

NANOTHERMODYNAMICS: SMALL-SYSTEM THERMODYNAMICS APPLIED TO LARGE SYSTEMS*

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EXTENDED ABSTRACT

Standard thermodynamics was developed to describe homogeneous changes in large systems, but now it is known that the primary response of most materials comes from a heterogeneous distribution of independently-relaxing nanometer-sized regions. Nanothermodynamics provides a foundation for understanding finite-size thermal effects inside bulk materials [1,2]. A key feature is the subdivision potential, which is added to the fundamental equation of thermodynamics. The subdivision potential can be understood by comparison to the chemical potential. The chemical potential is the change in energy to take a single particle from a bath of particles into the system, whereas the subdivision potential is the change in energy to take a cluster of interacting particles from a bath of clusters into the system, and in general N interacting particles do not have the same energy as N isolated particles. Thus, the subdivision potential facilitates the treatment of non-extensive and nonlinear contributions to energy, thereby allowing a system to adjust its internal dynamics to find the true thermal equilibrium. We have applied the ideas of nanothermodynamics to standard theoretical models and found improved agreement with measured response, including: non-exponential relaxation, non-Arrhenius activation, and non-classical critical scaling in liquids, glasses, polymers and crystals [3-5].

Nanothermodynamics is based on the assumption that entropy is extensive and additive for independent subsystems of all sizes, whereas most computer simulations of small systems show non-extensive entropy. We study computer simulations of Ising-like models with binary spins that can be up, or down. (Similar statistics applies to binary alloys with sites that can be occupied by atom A, or B; a lattice gas of sites that can be occupied, or empty; or ideal-gas particles in a box that can be on the left side, or right.) Simulations of the standard Ising model using the usual Metropolis algorithm show that the change in entropy more than doubles when one identical subsystem is added to another, similar to the $M \ln(N)$ term that gives Gibbs' paradox when combining identical systems of distinguishable particles. Thus, for the heterogeneous primary response of most materials, either the Boltzmann definition of statistical entropy must be modified, or the Metropolis algorithm is incomplete. The Metropolis algorithm is based on the Boltzmann factor, which requires the usual assumptions of the canonical ensemble [6,7]: the system must be able to borrow an unlimited amount of energy from an effectively infinite heat bath, the system and its bath must be in weak thermal contact without direct interaction, the heat bath must contain a smooth distribution of closely-spaced energies, and units of energy in the system and bath must be uncorrelated. In other words, adding one unit of energy to the system must not change the likelihood of adding a second unit. We investigate nonlinear corrections to the Boltzmann factor that come from the local entropy [8], similar to the Gaussian-fluctuation term first used by Einstein in 1910 to describe critical opalescence.

We have found a nonlinear correction to the Boltzmann factor that makes computer simulations of the Ising model consistent with the concepts of nanothermodynamics. This nonlinear correction comes from the configurational entropy of a local bath, which can be understood by comparison to temperature that comes from the thermal entropy of a heat bath. Specifically, at low temperatures where the heat bath has low entropy, the heat bath is unlikely to allow large increases in energy of the system. Similarly, if the local bath is highly aligned so that it has low entropy, the local bath is unlikely to allow large changes in configuration of the system. Thus, the local bath acts as a reservoir of configurational entropy (e.g angular momentum), similar to how the heat bath acts as a reservoir of thermal entropy. Perhaps the local bath is one way to add conservation of momentum to the laws of thermodynamics. In any case, the nonlinear correction to Boltzmann's factor ensures conservation of energy and maximum entropy during normal thermal fluctuations. Furthermore, the nonlinear correction improves agreement between Monte-Carlo simulations of the Ising model and the measured critical scaling in ferromagnetic materials and fluids, the measured specific heat in imperfect crystals, and the structural correlations found near the Jahn-Teller distortion in LaMnO_3 [9]. Moreover, the nonlinear correction yields particles that are statistically indistinguishable, thereby avoiding Gibbs' paradox in computer simulations of classical particles.

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