Letters

Melding Two Approaches to Entropy

Fortuitously, an interesting article by Ben-Naim *(1)* follows an article by us *(2)* in the January 2009 issue of this *Journal*. Ben-Naim discussed the second law of thermodynamics and entropy using a probabilistic-information-theoretic approach. We illustrated a strong connection between entropy and energy for solids. Here, we suggest how the two modes of thought can be usefully melded.

Ben-Naim envisaged an ensemble of many systems with the same macrostate, but different, time-varying quantum microstates. If a system is isolated, its accessible microstates are equally probable. When a constraint is removed, the number of accessible states increases and the probabilities change accordingly. The system moves toward a state that maximizes the sharply peaked new probability.

Physically, partition removal enables the reduction of existing chemical potential and pressure gradients as molecules carry their energies into new regions. Removal of an insulating constraint enables energy to spread from one spatial region to another and to become stored by a system′s molecules. For phase transitions, changes in energy spreading occur within the resulting phases plus surroundings.

As Ben-Naim observed *(1)*, a single system will spend a larger fraction of time in states that have larger probability. In a process, a system ultimately reaches thermodynamic equilibrium, with an unchanging, maximally probable macrostate and fluctuating microstate. A single system in a laboratory at fixed temperature *dances temporally* over states in the set of W accessible microstates, with entropy $S = k \ln W$.

Thus, entropy reflects the degree of temporal spreading of the system state over microstates with the same *macrostate*. These observations suggest that entropy is a *spreading function* in two ways *(3–5)*:

- In a thermodynamic process, energy spreads spatially, leading toward a more uniform spatial distribution of energy. The degree of spreading depends on the quantity of energy that spreads, available storage modes in the system, and volume.
- In an equilibrium thermodynamic state, the system spreads temporally over accessible microstates.

Notably, S can be viewed as connoting *spreading*.

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