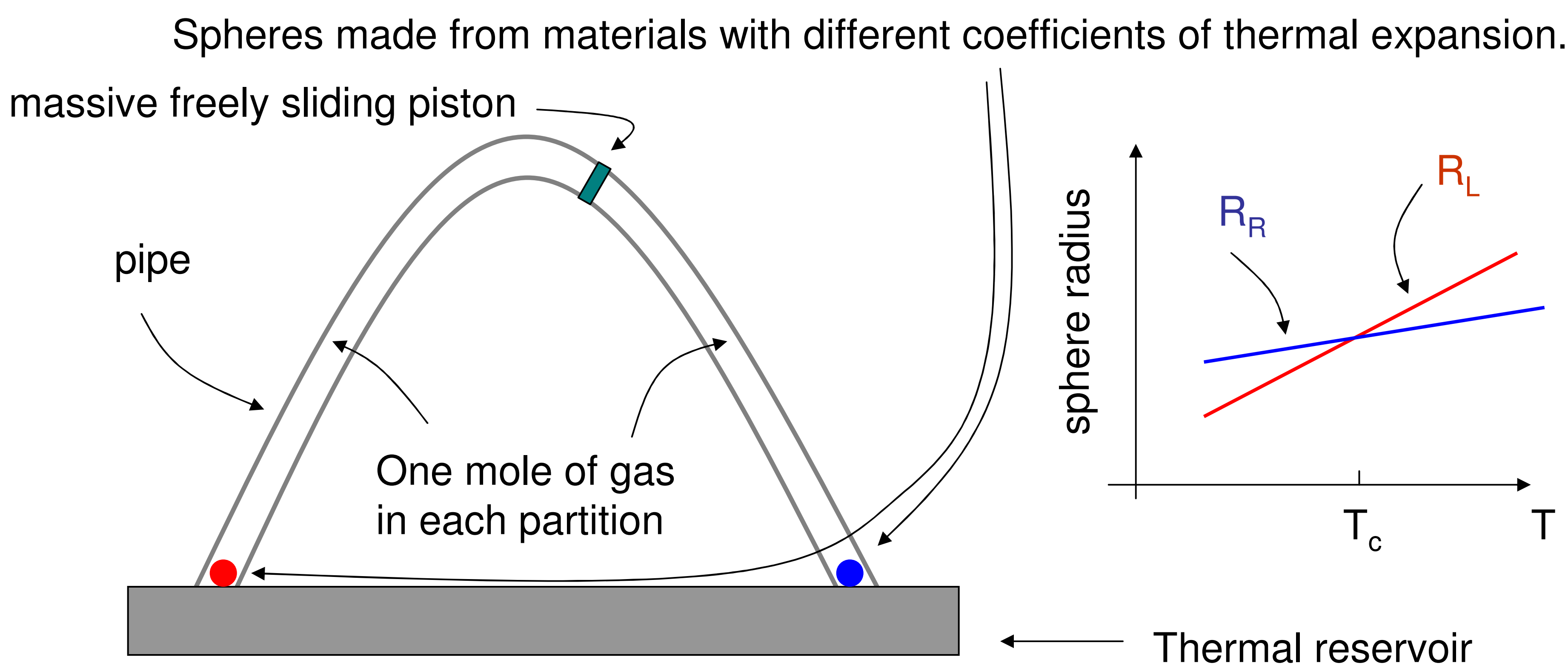
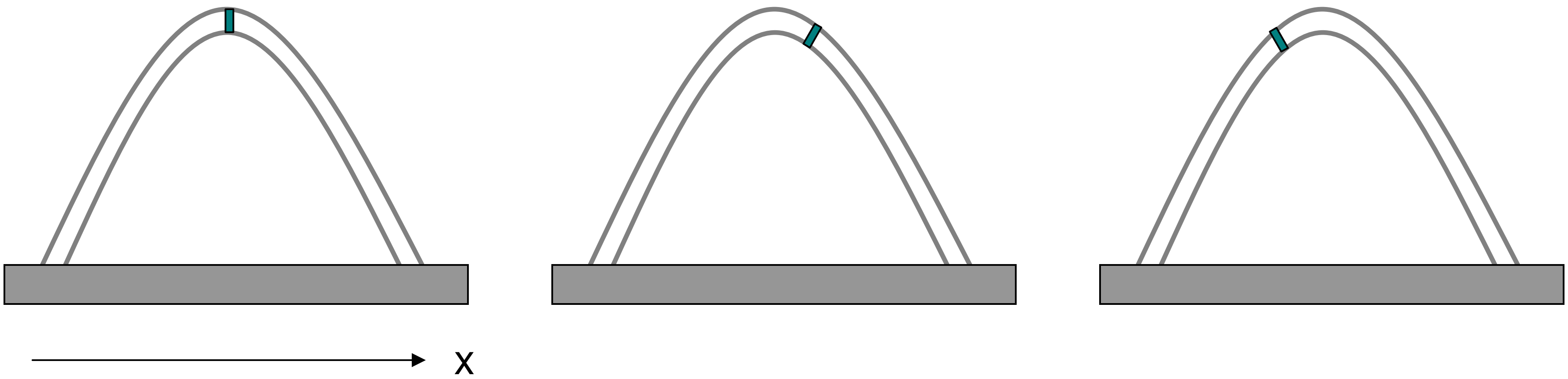
Mechanical Model of a First Order Phase Transition



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

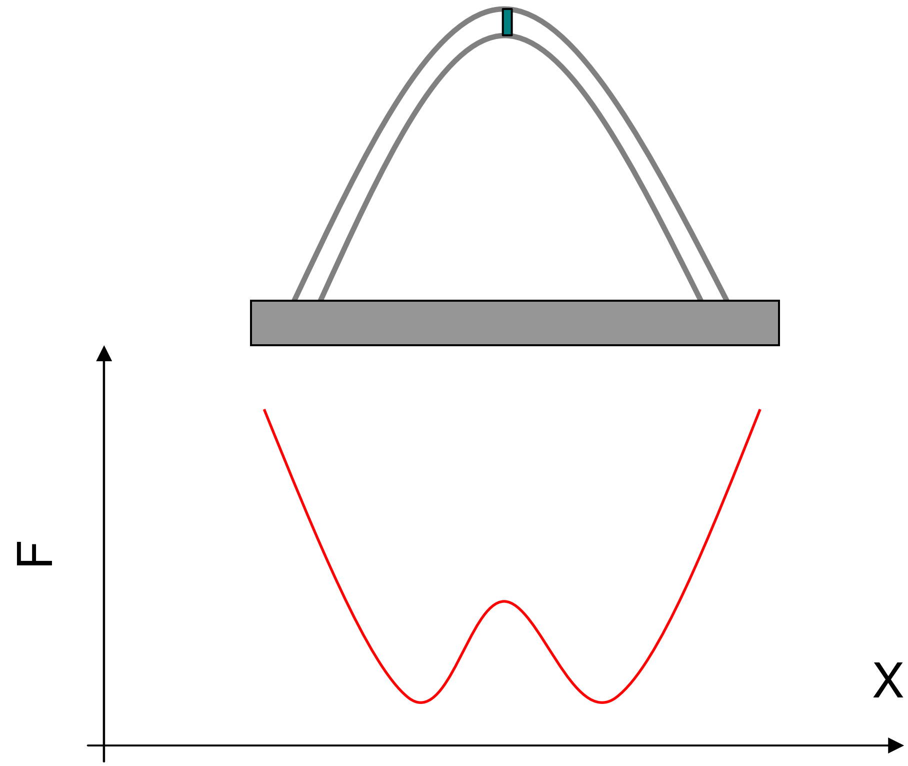
There are two equivalent stable equilibrium states.

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:

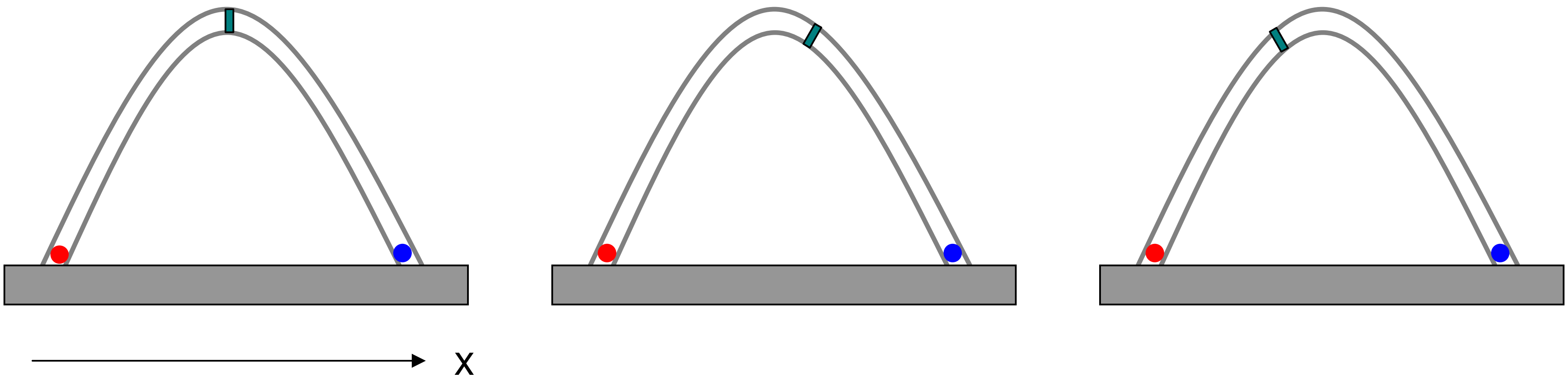
The system is best described by the Helmholtz free energy F (in contact with T but not P reservoir).



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

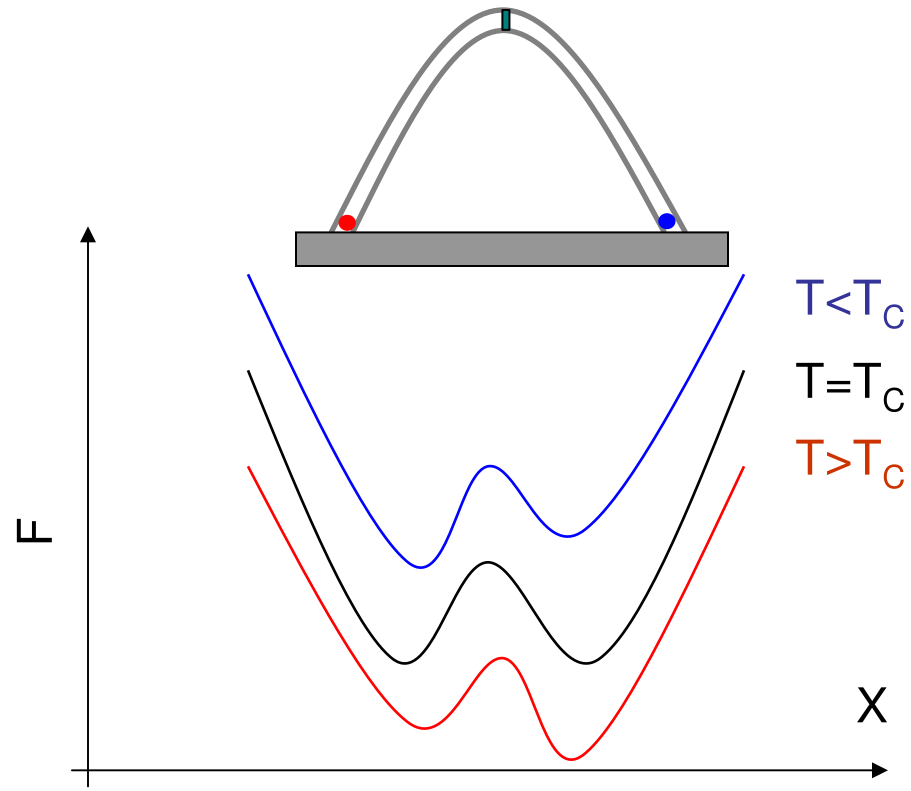
Notes

Mechanical Model of a First Order Phase Transition

x

Unstable equilibrium

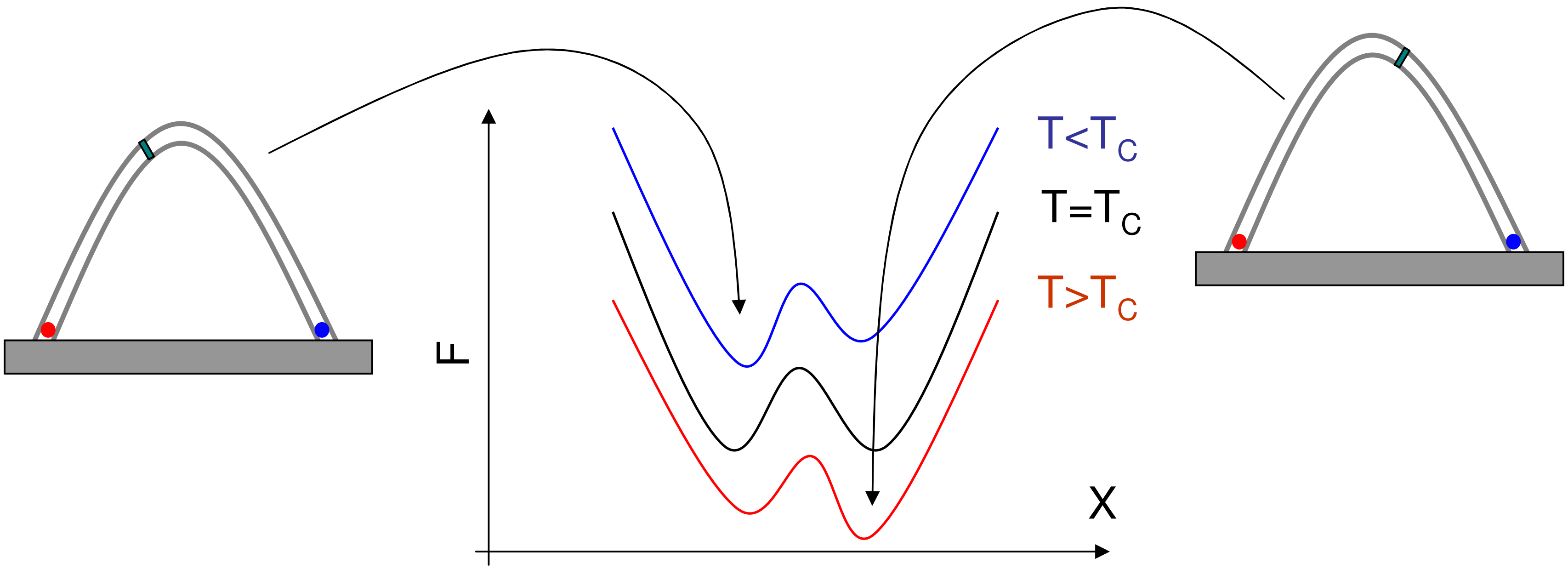
The total energy of the system as a function of position of the piston has two non-equivalent minima:



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.

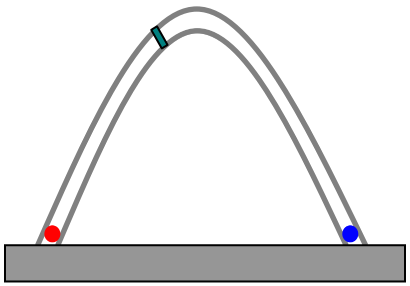


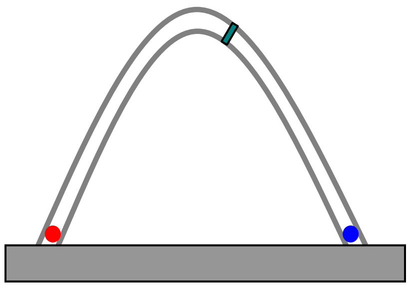
Notes

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.

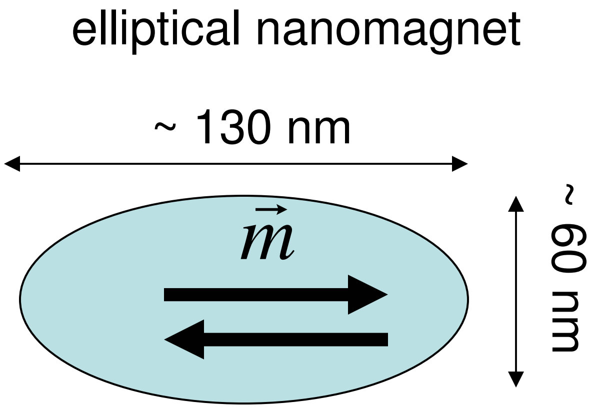
In macroscopic systems, fluctuations that take system back from the global energy minimum to the local one are extremely rare and thus the transition in practice happens just once. However, in microscopic systems fluctuations can take the system back and forth between the local and the global minima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



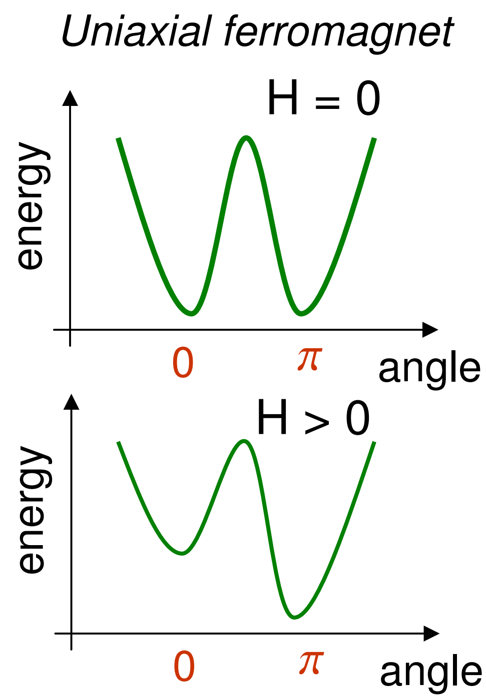


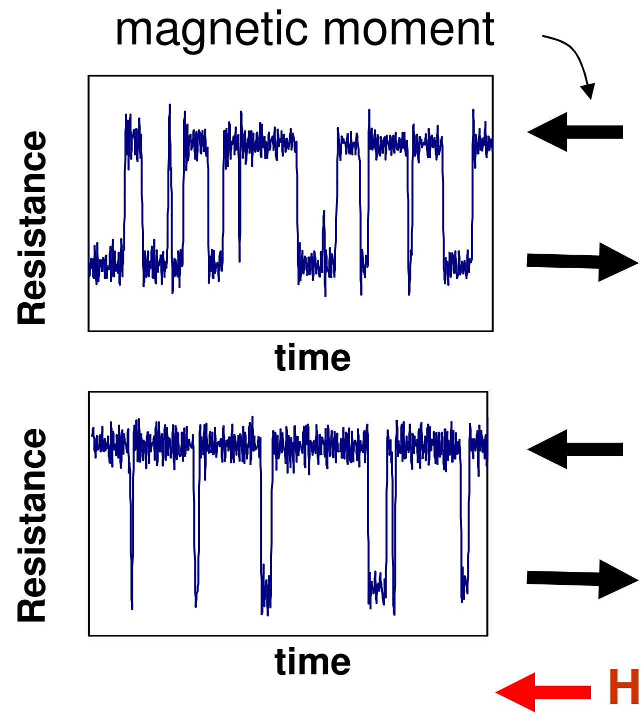
Notes

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.

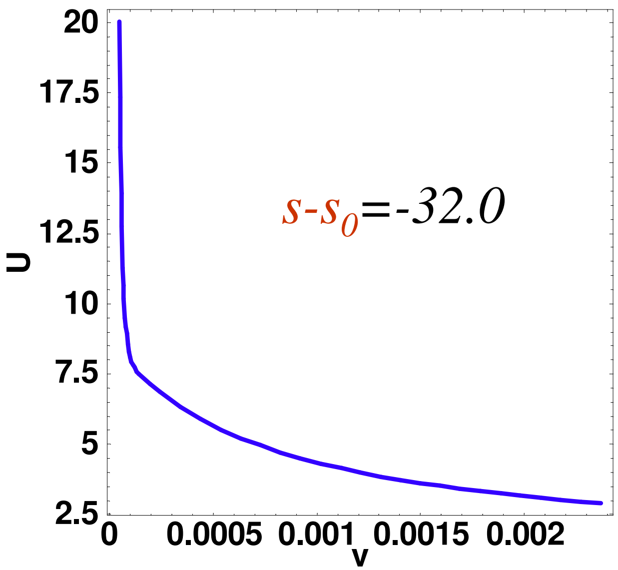
Notes

Van der Waals fluid

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

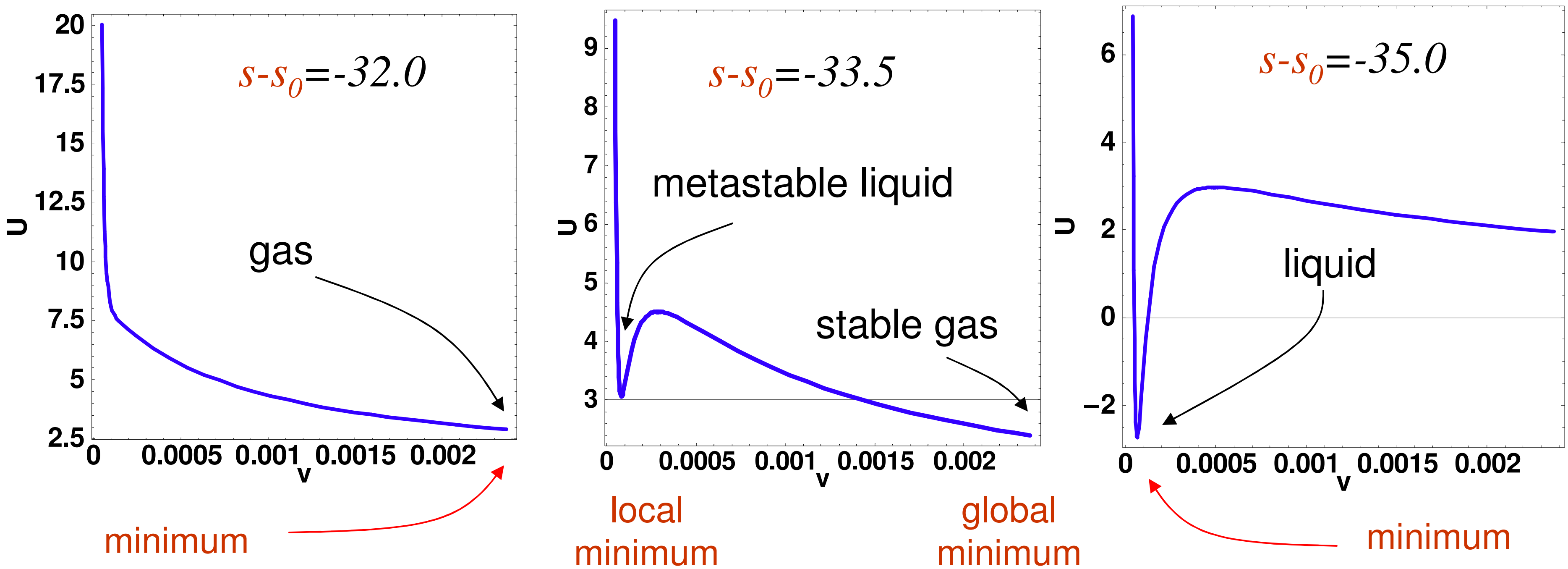
$$u = \frac{1}{(v-b)^{1/c}}\exp\left(\frac{s-s_0}{cR}\right) - \frac{a}{v}$$

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

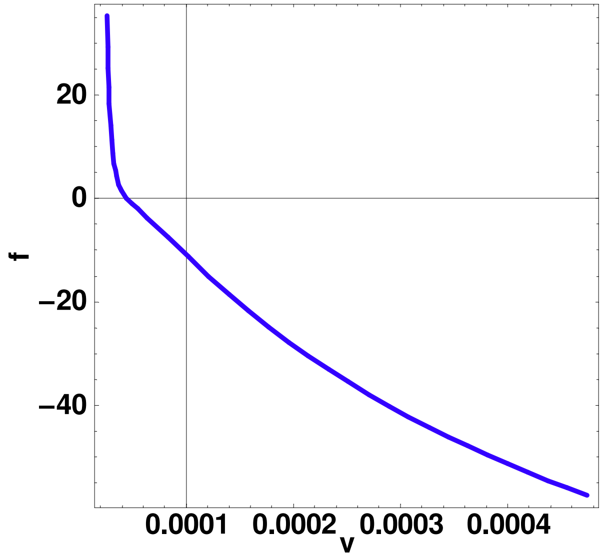
Van der Waals fluid

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:

$$f = u - Ts$$

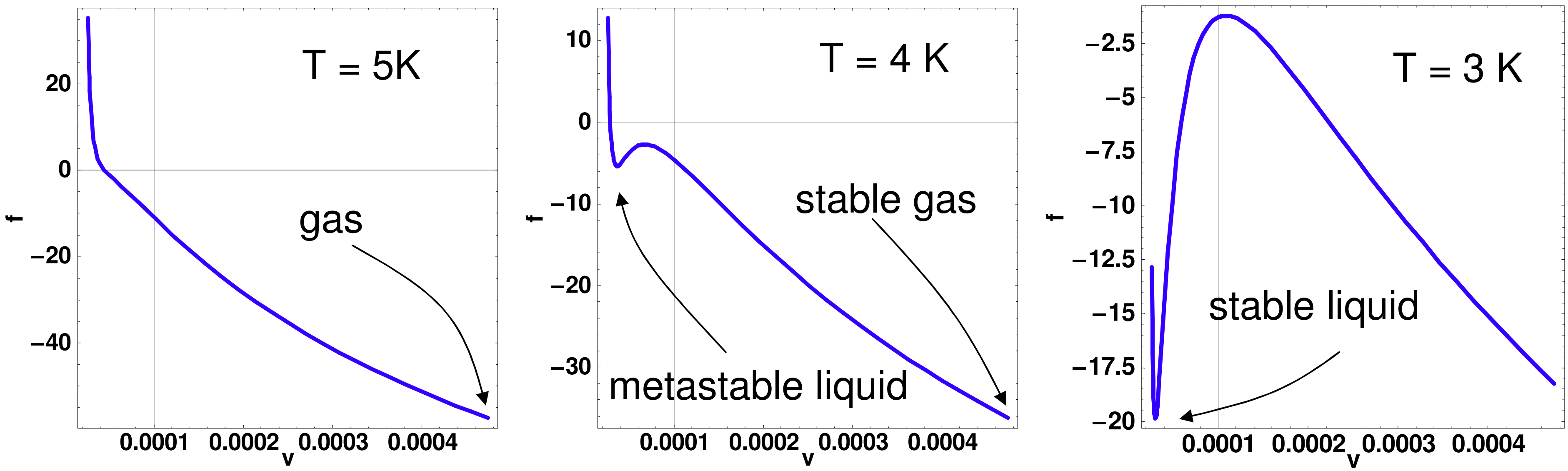
$$\Downarrow$$

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



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

Understanding the Gibbs Potential

We know that the Gibbs potential of a system $G(T,P,N)$ has to be minimum in equilibrium with respect to variation of any unconstrained coordinate of the system **if** T = const **and** P = const (the system in contact with temperature and pressure reservoirs).

What are these unconstrained internal parameters? They are not T and P because $T = T_0$ and $P = P_0$ are fixed.

However, volume V and entropy S are not constrained (their fluctuations between the system of interest and reservoir are allowed).

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \qquad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

Notes

Understanding the Gibbs Potential

We can formally solve these two equations:

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \qquad\qquad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

to obtain:

$$T = T(V,S) \qquad\qquad P = P(V,S)$$

And substitute them back into the expression for G:

$$G(T,P) = G(T(V,S),P(V,S)) = G(S,V)$$

The equilibrium values of V and S are fixed by the conditions $T=T_0$ and $P = P_0$
And the G(S,V) is at minimum with respect to S and V in equilibrium.

Notes

Understanding the Gibbs Potential

Also remember the local stability conditions for the Gibbs potential:

$$\frac{\partial^2 G}{\partial T^2} \leq 0 \qquad \frac{\partial^2 G}{\partial P^2} \leq 0$$

Therefore, the Gibbs potential for a system in equilibrium is at a maximum with respect to S and V but is at a minimum with respect to T and P.

Exercise: Write down G(T,P) and G(S,V) for a vdW fluid and show that in equilibrium G is at a minimum with respect to S and V but is at a maximum with respect to T and P.

Notes