitions is of historical significance, but not fully adequate.

Consider a 1-component fluid system. Here we focus on transitions between phases *I* and *II* upon variation of the intensive variables  $p$  and  $T$ .

Gibbs free energy:  $G(T, p, N) = U - TS + pV = \mu n$ .

Differential and first derivatives:  $dG = -SdT + Vdp + \mu dn$ .

- Volume:  $V = \left( \frac{\partial G}{\partial p} \right)_{T,n}$ .
- Entropy:  $S = - \left( \frac{\partial G}{\partial T} \right)_{V,n}$ .
- Chemical potential:  $\mu = \left( \frac{\partial G}{\partial n} \right)_{T,p} = \frac{G}{n}$ .

The Gibbs free energy has a different functional dependence on its natural independent variables in the two phases:

$$G^I(T, p, n) = \mu^I(T, p)n, \quad G^{II}(T, p, n) = \mu^{II}(T, p)n.$$

For given values of  $T$  and  $p$ , the phase realized at equilibrium is the one with the lowest Gibbs free energy, i.e the state with the lower chemical potential.

Condition for transition:  $G^I = G^{II}$ .

Implication:  $\mu_I(T, p) = \mu_{II}(T, p)$  at the transition.

### Discontinuous transition:

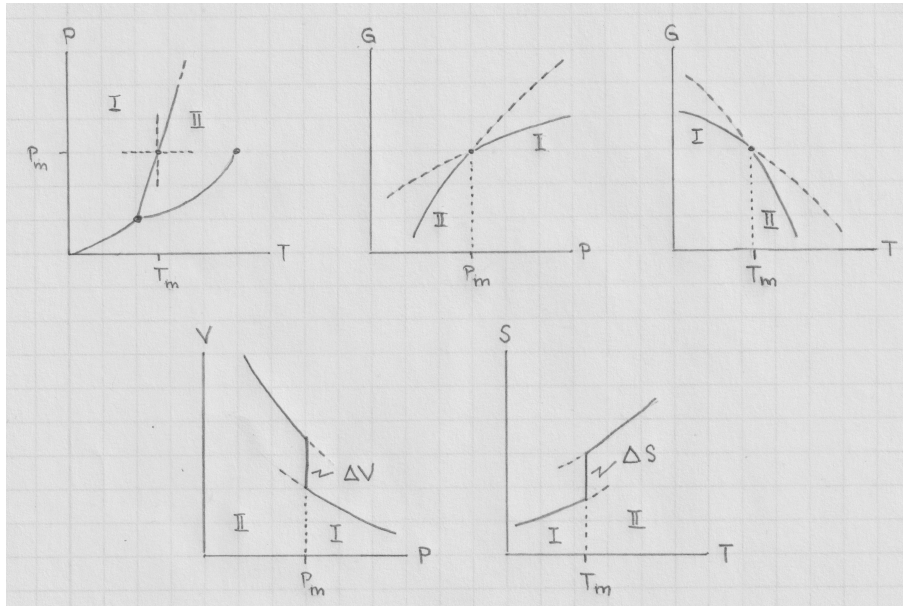
The volume and the entropy change discontinuously, whereas the chemical potential must change continuously:

$$\left(\frac{\partial G}{\partial p}\right)_{T,n}^I \neq \left(\frac{\partial G}{\partial p}\right)_{T,n}^{II} \Rightarrow V^I \neq V^{II}.$$

$$\left(\frac{\partial G}{\partial T}\right)_{n,p}^I \neq \left(\frac{\partial G}{\partial T}\right)_{n,p}^{II} \Rightarrow S^I \neq S^{II}.$$

$$\left(\frac{\partial G}{\partial n}\right)_{T,p}^I = \left(\frac{\partial G}{\partial n}\right)_{T,p}^{II} \Rightarrow \mu^I = \mu^{II}.$$

Latent heat (change in enthalpy):  $\Delta E = \Delta(G + TS) = T\Delta S$



**Continuous transition:**

The volume and the entropy change continuously:

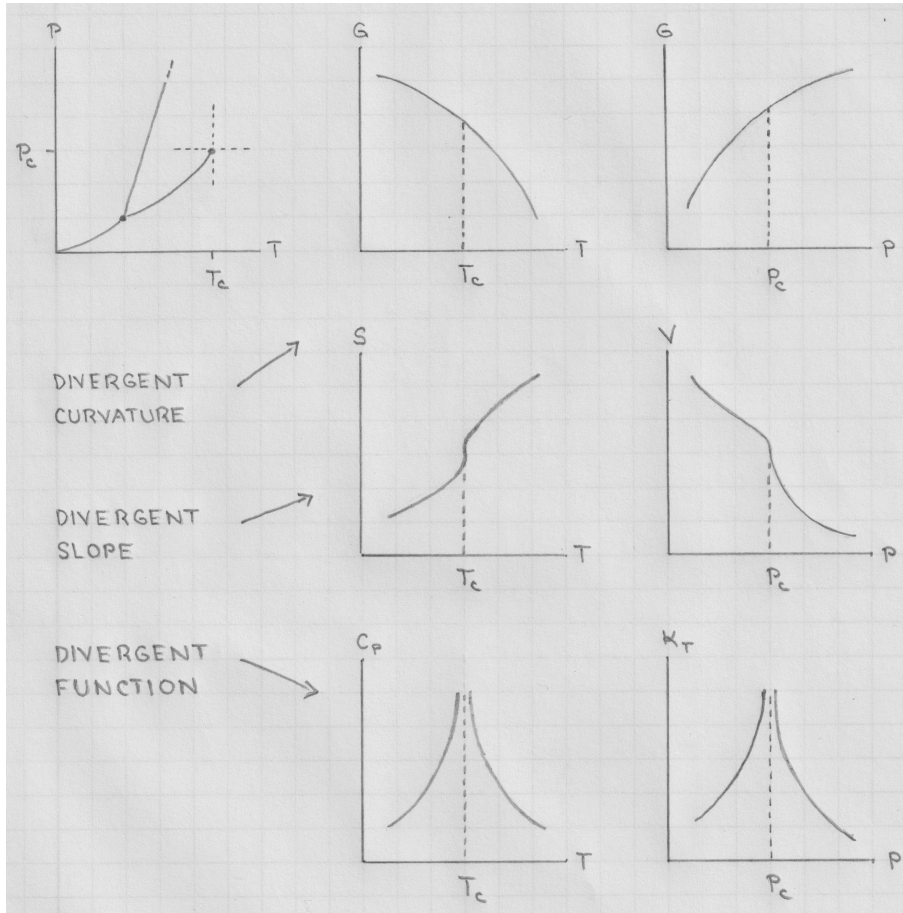
$$\left(\frac{\partial G}{\partial n}\right)_{T,p}^I = \left(\frac{\partial G}{\partial n}\right)_{T,p}^{II} \Rightarrow \mu^I = \mu^{II} = \mu^*.$$

$$\left(\frac{\partial G}{\partial p}\right)_{T,n}^I = \left(\frac{\partial G}{\partial p}\right)_{T,n}^{II} \Rightarrow V^I = V^{II}.$$

$$\left(\frac{\partial G}{\partial T}\right)_{n,p}^I = \left(\frac{\partial G}{\partial T}\right)_{n,p}^{II} \Rightarrow S^I = S^{II}.$$

Discontinuities or divergences occur in higher-order derivatives (e.g. heat capacity and compressibility):

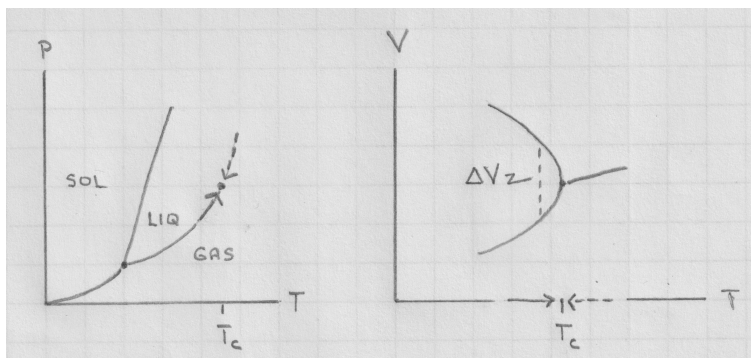
$$C_p = T \left(\frac{\partial S}{\partial T}\right)_{p,n}, \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_{T,n}.$$



### Order parameter:

A characteristic feature of continuous transitions is the cusp-like growth of an *order parameter* at the critical point.

In the context of the liquid-gas critical point, the order parameter is the emerging discontinuity in density between two fluid phases: the high-density liquid and the low-density gas.

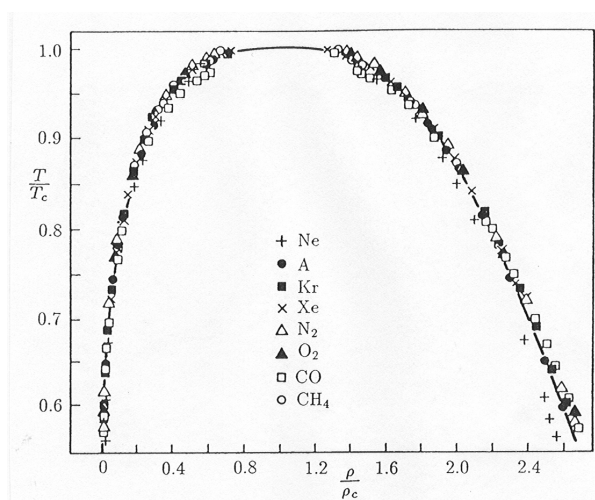


A characteristic feature of thermodynamic systems near critical points is *universality* (to be investigated later).

When suitably scaled, data for different substances that undergo the same kind of phase transitions follow the same universal curve.

The most prominent example is the *Guggenheim plot* for densities near the liquid-vapor transitions in comparison with the empirical law,

$$\frac{\rho_l + \rho_g}{2\rho_c} = 1 + \frac{3}{4} \left(1 - \frac{T}{T_c}\right), \quad \frac{\rho_l - \rho_g}{\rho_c} = \frac{7}{2} \left(1 - \frac{T}{T_c}\right)^{1/3}.$$



### Phase coexistence: Gibbs' phase rule:

Consider a fluid system with the following specifications:

- $K$ : number of components (chemically distinct atoms or molecules),
- $P$ : number of distinct phases that coexist under specific circumstances.

The system discussed earlier has  $K = 1$  and  $P = 3$  (solid, liquid, gas).

The internal energy (as a thermodynamic potential) of this system is a different function of  $K + 2$  extensive variables in each phase:

$$U^{(i)}(S^{(i)}, V^{(i)}, N_1^{(i)}, \dots, N_K^{(i)}), \quad i = 1, \dots, P.$$

Differential: 
$$dU^{(i)} = T^{(i)}dS^{(i)} - p^{(i)}dV^{(i)} + \sum_{\ell=1}^K \mu_{\ell}^{(i)}dN_{\ell}^{(i)}, \quad i = 1, \dots, P.$$

Total number of extensive variables:  $P(K + 2)$ . The number of intensive variables is the same.

Conditions for the coexistence of  $P$  phases:

- thermal equilibrium:  $T^{(1)} = T^{(2)} = \dots = T^{(P)}$ ,
- mechanical equilibrium:  $p^{(1)} = p^{(2)} = \dots = p^{(P)}$ ,
- chemical equilibrium:  $\mu_{\ell}^{(1)} = \mu_{\ell}^{(2)} = \dots = \mu_{\ell}^{(P)}$ ,  $\ell = 1, \dots, K$ .

These conditions amount to  $(P - 1)(K + 2)$  relations between intensive variables. If  $P$  phases coexist, then the number of independent (intensive or extensive) variables is reduced to

$$P(K + 2) - (P - 1)(K + 2) = K + 2,$$

which is independent of  $P$ .

In this set of  $K + 2$  variables,  $P$  must be extensive, e.g.  $V_1, \dots, V_P$ , to determine the fraction of each coexisting phase. The remaining independent state variables can be chosen to be intensive.

The number of independent intensive state variables required to describe the thermodynamic state of  $P$  coexisting phases in a  $K$ -component system is

$$F = K + 2 - P \quad (\text{Gibbs phase rule}).$$

The maximum number of coexisting phases is  $K + 2$ , which is realized for  $F = 0$ . In this case, no intensive variables need to be specified. All are determined by the conditions of phase coexistence.

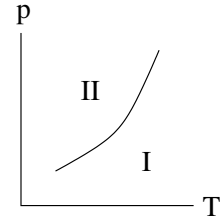
Example: 1-component fluid ( $K = 1$ ) from earlier.

- ▷  $P = 1$  (solid or liquid or gas): realization of  $F = 2$ . Both  $p$  and  $T$  must be specified to locate the equilibrium state in the  $(p, T)$ -plane.
- ▷  $P = 2$  (solid/liquid or solid/gas or liquid gas): realization of  $F = 1$ . Only  $p$  or  $T$  must be specified to locate the equilibrium state in the  $(p, T)$ -plane. The coexistence line is characterized by a function  $p_{\text{coex}}(T)$ .
- ▷  $P = 3$  (solid/liquid/gas): realization of  $F = 0$ . The coexistence condition alone determines the values of  $p$  and  $T$ . The equilibrium state is located at the triple point in the  $(p, T)$ -plane.

### Clausius-Clapeyron equation:

On the coexistence line of two phases  $I$  and  $II$ , the Gibbs free energies are equal, which determines the course of the coexistence line in the  $(T, p)$ -plane:

$$G_I(T, p) = G_{II}(T, p) \quad \Rightarrow \quad p = p_{\text{coex}}(T).$$



It follows that the variation of the Gibbs free energy in the two phases along their coexistence line are also equal:

$$dG^I = dG^{II} \quad \Rightarrow \quad V^I dp - S^I dT = V^{II} dp - S^{II} dT.$$

Clausius-Clapeyron equation (from the slope of the coexistence line):

$$\left( \frac{dp}{dT} \right)_{\text{coex}} = \frac{S^I - S^{II}}{V^I - V^{II}} = \frac{\Delta S}{\Delta V} = \frac{\Delta E}{T \Delta V}.$$

Latent heat (change in enthalpy):  $\Delta E = T \Delta S$ .

Fact:  $\Delta S > 0$  if  $dT > 0$ .

Consequence:  $\left( \frac{dp}{dT} \right)_{\text{coex}} > 0$  if  $\Delta V > 0$ ;  $\left( \frac{dp}{dT} \right)_{\text{coex}} < 0$  if  $\Delta V < 0$ .

Peculiarity of  $\text{H}_2\text{O}$ : Ice contracts upon melting. The fusion curve has negative slope. Ice under pressure tends to melt, which makes skating possible.



(i) *Vaporization curve* (liquid-gas coexistence line):

The equilibrium pressure,  $p(T)_{\text{coex}}$ , is named *saturated vapor pressure*.

For this case the Clausius-Clapeyron equation can be integrated with mild assumptions, producing an explicit expression for the coexistence line:

$$\begin{aligned} \left(\frac{dp}{dT}\right)_{\text{coex}} &= \frac{\Delta E}{T\Delta V} \simeq \frac{\Delta E}{TV_{\text{vap}}} \simeq \frac{p}{nRT^2}\Delta E \Rightarrow \ln \frac{p}{p_0} = -\frac{\Delta E}{nR} \left(\frac{1}{T} - \frac{1}{T_0}\right) \\ &\Rightarrow p(T)_{\text{coex}} = p(T_0)_{\text{coex}} \exp\left(-\frac{\Delta E}{nR} \left[\frac{1}{T} - \frac{1}{T_0}\right]\right). \end{aligned}$$

(ii) *Fusion curve* (solid-liquid coexistence line):

The fusion curve does not terminate in a critical point. The solid and liquid phases have different symmetries.

(iii) *Sublimation curve* (solid-gas coexistence line):

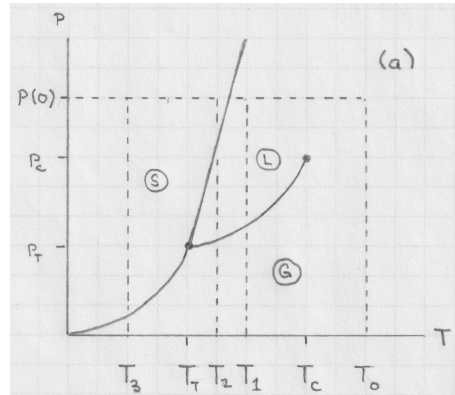
The sublimation curve ends in the triple point.

### Effects of a uniform gravitational field:

Next we discuss density profiles of an infinitely high column of a normal substance with solid/liquid/gas phases in a uniform gravitational field.

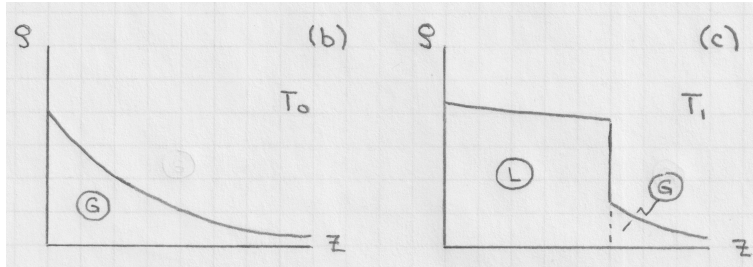
The phase diagram in the  $(T, p)$ -plane is redrawn in panel (a) with additional landmarks.

With coordinate  $z$  measuring altitude, the pressure  $p(0)$  at the bottom is independent of  $T$ , here assumed to be larger than  $p_C$ .



Mechanical stability requires that  $p(z)$  is continuous and monotonically decreasing. Otherwise, fluid phases are unstable against convective flow and solid phases against motion propelled by buoyancy.

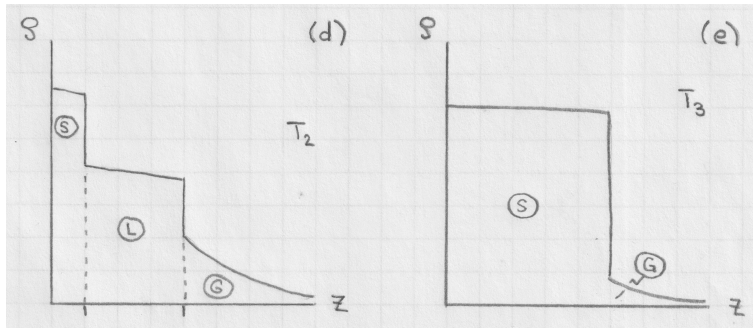
Continuity of density does not follow from continuity of pressure. Discontinuities in density are a common occurrence at phase boundaries. They are caused by cohesive molecular interactions.



At sufficiently high temperature, e.g. at  $T_0$ , the column exhibits the standard exponential profile of the isothermal atmosphere as sketched in panel (b).

Upon quasistatic cooling, the density profile changes gradually down to  $T_C$ . A phase boundary nucleates at the elevation of critical pressure:  $p(z) = p_C$ . A discontinuity emerges in the density profile, but not in the pressure profile.

Further cooling makes the fluid phase near the bottom look more like a liquid and the fluid phase near the top more like a gas as indicated in panel (c).



Before the temperature has dropped to  $T_2$ , a solid phase starts to grow at the bottom at the expense of the liquid phase as shown in panel (d). At the same time, gas is condensing at diminishing vapor pressure.

At the triple-point temperature  $T_T$ , the liquid phase disappears. The solid is now in direct contact with the gas. At  $T_3$ , below the triple point, only the solid-gas phase boundary is present. More of the gas condenses and solidifies.

All these processes are perfectly reversible when we start from  $T = 0$  and add heat quasistatically.

Noteworthy points:

- Multiple phase changes can be in process simultaneously.
- Discontinuities can emerge in the middle of smooth density profiles.
- The temperature of coexisting phases (in general) varies while (quasi-static) phase changes are in process.