

# STABLE NANOTHERMODYNAMICS: BEYOND BOLTZMANN'S FACTOR FOR THERMAL EQUILIBRIUM AND NANOSCALE FLUCTUATIONS

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## ABSTRACT

In his lectures on statistical mechanics [1] Feynman calls Boltzmann's factor a "fundamental law," but then he lists several assumptions needed for a system to obey this "law." Two key assumptions are 1) the system must be coupled to an ideal heat bath yielding temperature ( $T$ ) and 2) this coupling must be very weak, yet faster than any fluctuations in local energy. Now it is known that many measurements and computer simulations show clear deviations from these assumptions [2]. Most deviations are due to localized energy fluctuations that are too fast to fully couple to the heat bath, so that conservation of local energy dominates over the very weak coupling needed for Boltzmann's factor. In such cases, we have found that it may be necessary to return to the fundamental laws of thermodynamics to understand the thermal behavior. For example, local energy fluctuations are often best analyzed in a microcanonical ensemble (Fig. 1A, upper left), because conservation of local energy is a more-basic law than Boltzmann's factor.

Hill's theory of small system thermodynamics [3] has been called "the most extensive addition to equilibrium thermodynamics since Gibbs." Indeed, Hill and Gibbs made mathematically similar (and comparably important!) contributions to the laws of thermodynamics. Specifically, conservation of energy during reversible processes (equation in inset of Fig. 1B) requires the term introduced by Gibbs ( $\mu dN_t$ ) if the total number of particles changes ( $dN_t \neq 0$ ), plus the term introduced by Hill ( $\mathcal{E} d\eta$ ) if the number of independent clusters of interacting particles ("subsystems") changes ( $d\eta \neq 0$ ). Gibbs' chemical potential is set to zero ( $\mu = 0$ ) for the stable equilibrium of quantized waves, e.g. photons or phonons. Similarly, Hill's subdivision potential is set to zero ( $\mathcal{E} = 0$ ) to minimize the free energy (Fig. 1B) for the stable equilibrium of independent subsystems in the nanocanonical ensemble. Hill discussed this stability condition at length in section 10-3 of his 1964 book. To my knowledge, since 1964 only our group has applied  $\mathcal{E} = 0$  to any system, allowing us to solve, resolve, or at least clarify several "unsolved" problems in physics [2]. Here I will focus on the stable solution (Fig. 1C) of Ising's original (1925) model for finite chains of interacting binary degrees of freedom ("spins"), which goes beyond Boltzmann's factor by utilizing  $\mathcal{E} = 0$ . Ising could not have found this solution 40 years before Hill's work.

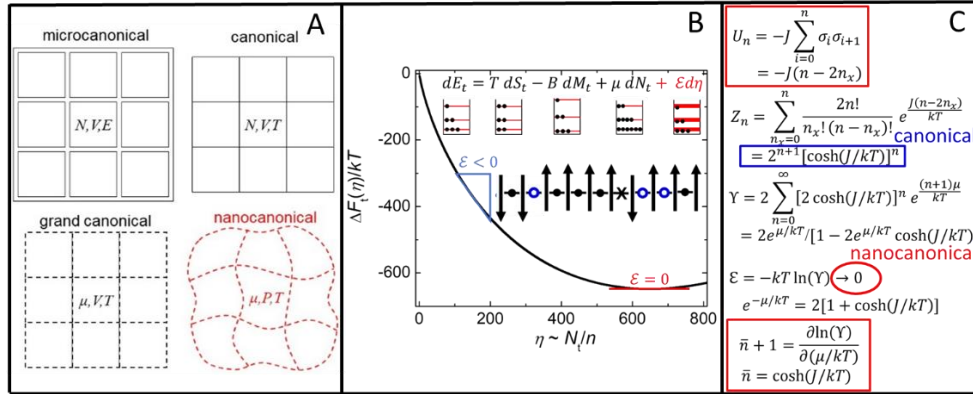


Figure 1. A) Sketch of various ensembles, from subdividing a larger system into  $\eta = 9$  subsystems, with their environmental variables for a simple gas. B) Main figure shows the total free energy versus number of subdivisions for a system of  $N_t = 1000$  Ising spins at  $kT/J = 1$ . The system subdivides until it reaches its stable equilibrium at  $\mathcal{E} = 0$ , yielding subsystems of average size  $\bar{n} + 1 \approx 1000/642 + 1 \approx 2.54$  spins. Upper inset gives the fundamental equation of thermodynamics, including Hill's pair of conjugate variables (in red), with a simple (three-energy-level) diagram showing how energy might change from each term in the equation. Other inset shows  $N_t = 10$  Ising spins with low-energy ( $\bullet$ ) and high-energy ( $\times$ ) interactions, plus no-energy "breaks" ( $\circ$ ) that subdivide the system into  $\eta = 4$  subsystems. C) The Ising model requires  $\mathcal{E} = 0$  for stability in the nanocanonical ensemble.

**Keywords:** Nanothermodynamics, nanocanonical ensemble, nanoscale fluctuations, stable equilibrium, Ising model.

**PACS:** 05.20.Gg; 05.50.+q; 82.60.Qr

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