Statistical Molecular Thermodynamics

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Video 5.6

Microscopic Origin of Pressure

Statistical Mechanics of w and q

Recall from stat mech: $U = \sum_j p_j(N,V,\beta)E_j(N,V)$ with $p_j(N,V,\beta) = \dfrac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)}$

Differentiate: $dU = \sum_j p_j dE_j + \sum_j E_j dp_j = \sum_j p_j \left(\dfrac{\partial E_j}{\partial V}\right)_N dV + \sum_j E_j dp_j$

$E_j = E_j(N,V)$

Compare this to $dU = \delta w_{\text{rev}} + \delta q_{\text{rev}}$

$$\delta w_{\text{rev}} = \sum_j p_j(N,V,\beta)\left(\frac{\partial E_j}{\partial V}\right)_N dV$$

Infinitesimal change in the energy levels, probability remains the same.

$$\delta q_{\text{rev}} = \sum_j E_j(N,V)\,dp_j(N,V,\beta)$$

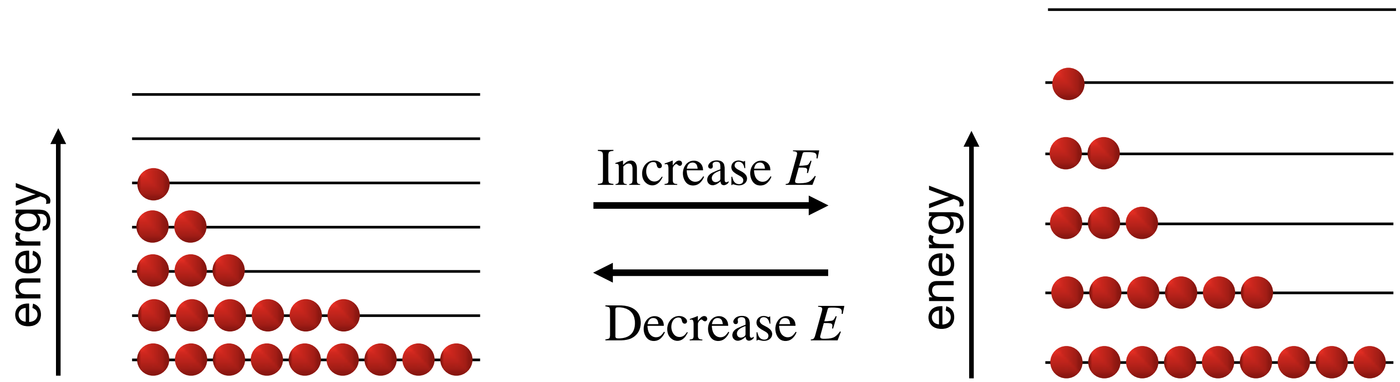
Infinitesimal change in the probability of levels, energy levels remain the same.

Statistical Mechanics of *w* and *q*

WORK

$$\delta w_{\text{rev}} = \sum_j p_j(N,V,\beta)\left(\frac{\partial E_j}{\partial V}\right)_N dV$$

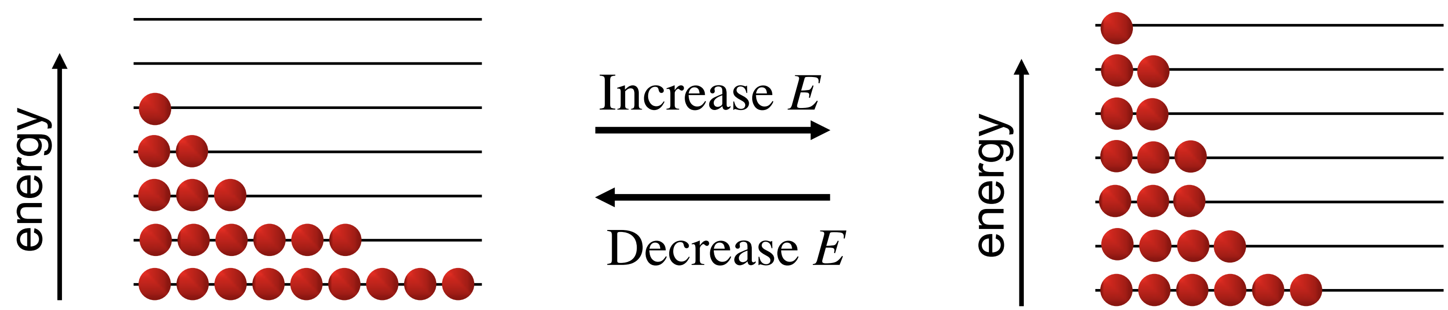
Infinitesimal change in the energy levels, probability remains the same.



HEAT

$$\delta q_{\text{rev}} = \sum_j E_j(N,V)\,dp_j(N,V,\beta)$$

Infinitesimal change in the probability of levels, energy levels remain the same.



Pressure

Given,

$$\delta w_{\mathrm{rev}} = \sum_j p_j(N,V,\beta)\left(\frac{\partial E_j}{\partial V}\right)_N dV$$

And the definition of pressure-volume work,

$$\delta w_{\mathrm{rev}} = -P\,dV$$

We can determine the pressure as,

$$P = -\sum_j p_j(N,V,\beta)\left(\frac{\partial E_j}{\partial V}\right)_N = -\left\langle\left(\frac{\partial E_j}{\partial V}\right)_N\right\rangle$$

Cf. Video 3.4 where we used this relationship without derivation to prove that the partition function for the monatomic ideal gas is consistent with the ideal gas equation of state