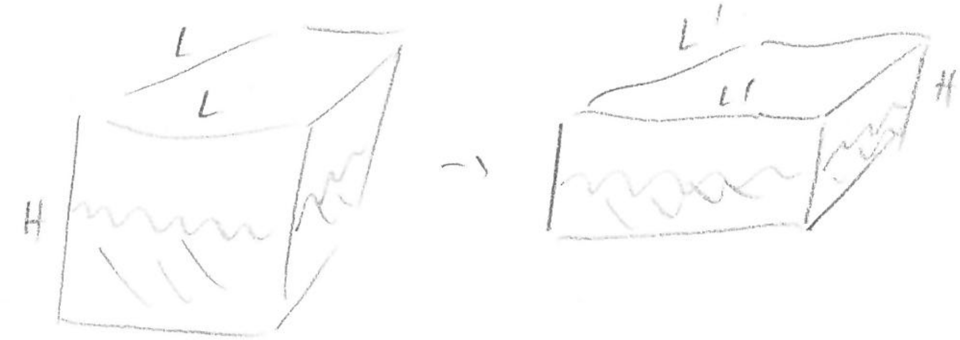
To derive the formula for surface tension, use $\gamma = \left(\frac{\partial F}{\partial A}\right)_{V,T}$

for a system in equilibrium. Note that whether or not an interface is present $F = -k_B T \log Z$ with

$$Z = \frac{1}{N!}\int \prod_1^N d^3r_i\, d^3p_i \exp -\beta\left(\sum p_i^2/2m + V(\{r_i\})\right).$$

Deform the box:



conservation of volume $\Rightarrow H' = V/L'^2$

the interfacial area was $L^2 \Rightarrow L'^2$

so $\left(\frac{\partial F}{\partial A}\right)_{VT} = \frac{\partial L}{\partial A}\left(\frac{\partial F}{\partial L}\right)_{VT} = \frac{1}{2L}\left(\frac{\partial F}{\partial L}\right)_{VT}.$

In Z, introduce scaled coordinates $r_i \to \left(Ls_{ix}, Ls_{iy}, \frac{V}{L^2}s_{iz}\right)$

and integrate out the momenta:

$$Z \sim \frac{V^N}{N!}\Lambda_T^{-3N}\int \prod_{i=1}^N d^3s_i\, e^{-\beta V\left(\{Ls_{ix}, Ls_{iy}, \frac{V}{L^2}s_{iz}\}\right)}$$

Then $\frac{\partial F}{\partial L} = -\frac{k_B T}{Z}\frac{\partial}{\partial L}\int\left(\quad\right) = \left\langle\frac{\partial V}{\partial L}\right\rangle$

$$\frac{\partial V}{\partial L} = \frac{\partial}{\partial L} \sum_{i<j} V_{ij} \left(\left[L^2 (s_{ix} - s_{jx})^2 + L^2 (s_{iy} - s_{jy})^2 + \right.\right.$$
$$\left.\left. + \frac{V^2}{L^4} (s_{iz} - s_{jz})^2 \right]^{\frac{1}{2}} \right)$$

$$= \sum_{i<j} V'(r_{ij}) \cdot \left[L \frac{(s_{ix} - s_{jx})^2}{r_{ij}} + L \frac{(s_{iy} - s_{jy})^2}{r_{ij}} - \right.$$
$$\left. - 2 \frac{V^2}{L^5} \frac{(s_{iz} - s_{jz})^2}{r_{ij}} \right]$$

$$= \sum_{i<j} V'(r_{ij}) \left[\frac{x_{ij}^2 + y_{ij}^2 - 2 z_{ij}^2}{L r_{ij}} \right]$$

and $\gamma = \frac{1}{2A} \left\langle \sum_{i<j} V'(r_{ij}) \frac{r_{ij}^2 - 3 z_{ij}^2}{r_{ij}} \right\rangle$