NL2603 Free energy

The concept of "free energy" is a key concept to characterize physically relevant states in statistical mechanics (see e.g. Mandl, 1988; Reichl, 1998). Given an equilibrium system of statistical mechanics with energy levels E_i of the microstates i, the (Helmholtz) free energy is defined as

$$F(\beta) = -\frac{1}{\beta} \log Z(\beta), \tag{1}$$

where

$$Z(\beta) = \sum_i e^{-\beta E_i} \tag{2}$$

is the partition function and β is the inverse temperature. Apparently, the free energy is different from the internal energy U given by

$$U = -\frac{\partial}{\partial \beta} \log Z(\beta) = \langle E_i \rangle. \tag{3}$$

The difference is given by the entropy times the temperature. One has

$$F = U - TS. \tag{4}$$

This equation can also be regarded as describing a Legendre transformation from U to F. Equilibrium states minimize the free energy (rather than the internal energy) — in this sense F is more relevant than U. The minimum of F can be achieved in two competing ways: Either by making the internal energy U small or by making the entropy S large (or both).

The basic principle underlying statistical mechanics, the maximum entropy principle, can also be formulated as a "principle of minimum free energy" (Beck & Schlögl, 1993). In this formulation one starts from fixed intensive quantities (e.g. the inverse temperature β) and considers a free energy function $F[p]$ as a function of an *a priori* arbitrary set of probabilities $[p] = \{p_1, p_2, \ldots\}$. These p_i can describe any state, for example also nonequilibrium and nonthermal states. One then requires

$$F[p] := \sum_i p_i E_i + \beta^{-1} p_i \log p_i = U - \beta^{-1} S \tag{5}$$

to have a minimum in the space of all possible probability distributions. This minimum is achieved for the canonical distribution

$$p_i = \frac{1}{Z} e^{-\beta E_i}. \tag{6}$$

There are straightforward generalizations of this principle for systems with several intensive quantities, for example grand canonical ensembles.

For nonlinear dynamical systems, the concept of free energy is often seen in a much broader sense. Various generalized types of free energies can be defined. A key ingredient for this more general approach is the so-called thermodynamic formalism of dynamical systems (Beck & Schlögl, 1993). One defines partition functions which contain information on certain fluctuating quantities associated with the dynamical system, for example local singularities of the invariant density or local Liapunov exponents. To proceed to a (formal) statistical mechanics description one then defines a free energy function for these partition functions quite analogous to eq. (1).

Examples are "static", "dynamic", and "expansion" free energies of dynamical systems, as well as the so-called "topological pressure". Let us here consider the "static" free energy in somewhat more detail. This free energy function contains information on the spectrum of singularities of the invariant density of the dynamical system and is closely related to very important quantities to characterize multifractals, the so-called Rényi dimensions. One covers the attractor (or repeller) under consideration with small d-dimensional cubes ("boxes") of volume ϵ^d, where d is an integer dimension large enough to embed the attractor. The static partition function is then defined as

$$Z(\beta) = \sum_i p_i^\beta = \sum_i e^{-\beta\alpha_i V}, \tag{7}$$

where p_i is the invariant probability measure associated with box i and β is a formal "inverse temperature" parameter. To illustrate the similarites with statistical mechanics, we have written in the above equation $p_i =: \epsilon^{\alpha_i} = e^{-\alpha_i \cdot V}$, where α_i is like a fluctuating energy associated with each box i and $V = -\log \epsilon$ plays the role of a formal volume variable. One can then study the free energy density associated with this partition function,

$$f(\beta) := \lim_{V\to\infty} -\frac{1}{\beta V} \log Z(\beta) \tag{8}$$

This static free energy, up to a trivial factor, is indeed identical with the Rényi dimensions D_β:

$$f(\beta) = \frac{\beta - 1}{\beta} D_\beta \tag{9}$$

In this way methods borrowed from statistical mechanics play an important role for the statistical description of dynamical systems.

While the above generalized free energies, of relevance for nonlinear dynamical systems, have only formal analogies with conventional free energies, a more fundamental generalization of statistical mechanics suitable for complex systems has been suggested by Tsallis (Tsallis, 1988). In this so-called nonextensive statistical mechanics approach (Abe & Okamoto, 2001; Kaniadakis et al., 2002) the entire formalism of statistical mechanics is generalized by starting from more general entropy measures, the Tsallis entropies. These are defined by

$$S_q = \frac{1}{q-1}(1 - \sum_i p_i^q). \tag{10}$$

Here the p_i are probabilities associated with the microstates i of a physical system. Note that the Tsallis entropies look somewhat similar to the Rényi information measures but are indeed different (there is no logarithm). The parameter q, called "entropic index", can take on any real value but is in practice often close to 1. For $q \to 1$, one can esily check that the Tsallis entropies reduce to the ordinary Shannon entropy $S_1 = -\sum_i p_i \log p_i$. The principal idea of nonextensive statistical mechanics is to do everything we know from ordinary statistical mechanics, but start from the more general entropy measures. Naturally, ordinary statistical mechanics is contained as a special case ($q = 1$) in this more general formalism. The maximum entropy principle yields power-law generalizations of the canonical ensemble,

$$p_i = \frac{1}{Z_q(\beta)}(1 + (q-1)\beta E_i)^{-1/(q-1)}, \tag{11}$$

which reduce to eq. (6) for $q \to 1$. As a consequence, there is then also a more general free energy $F_q(\beta)$, which is parametrized by the entropic index q. One can basically show that the entire formalism of thermodynamics has simple q-generalizations, for example for the generalized free energy there is a relation of the form

$$F_q = U_q - TS_q, \tag{12}$$

where the index q indicates that the q-generalized canonical ensemble is chosen. This type of formalism has interesting physical applications, for example for fully developed turbulence and for scattering processes in high energy physics (Beck, 2002).

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see also entropy, multifractal analysis, chaotic dynamics

Further reading:

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Reichl L.E. 1998. *A Modern Course in Statistical Physics*, New York: John Wiley

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Abe S. & Okamoto Y. (eds.) 2001. *Nonextensive Statistical Mechanics and its Applications*, Berlin and New York: Springer

Kaniadakis G., Lissia M. & Rapisarda A. (eds.) 2002. *Nonextensive Thermodynamics and Physical Applications*, Physica A, 305 (special volume)

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