(important tangent continued...)

What controls $U_i - U_0$?

Focus on the form of U possessed by all gases: translation.

Consider a particle of mass m in a cube with sides of length l.

Quantum mechanics tells us that allowed translational energies given by

$$U = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8}\left(\frac{1}{ml^2}\right)$$

where $h = 6.626 \times 10^{-34}$ J s

and n_x, n_y, n_z are positive integers ("quantum numbers") proportional to the particle's speed in the x, y, and z directions.

The smallest difference in the energies of two translational states (when one quantum number increases by 1, and the other quantum numbers don't change) is given by

$$U_i - U_0 = \frac{3}{8}\frac{h^2}{m}\left(\frac{1}{l^2}\right)$$

or, since $V = l^3 \Rightarrow l^2 = V^{2/3}$

$$U_i - U_0 = \frac{3}{8}\frac{h^2}{m}\left(\frac{1}{V^{2/3}}\right)$$

$\therefore \uparrow V \Rightarrow \downarrow (U_i - U_0) \Rightarrow$ more ways to distribute E!

$\therefore S = f(V)$ and $\left(\frac{\partial S}{\partial V}\right)_T > 0$ (Consistent with our earlier statistical arguments)