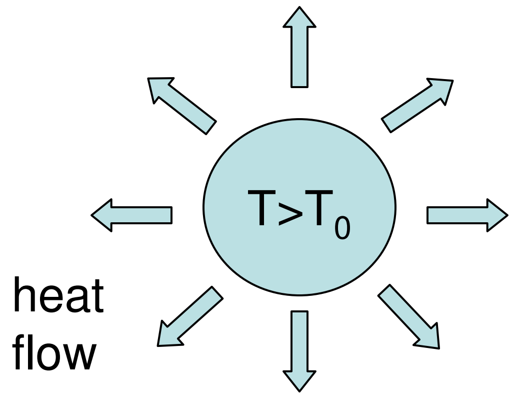
Le Chatelier's Principle

Any inhomogeneity (fluctuation) that develops in a system should induce a process that tends to eradicate this inhomogeneity.

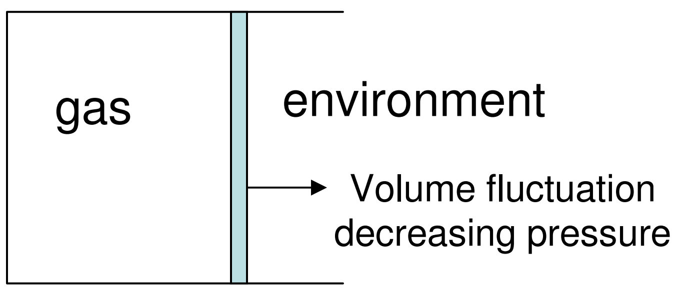
Example: A high temperature region in gas (a temperature fluctuation) will induce (due to the second law) heat flow out of this region to colder regions. Since heat capacity is positive for a stable system, this heat flow will result in a decrease of temperature and thus this process will eradicate the temperature inhomogeneity.



Le Chatelier-Braun principle states that various secondary processes induced by the fluctuation also tend to restore a homogeneous state of the system.

Notes

Le Chatelier - Brown Principle: Example



diathermal wall
movable piston

Consider a fluctuation of the piston position

Primary effect: change of pressure, restores equilibrium

Secondary effect: change of temperature:

$$dT = \left(\frac{\partial T}{\partial V}\right)_S dV = -\frac{T\alpha}{Nc_v\kappa_T} dV$$

dT induces heat flow $\delta Q \sim sign(\alpha)$, that tends to change the pressure:

$$dP = \frac{1}{T}\left(\frac{\partial P}{\partial S}\right)_V \delta Q = \frac{\alpha}{NT^2 c_v \kappa_T} \delta Q$$

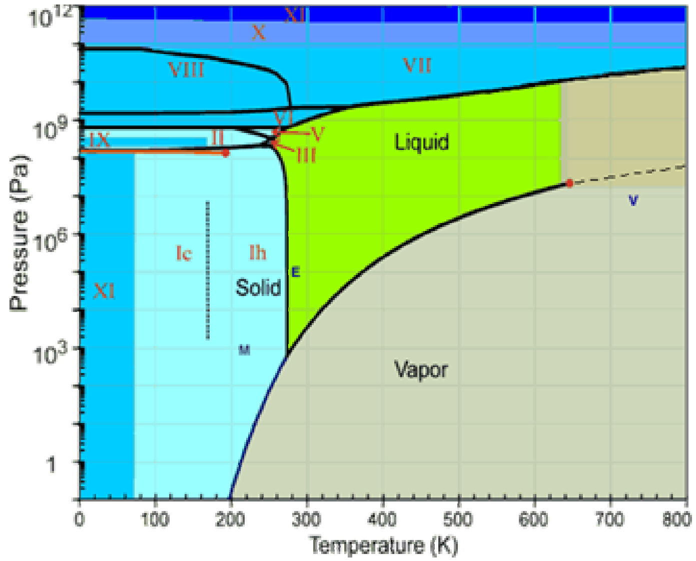
$$\boxed{dP > 0}$$

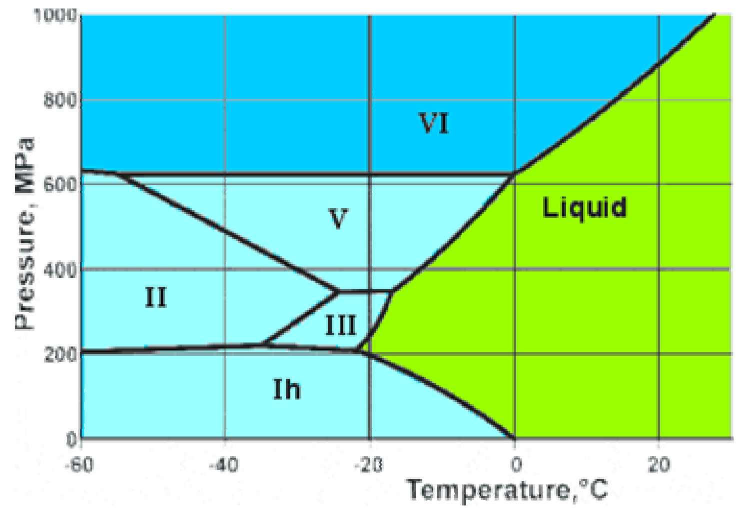
Notes

First Order Phase Transitions

A phase transition is an abrupt or a qualitative change of some macroscopic property of a thermodynamic system as a function of a thermodynamic coordinate. For example, in a liquid-gas phase transition, density of the material undergoes an abrupt change. The qualitatively different states of the system are called phases.

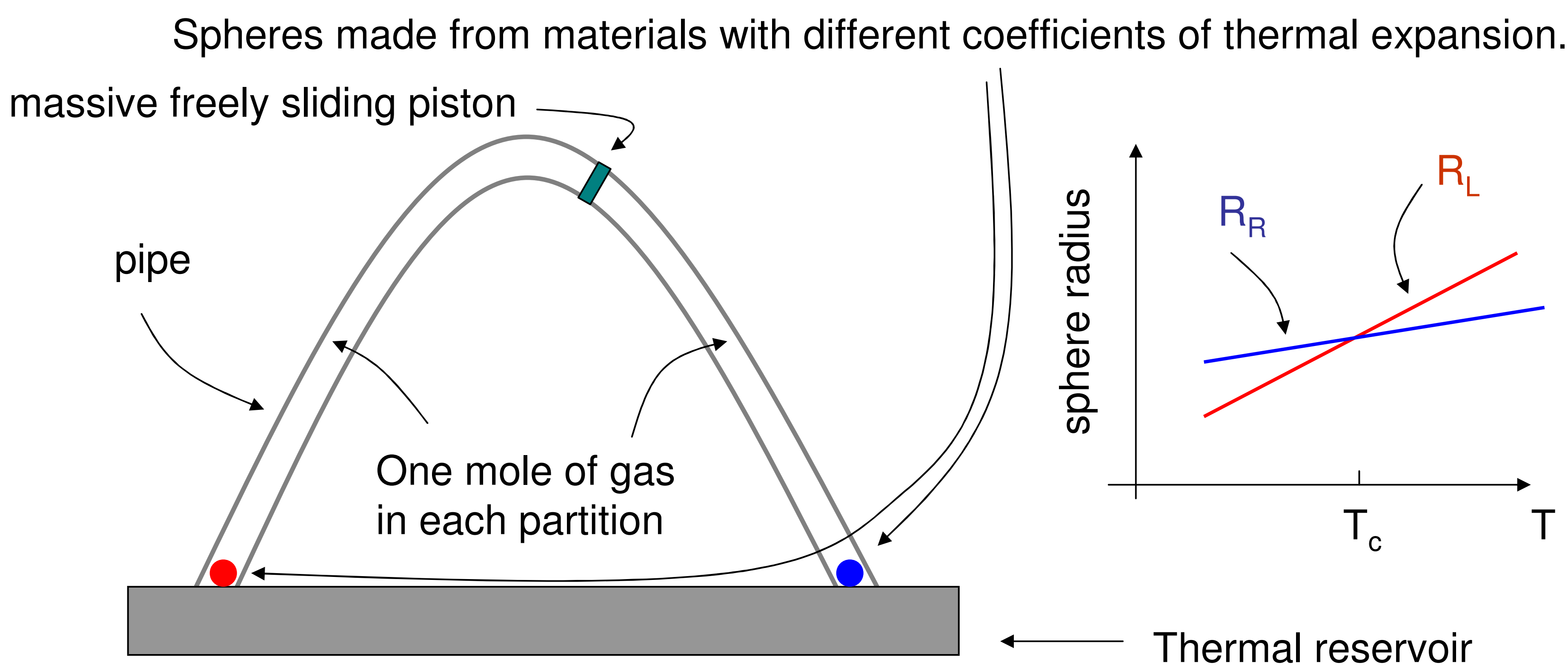
For example, water has a number of (mostly solid) phases:





Notes

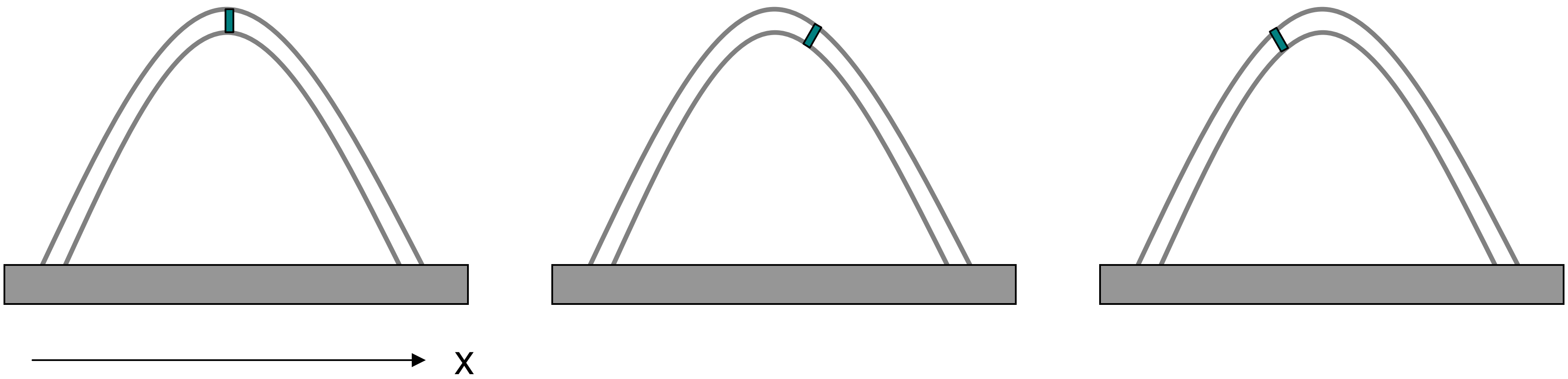
Mechanical Model of a First Order Phase Transition



Notes

Mechanical Model of a First Order Phase Transition

In the absence of spheres and at low enough temperature, the position of the piston at the apex of the pipe is unstable equilibrium due to the gravitational energy cost.



Unstable equilibrium

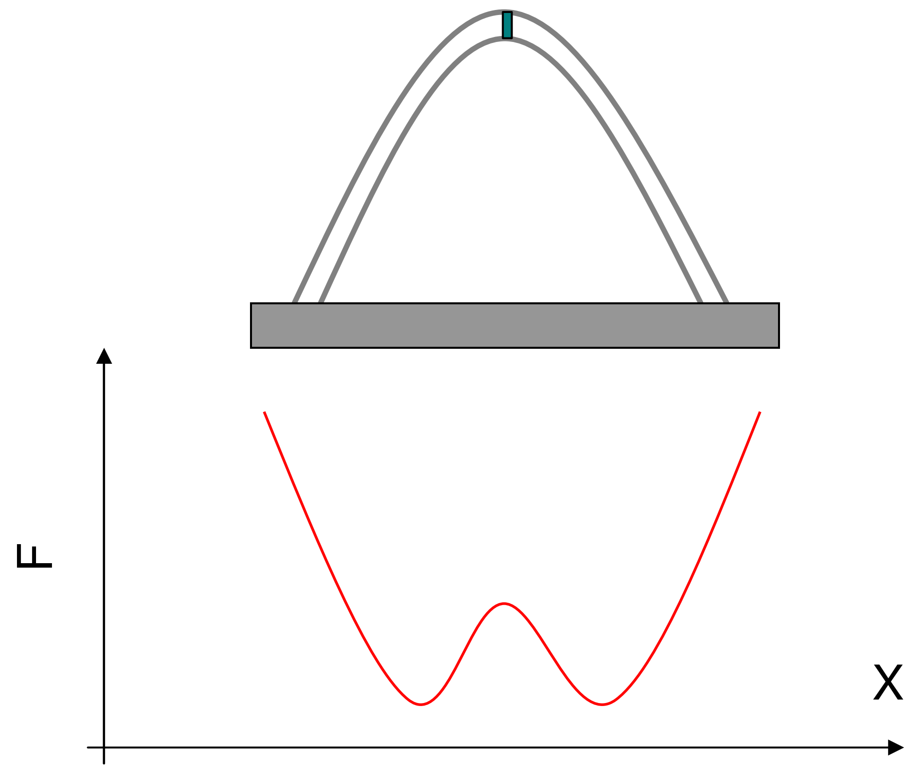
There are two equivalent stable equilibrium states.

Notes

Mechanical Model of a First Order Phase Transition

The total energy of the system as a function of position of the piston has two equivalent minima:

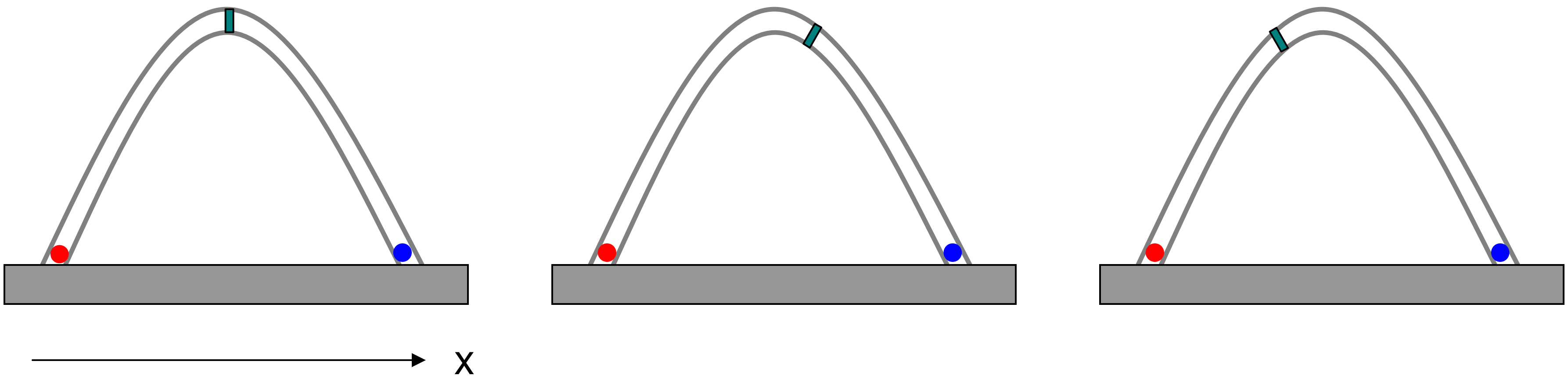
The system is best described by the Helmholtz free energy F (in contact with T but not P reservoir).



Notes

Mechanical Model of a First Order Phase Transition

In the presence of spheres and at low enough temperature, the position of the piston at the apex of the pipe is still unstable but the two minima are not equivalent at any temperature other then T_c.



Unstable equilibrium

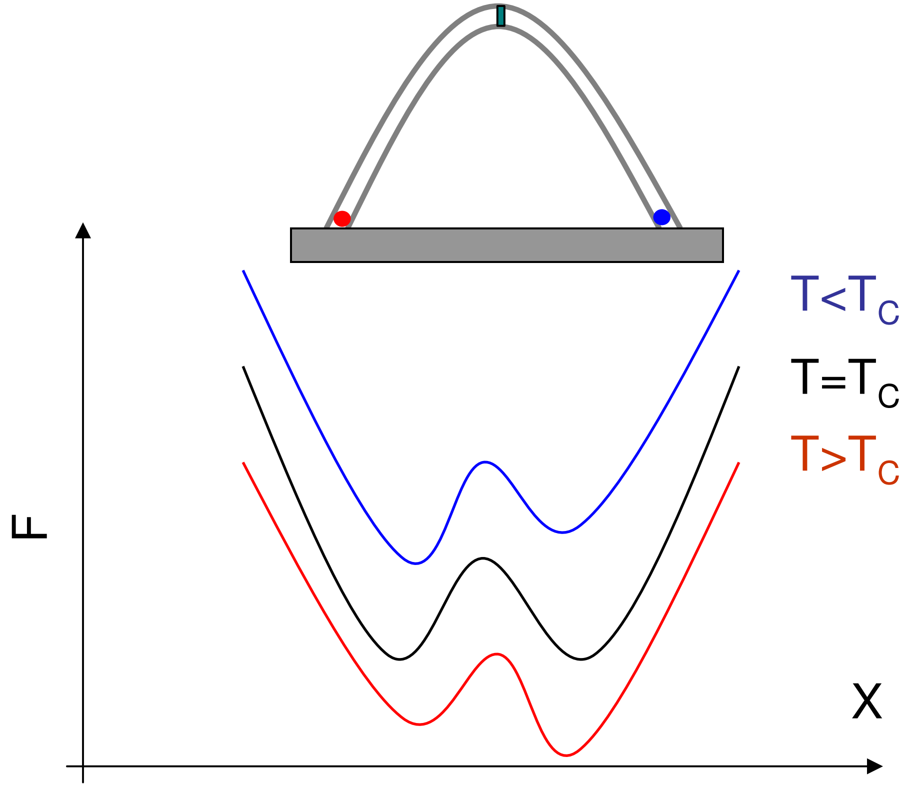
Notes

Mechanical Model of a First Order Phase Transition

x

Unstable equilibrium

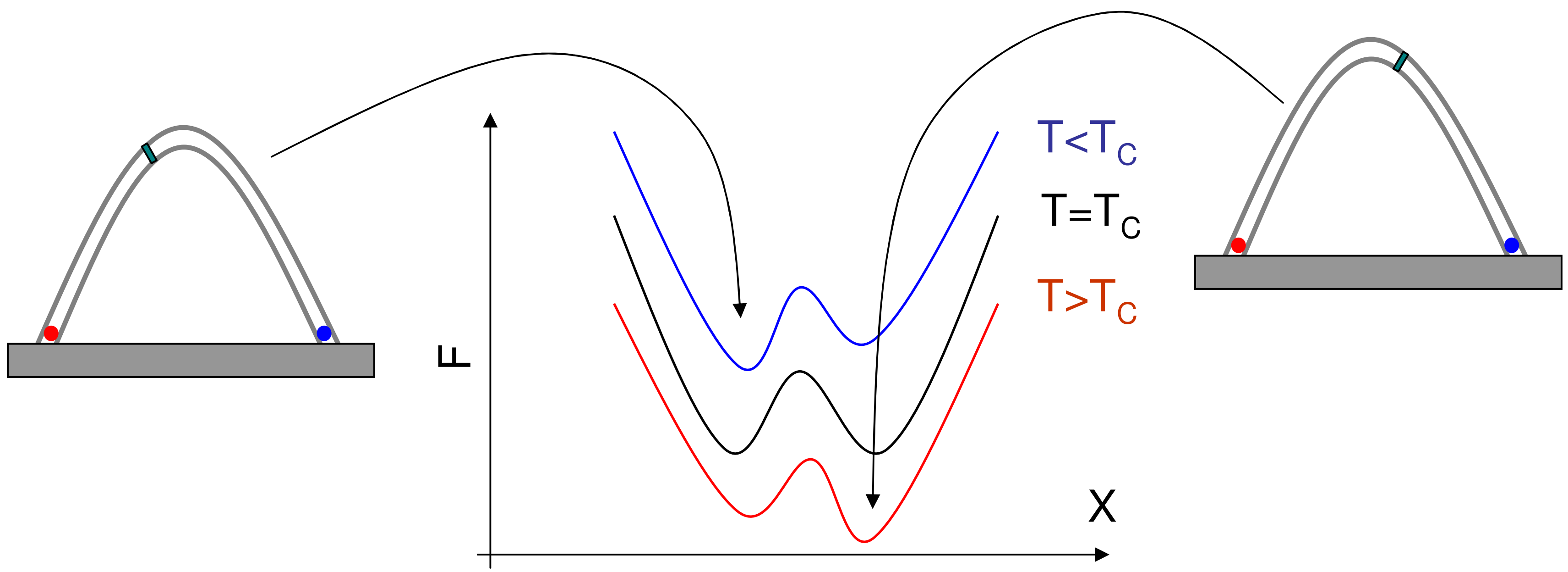
The total energy of the system as a function of position of the piston has two non-equivalent minima:



Notes

Mechanical Model of a First Order Phase Transition

As the temperature of the system is lowered through the transition temperature T_c, the global energy minimum shifts from right to left. This change is discontinuous, a macroscopic coordinate of the system, x, changes by a discontinuous jump.

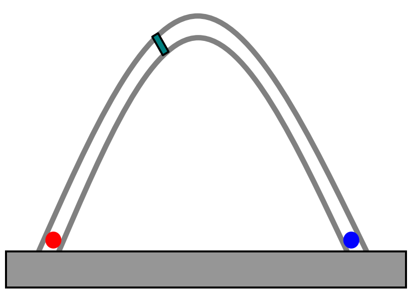


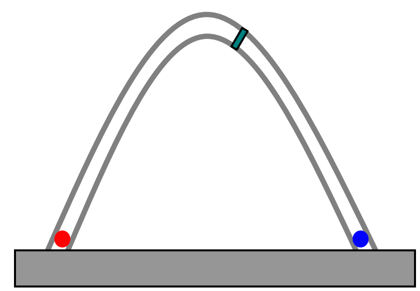
Notes

Role of fluctuations

As the temperature is lowered through T_c, the system initially finds itself in a local energy minimum (a meta-stable state). Then, as time progresses, a fluctuation will take the system from the local energy minimum to the global energy minimum.

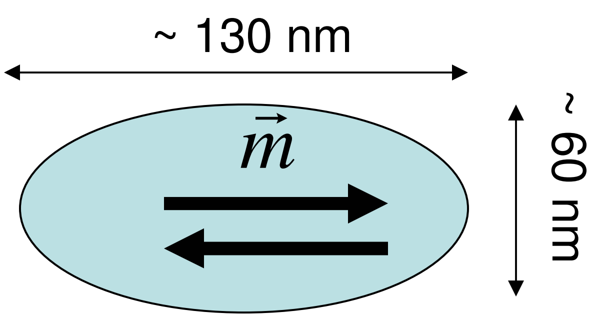
In macroscopic systems, fluctuations that take system back from the global energy minimum to the local one are extremely rare and thus the transition in practice happens just once. However, in microscopic systems fluctuations can take the system back and forth between the local and the global minima many times.

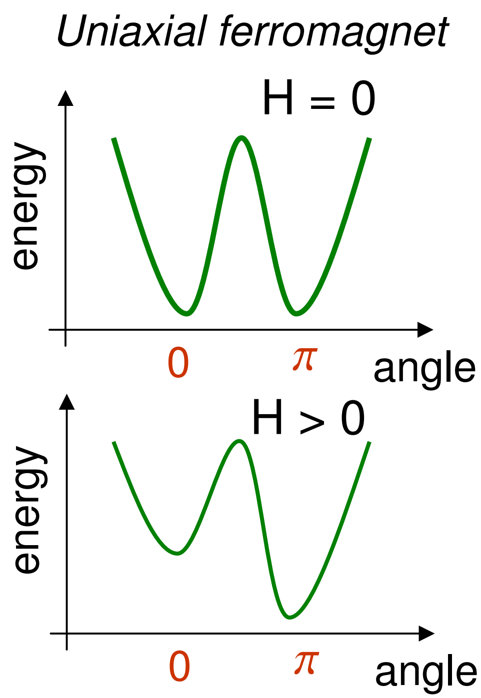


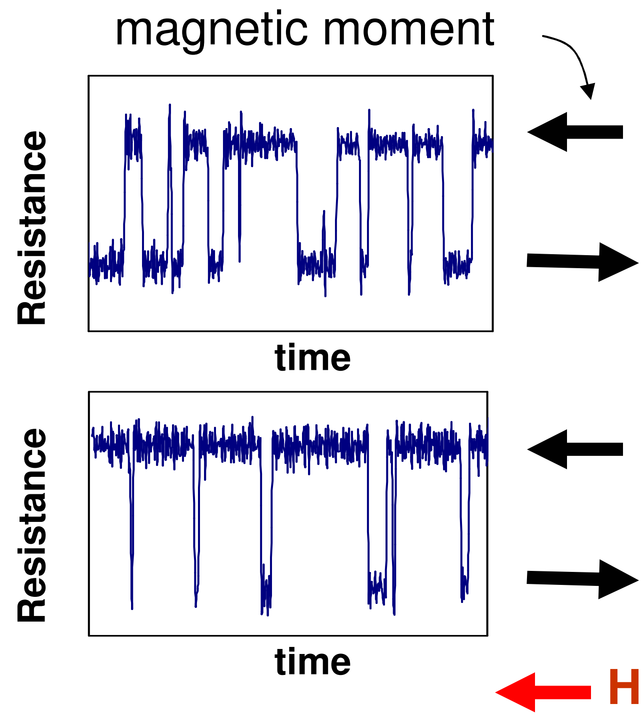


Notes

Example: fluctuations of magnetic moment of a nanomagnet







Two low energy states for the magnetic moment.

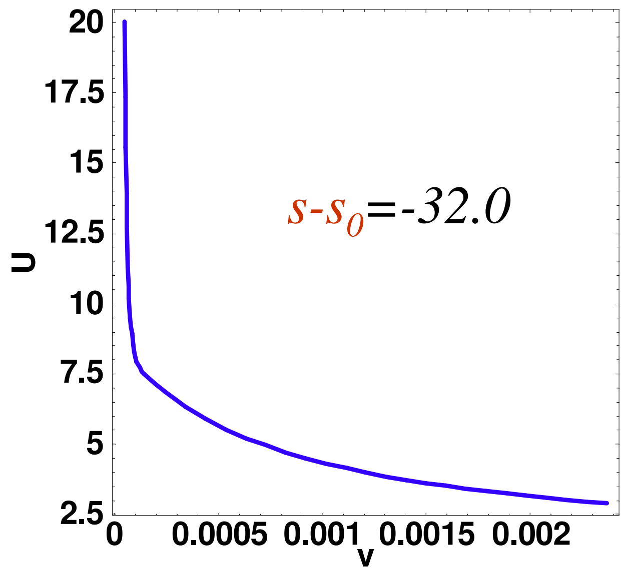
Since the magnet is small enough, fluctuations constantly take the magnet between the states of two opposite directions of magnetic moment.

Notes

Van der Waals fluid

$$S = S_0 + NR\ln\left((v-b)\left(u+\frac{a}{v}\right)^c\right)$$

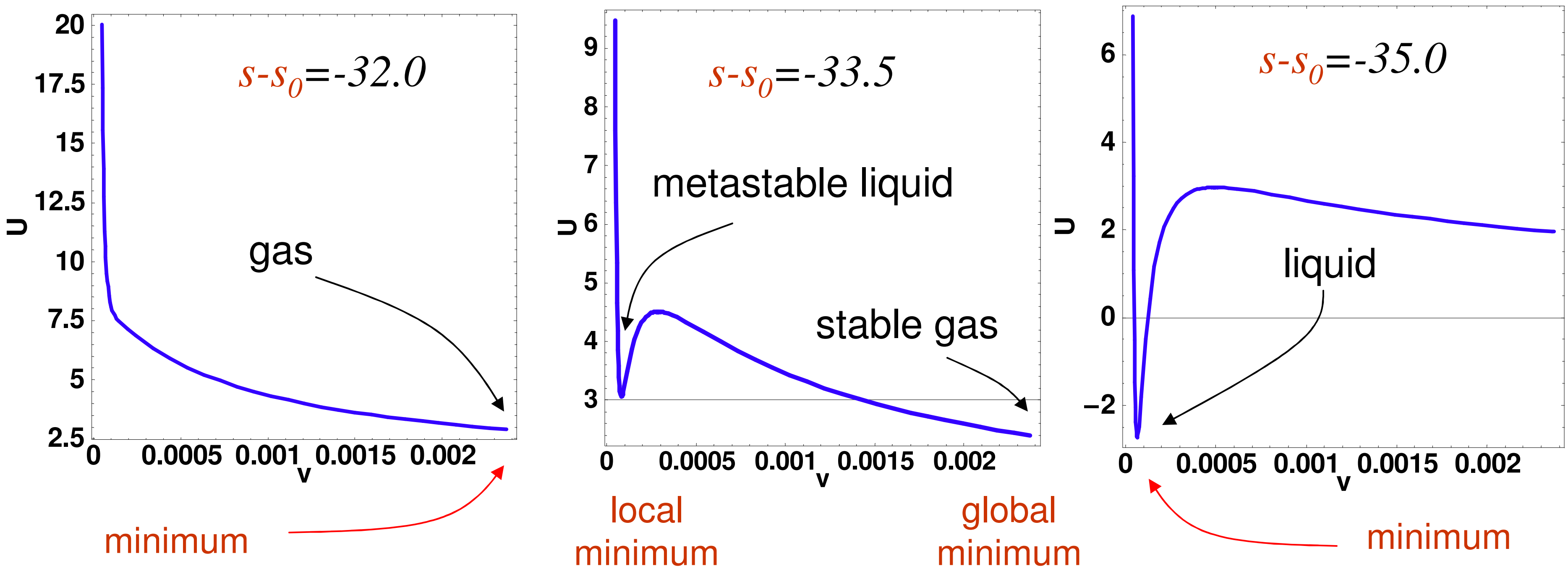
$$u = \frac{1}{(v-b)^{1/c}}\exp\left(\frac{s-s_0}{cR}\right) - \frac{a}{v}$$



Using vdW parameters for He gas, we plot the internal energy as a function of molar volume for fixed entropy

Notes

Van der Waals fluid



According to the energy minimum principle, internal energy of the equilibrium state should be at minimum at constant entropy as a function of other extensive parameters

Notes

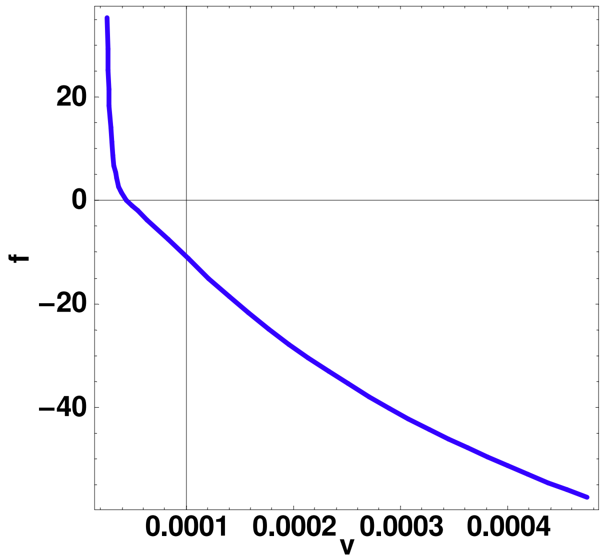
Van der Waals fluid

Now let us consider a situation when He gas is in a thermal contact with a thermal reservoir.
In this case, the free energy of gas has to be at minimum:

$$f = u - Ts$$

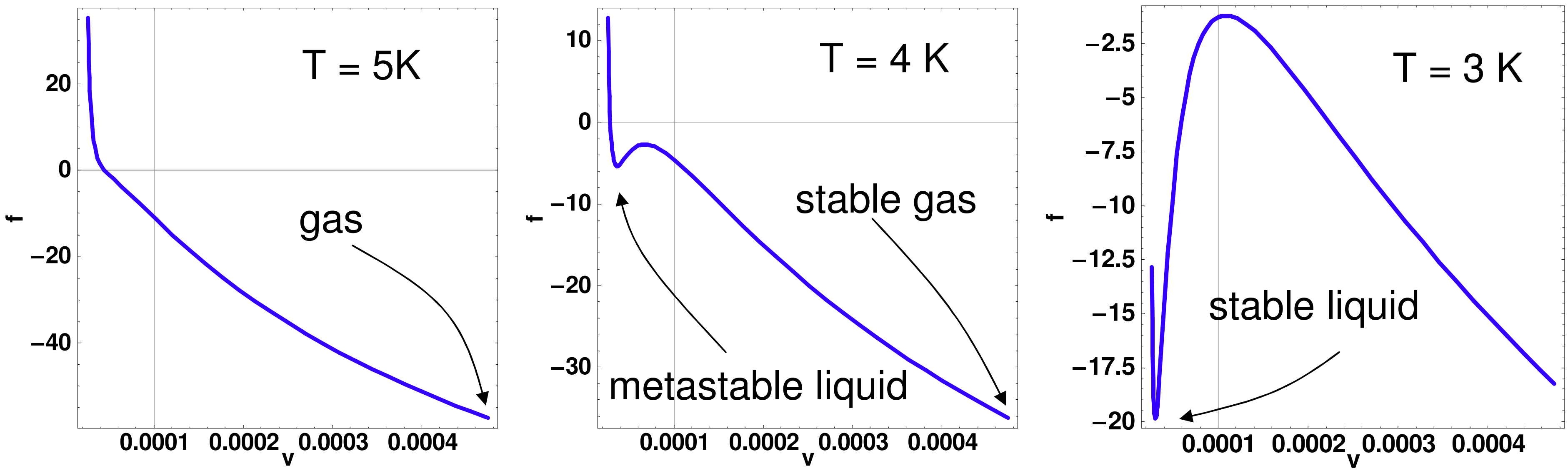
$$\Downarrow$$

$$f = cRT - \frac{a}{v} - T\left(R\ln\left((v-b)(cRT)^{c}\right) + s_0\right)$$



Notes

Van der Waals fluid



Note that at these low temperatures, vdW description of He gas is only approximate as quantum mechanical effects neglected by vdW become important for He at these low temperatures.

Notes