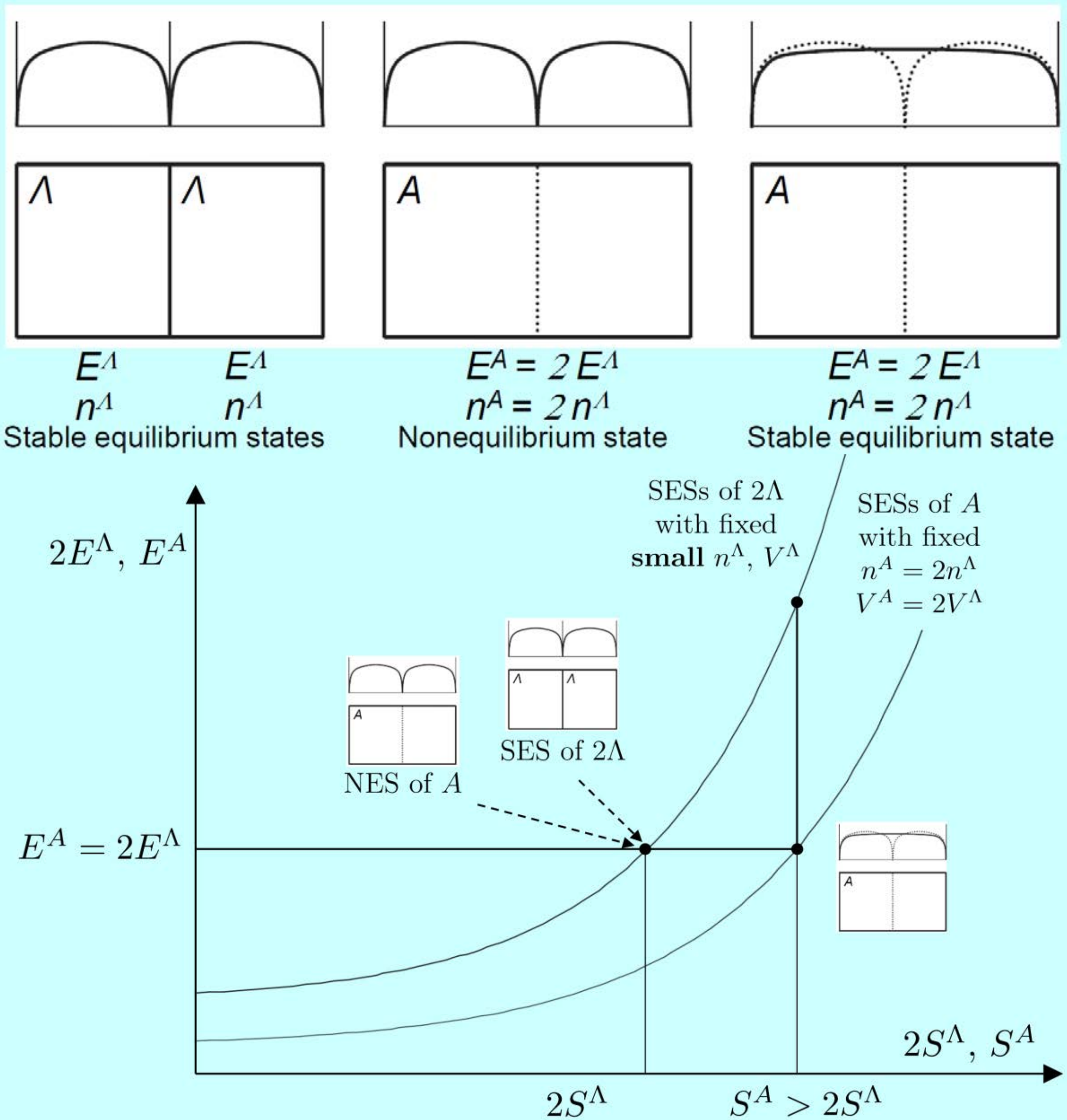
This is the third take-home quiz: Q3

Make another max-5-min video in which using the following slides (the same I used in class) you explain (like I did in class) the key observations that lead to the simple system model and the Euler free energy for small systems. Avoid spending time on the mathematical derivations in slides 4-5-7 below. Rather, focus on graphical representations in slides 2-3-6 and try to explain their physical meaning.

rarefaction effects near walls at SE



Few particles

per partition:

at SES

(micro or mesoscopic systems)

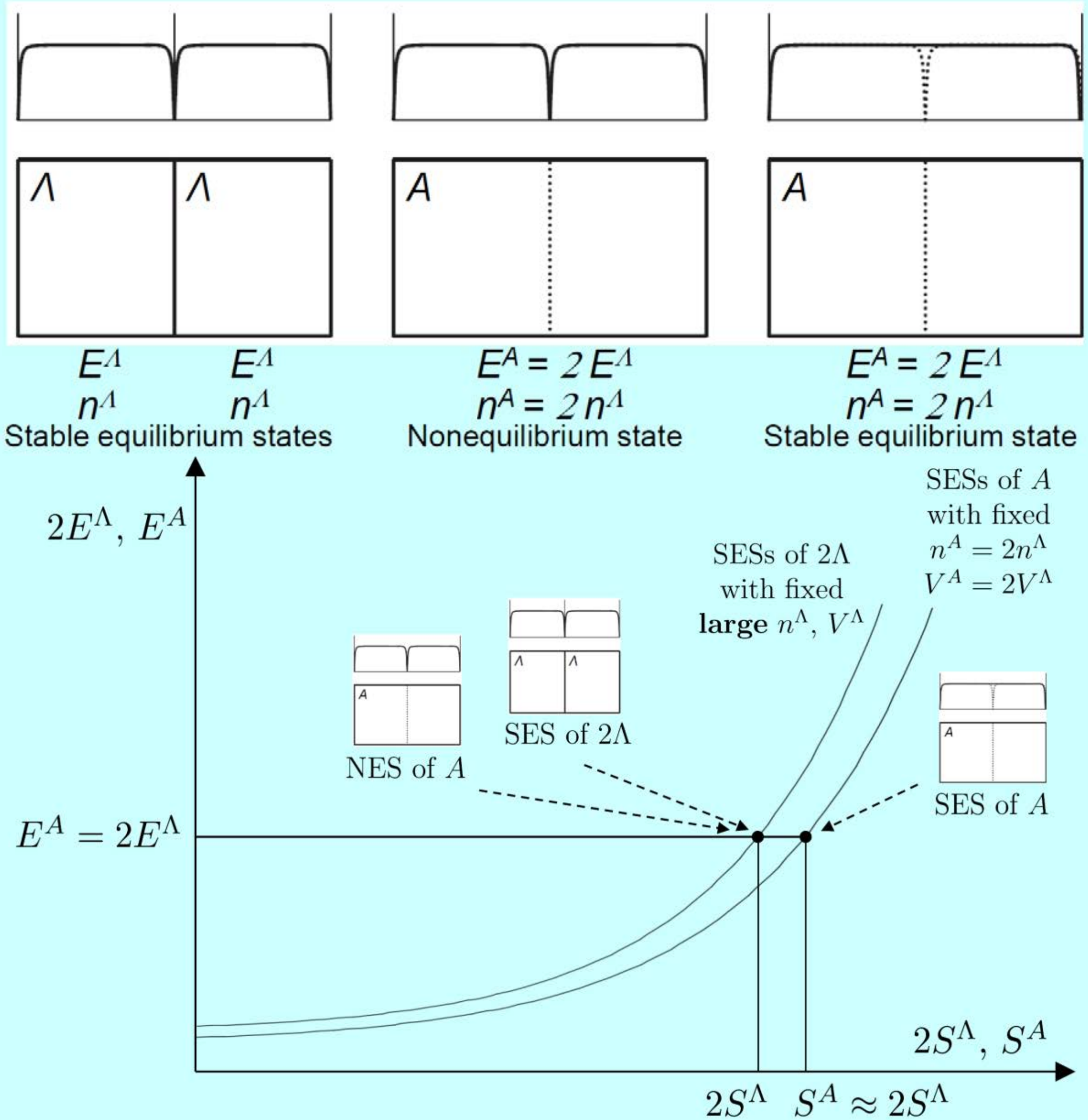
$$S^A > 2S^\Lambda$$

$$S^\Lambda = S_{\rm SES}(E^\Lambda, n^\Lambda, V^\Lambda)$$

$$S^A = S_{\rm SES}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda)$$

$$S_{\rm SES}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda) >$$
$$2\,S_{\rm SES}(E^\Lambda, n^\Lambda, V^\Lambda)$$

rarefaction effects near walls at SE



Many particles
per partition:
at SES
(macroscopic systems)

$$S^A \approx 2S^\Lambda$$

$$S^\Lambda = S_{\text{SES}}(E^\Lambda, n^\Lambda, V^\Lambda)$$

$$S^A = S_{\text{SES}}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda)$$

$$S_{\text{SES}}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda) \approx 2\, S_{\text{SES}}(E^\Lambda, n^\Lambda, V^\Lambda)$$

Simple System Model
assumes:

$$S_{\text{SES}}(2E^\Lambda, 2n^\Lambda, 2V^\Lambda) = 2\, S_{\text{SES}}(E^\Lambda, n^\Lambda, V^\Lambda)$$

Review of basic concepts: simple-system model (macroscopic limit)

proof of the Euler relation

The condition of homogeneity of first degree in all variables

$$U(S,V,\boldsymbol{n}) = \lambda\, U\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \text{ for any real } \lambda \qquad (1)$$

implies the Euler relation

$$U = TS - pV + \boldsymbol{\mu}\cdot\boldsymbol{n}$$

It also implies that the potentials conjugated with S, V, $\boldsymbol{n}$ are homogeneous of zero degree in all variables, i.e., for any real λ,

$$T(S,V,\boldsymbol{n}) = T\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \quad p(S,V,\boldsymbol{n}) = p\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \quad \boldsymbol{\mu}(S,V,\boldsymbol{n}) = \boldsymbol{\mu}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) \quad (2)$$

Proof of (1): compute the partial derivative of Equation (1) with respect to λ

$$0 = U\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) + \lambda\, T\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{S}{\lambda^2}\Big) - \lambda\, p\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{V}{\lambda^2}\Big) + \lambda\,\boldsymbol{\mu}\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\cdot\Big(-\frac{\boldsymbol{n}}{\lambda^2}\Big)$$

and let $\lambda = 1$ to get $0 = U(S,V,\boldsymbol{n}) - T(S,V,\boldsymbol{n})\,S + p(S,V,\boldsymbol{n})\,V - \boldsymbol{\mu}(S,V,\boldsymbol{n})\cdot\boldsymbol{n}$.
Proof of (2): compute the partial derivatives of Equation (1) with respect to S, V, and $\boldsymbol{n}$, respectively.

Review of basic concepts: **(small systems)**

specific properties depend on the total amount of constituents

$$\mathcal{E}u = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n} \qquad \mathrm{d}\mathcal{E}u = -S\,\mathrm{d}T + V\,\mathrm{d}p - \boldsymbol{n}\cdot\mathrm{d}\boldsymbol{\mu} \qquad n_i = -\left(\frac{\partial \mathcal{E}u}{\partial \mu_i}\right)_{T,p,\boldsymbol{\mu}'_i}$$

$\mathcal{E}u = \mathcal{E}u(T,p,\boldsymbol{\mu})$ $\quad T,p,\boldsymbol{\mu}$ for a small system are all independent

$$\epsilon u = e - Ts + pv - \boldsymbol{\mu}\cdot\boldsymbol{y} \qquad \mathrm{d}\epsilon u = -s\,\mathrm{d}T + v\,\mathrm{d}p - \boldsymbol{y}\cdot\mathrm{d}\boldsymbol{\mu} \qquad \sum_{i=1}^r y_i = 1 \qquad \sum_{i=1}^r \mathrm{d}y_i = 0$$

$\epsilon u = \epsilon u(T,p,\boldsymbol{\mu})$ $\quad T,p,\boldsymbol{\mu}$ for a small system are all independent

$$s = \frac{S}{n} = \frac{1}{n}S(nu,nv,n\boldsymbol{y}) = s(u,v,\boldsymbol{y},n) \qquad \left(\frac{\partial s}{\partial n}\right)_{u,v,\boldsymbol{y}} = \frac{1}{n^2}\frac{\mathcal{E}u}{T} = \frac{1}{n}\frac{\epsilon u}{T}$$

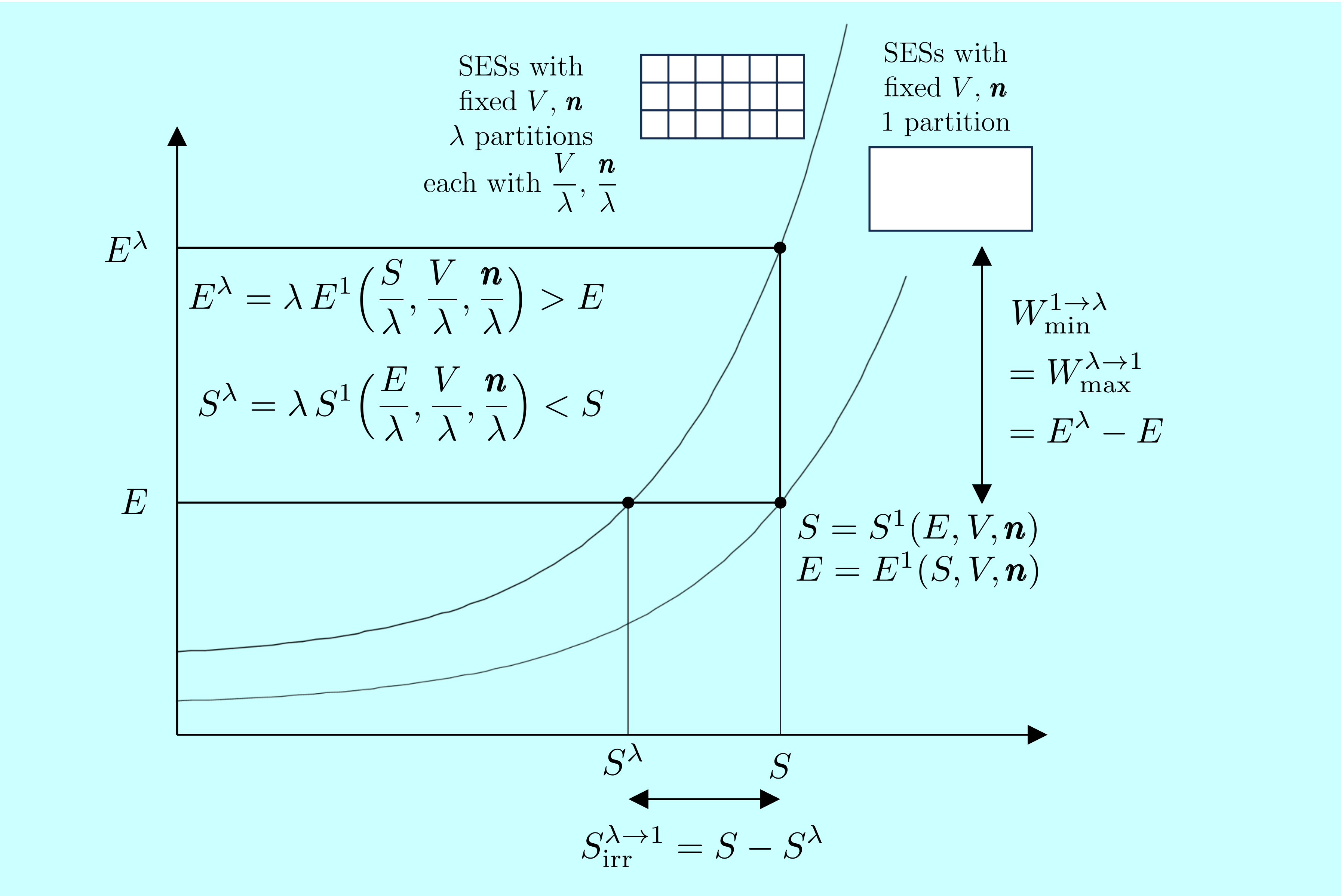
$$e = \frac{E}{n} = \frac{1}{n}E(ns,nv,n\boldsymbol{y}) = e(s,v,\boldsymbol{y},n) \qquad \left(\frac{\partial e}{\partial n}\right)_{s,v,\boldsymbol{y}} = -\frac{1}{n^2}\mathcal{E}u = -\frac{1}{n}\epsilon u$$

$$h = \frac{H}{n} = \frac{1}{n}H(ns,p,n\boldsymbol{y}) = h(s,p,\boldsymbol{y},n) \qquad \left(\frac{\partial h}{\partial n}\right)_{s,p,\boldsymbol{y}} = -\frac{1}{n^2}\mathcal{E}u = -\frac{1}{n}\epsilon u$$

$$f = \frac{F}{n} = \frac{1}{n}F(T,nv,n\boldsymbol{y}) = f(T,v,\boldsymbol{y},n) \qquad \left(\frac{\partial f}{\partial n}\right)_{T,v,\boldsymbol{y}} = -\frac{1}{n^2}\mathcal{E}u = -\frac{1}{n}\epsilon u$$

$$g = \frac{G}{n} = \frac{1}{n}G(T,p,n\boldsymbol{y}) = g(T,p,\boldsymbol{y},n) \qquad \left(\frac{\partial g}{\partial n}\right)_{T,p,\boldsymbol{y}} = -\frac{1}{n^2}\mathcal{E}u = -\frac{1}{n}\epsilon u$$

Review of basic concepts: (small systems)
minimum work of partitioning



minimum work of partitioning

Minimum work of partitioning into λ identical compartments in identical SES:

$$W_{\min}^{1\to\lambda} = W_{\max}^{\lambda\to 1} = E^{\lambda} - E = \lambda\, E^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) - E^1(S,V,\boldsymbol{n})$$

Minimum work to increment or decrement λ by one:

$$W_{\min}^{\lambda\to\lambda+1} = \frac{W_{\min}^{1\to\lambda+1} - W_{\min}^{1\to\lambda}}{(\lambda+1)-\lambda} = \frac{W_{\min}^{1\to\lambda} - W_{\min}^{1\to\lambda-1}}{\lambda-(\lambda-1)} = \frac{\partial W_{\min}^{1\to\lambda}}{\partial\lambda}$$

$$= E^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) + \lambda\, T^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{S}{\lambda^2}\Big)$$

$$- \lambda\, p^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\Big(-\frac{V}{\lambda^2}\Big) + \lambda\,\boldsymbol{\mu}^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\cdot\Big(-\frac{\boldsymbol{n}}{\lambda^2}\Big)$$

$$= E^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) - \frac{S}{\lambda}\, T^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)$$

$$+ \frac{V}{\lambda}\, p^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big) - \boldsymbol{\mu}^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)\cdot\frac{\boldsymbol{n}}{\lambda}$$

$$= Eu^1\Big(\frac{S}{\lambda},\frac{V}{\lambda},\frac{\boldsymbol{n}}{\lambda}\Big)$$

where we recall that we defined the Euler free energy

$$Eu = E - TS + pV - \boldsymbol{\mu}\cdot\boldsymbol{n}$$

So we see that its value for one of the λ partitions equals the minimum work to increase or decrease by one the number of partitions.

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