DEFINING THE EULER FREE ENERGY (OR SHOULD WE CALL IT HILL FREE ENERGY?): A GENERAL STABLE-EQUILIBRIUM PROPERTY, NON-TRIVIAL FOR SMALL-SYSTEMS

Gian Paolo Beretta

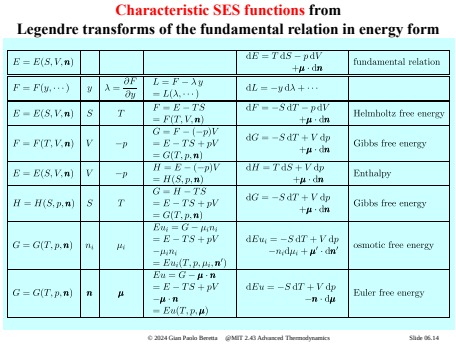
Università di Brescia, Italy
gianpaolo.beretta@unibs.it

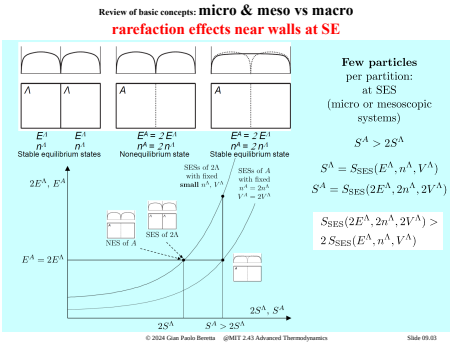
ABSTRACT

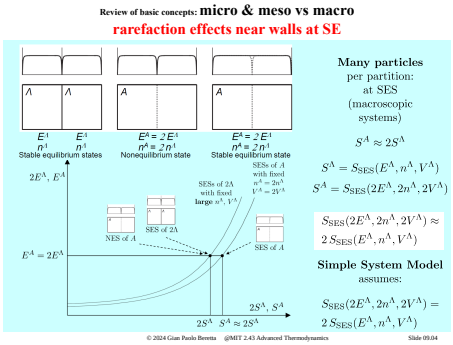
In thermodynamics, the state principle [1, Ch. 8] implies for all confined systems, large and small, the existence of the relation $S = S(E,V,N_1,\ldots,N_r)$. Its Legendre transform with respect to all its variables, is the stable-equilibrium characteristic function $Eu = E - TS + pV - \sum_i \mu_i N_i = Eu(T,p,\mu_1,\ldots,\mu_r)$ that in Ref. [2, Slide 06 s 14], I decided to name "Euler Free Energy." In [1, Ch. 17] and [2, Slides 09 s 03 and 09 s 04], we show that this function does not vanish for small systems due to rarefaction effects near boundaries and partitions. As a consequence, properties like energy E, entropy S, enthalpy H, Helmholtz and Gibbs free energy, F and G, which are extensive in the macroscopic limit $N \to \infty$, are not extensive for small N's. Indeed, for the respective specific properties we proved the following general relations (see [1, Eqs. (17.19) and (17.22)] and [2, Slide 09 s 09])

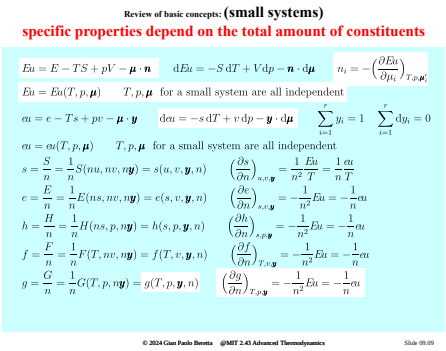
$$\left(\frac{\partial e}{\partial N}\right)_{s,v,\mathbf{y}} = \left(\frac{\partial h}{\partial N}\right)_{s,p,\mathbf{y}} = \left(\frac{\partial f}{\partial N}\right)_{T,v,\mathbf{y}} = \left(\frac{\partial g}{\partial N}\right)_{T,p,\mathbf{y}} = -T\left(\frac{\partial s}{\partial N}\right)_{u,v,\mathbf{y}} = -\frac{1}{N^2}Eu\,.$$

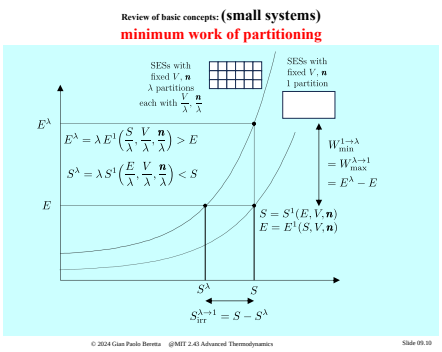
In this presentation, like in [2, Slides 09 s 10 and 09 s 11], I explain how the Euler free energy is also related to the minimum work required to increase (maximum work extractable by decreasing) the number of partitions by one. This can be illustrated very effectively by means of the representation of equilibrium and nonequilibrium states on energy–entropy diagrams we developed in [1, Ch. 13], as shown in the slides reproduced below.

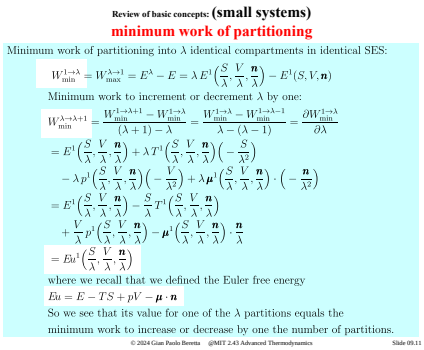












I hope my presentation will inspire further exploration of the connections between these general thermodynamic concepts applied to small systems and both classical and recent formulations of equilibrium thermodynamics for small systems [3] and nanothermodyamics [4], based on Hill's ensemble procedure, which we did not invoke to derive the presented relations and results and which, therefore, appears conceptually unnecessary. So, one question is: Does the Euler free energy coincide with Hill's subdivision potential? If so, I would agree to call *Eu* the "Hill Free Energy."

REFERENCES

[1] E.P. Gyftopoulos and G.P. Beretta, *Thermodynamics. Foundations and Applications*, Macmillan, 1991 (reprinted by Dover, 2005).

[2] MIT OpenCourseWare (2024). *Advanced Thermodynamics* (2.43). https://ocw.mit.edu/courses/2-43-advanced-thermodynamics-spring-2024/. The s and v symbols in the citations above are hyperlinks that point to the specific original slides and the corresponding timestamps in the video lectures. To see the full analytical index with hyperlinks for the whole lecture series click here.

[3] T.L. Hill, *Nano Letters*, vol. 1, 273–275 (2001); doi:10.1021/nl010027w. R.V. Chamberlin, *Entropy*, vol. 17, 52–73 (2015); doi:10.3390/e17010052. R.V. Chamberlin, S.M. Lindsay, *Nanomaterials*, vol. 14, 1828 (2024); doi:10.3390/nano14221828.

[4] D. Bedeaux, S. Kjelstrup, and S.K. Schnell, *Nanothermodynamics: Theory and Application*, World Scientific, 2023.