HELMHOLTZ ENERGY AS A FUNCTION OF VOLUME

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.19.

From the thermodynamic identity for the Helmholtz free energy we can obtain the derivative

$$\left(\frac{\partial F}{\partial V}\right)_{T,N}=-P \tag{1}$$

The Helmholtz energy is defined as

$$F\equiv U-TS \tag{2}$$

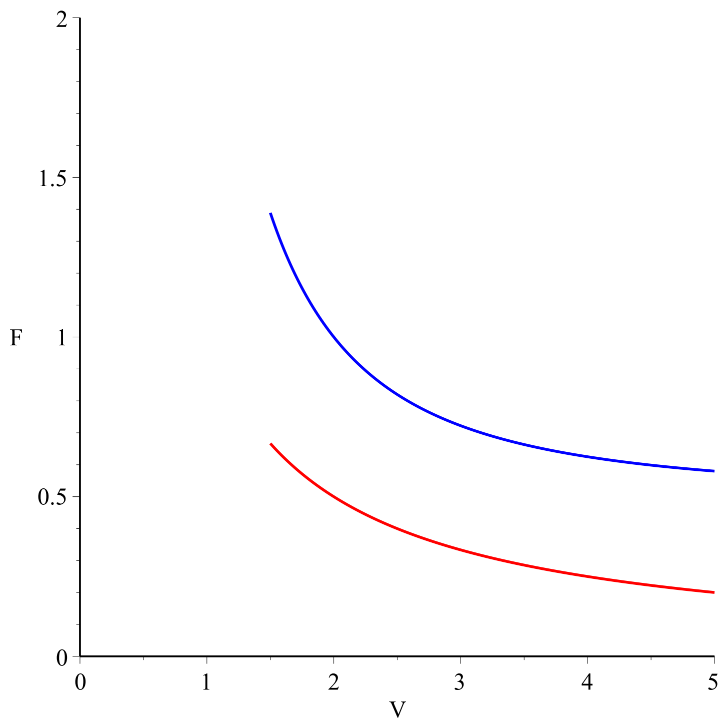
To get an intuitive feel for 1, we recall the definition of temperature in terms of the derivative of entropy. The idea there was that if we have two interacting systems, the equilibrium state is the one with the maximum overall entropy. To apply this idea to the current case, we can use the fact that if we have two interacting systems, the equilibrium state is the one with the minimum Helmholtz energy. So suppose we have two systems that each have a fixed number of molecules and that both systems are in contact with a thermal reservoir so their temperatures are equal and constant. Also suppose that these two systems are allowed to exchange volume (say, by means of a moveable boundary between them), but that the total volume is constant.

The condition that the total free energy is minimum is then

$$\begin{aligned}
\left(\frac{\partial F_{total}}{\partial V}\right)_{T,N} &= 0 && (3)\\
&= \left(\frac{\partial F_A}{\partial V}\right)_{T,N}-\left(\frac{\partial F_B}{\partial V}\right)_{T,N} && (4)\\
\left(\frac{\partial F_A}{\partial V}\right)_{T,N} &= \left(\frac{\partial F_B}{\partial V}\right)_{T,N} && (5)
\end{aligned}$$

where the minus sign in the second line is because an increase in volume A means a decrease in volume B. Thus we end up with an equilibrium condition that the magnitudes of the slopes of a graph of F versus V are equal. Since the units of this slope are (energy)/(volume) = (pressure) we can postulate that this derivative is proportional to the pressure.

A qualitative plot of F versus V for given values of T and N looks like this (for two different values of N):



With N and T fixed, an increase in volume usually implies an increase in entropy, so we'd expect F to decrease as volume is increased, which gives the general shape of the curve. Thus in general $\left(\frac{\partial F}{\partial V}\right)_{T,N} < 0$ which explains the minus sign in 1.

With a higher value of N, at a given temperature and volume, both U and S increase (in roughly the same proportion) so F would increase with N, thus the blue curve is for higher N. Note that the slope of the blue curve is steeper than that of the red curve, which also makes sense since increasing N within a fixed volume increases the pressure.

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