

Statistical Thermodynamics

Basic Theory and Equations: A White Paper

Alianna J. Maren, Ph.D.

Themasis

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1 Goal of This Paper

Identify and present basic equations from statistical thermodynamics, with the purpose of defining the theoretical framework on which certain inventions will rest, and creating a consistent set of notation that will be used throughout other works.

2 The Partition Function

Our goal is to compute the partition function, Z . To do this, we define a system of interest in a sample region Ω , and specify a Hamiltonian function H_Ω . We identify this region as having volume $V(\Omega)$ and surface area $S(\Omega)$. (Note: The source for the following and most of the succeeding equations is Goldenfeld, starting with Chapter 2, Eqn. 2.1).¹

We write the Hamiltonian for the system as:

$$-\frac{H_\Omega}{k_B T} = \sum_n K_n \Theta_n$$

Equation 1

Where the K_n are the **coupling constants** and the Θ_n are combinations of the dynamical degrees of freedom, summed over in the partition function. The Θ_n may also be referred to as **local operators**. The coupling constants K_n are the external parameters, e.g., fields, exchange interaction parameters, temperature, etc.

As a simple example for expressing a term in H_Ω , we take the Zeeman effect. The coupling constant here is the external magnetic field H , and the corresponding local operator is the magnetic moment at a lattice site i , S_i . Then the contribution of these terms to H_Ω is $-\sum_i H S_i$.

¹ Goldenfeld, N. (1992). Lectures on Phase Transitions and the Renormalization Group (Addison-Wesley). Eqn. 2.3, pg. 24, ff.

The partition function using Goldenfeld's notation is:

$$Z[\{K_n\}] \stackrel{\text{def}}{=} \text{Tr} e^{-\beta H_\Omega}$$

Equation 2

where $\beta = 1/k_B T$, and the operator Tr means “sum over all degrees of freedom, the sum including every possible value of each degree of freedom.”²

After carrying out the trace, Z depends on all of the K_n as indicated by the notation [...].

We simplify notation for the set of coupling constants; $[K] = [\{K_n\}]$, and then we can express the partition function as $Z[K]$.

NOTE: As a point of comparison, the same partition function (canonical ensemble), expressed in Hill's *Statistical Mechanics*³, is given as:

$$Q_n(N, \mathcal{F}, T) = j_n(T)^N \sum_{i=1}^{\Omega} e^{-E_i/kT}$$

where E_i is the sum of nearest-neighbor pair energies for the i^{th} configuration and j_n is the nonconfigurational partition function of each of the N items in the system. (We assume that j_n can be separated from the configurational partition function.)

The correspondence between notational terms is:

Meaning	Goldenfeld	Hill
Partition Function	$Z[\{K_n\}]$	$Q_n(N, \mathcal{F}, T)$
Coupling Constants / External Parameters	K_n	\mathcal{F}, T
Region under Consideration / Total Number of Elements in System	Ω	N
Total Number of Configurations	Tr (Eqn. 2)	Ω

Where given a fixed number of units or sites N , and also a fixed “external parameter” \mathcal{F} , we identify the total number of configurations as:

$$\Omega = \frac{N!}{N_A! N_B!}$$

and thus Ω expresses the number of ways of assigning “spins” among the different N sites.

² Goldenfeld, N. (1992). *Lectures on Phase Transitions and the Renormalization Group* (Addison-Wesley). Eqn. 2.3, pg. 24, ff.

³ Hill, T.L. (1956), *Statistical Mechanics* (McGraw-Hill). Section 41, pgs 288 ff.

3 Applying Statistical Thermodynamics to an Information Corpus

Periodically, throughout this and other works, I will take a moment to link the concepts of basic statistical thermodynamics to potential applications – and interpreting the meaning of these applications – in a large-scale data (information) corpus.

Statistical Thermodynamics	Notation	Application
Coupling Constants / External Parameters	K_n	System “stimulus” by presenting a search / query (for entities/concepts)
Region under Consideration / Total Number of Elements in System	Ω	Region of a data corpus
Total number of lattice sites in region Ω	$N(\Omega)$	Total number of items (web pages, documents, etc.) within corpus region
“Active” state A vs. “non-active” B	A, B	Active “item” in response to a query that identifies presence of a concept / entity in item whose frequency (tf/idf, or other designated function) crosses a defined threshold.
Correlation length: <i>Spatial extent of fluctuations</i> in a physical quantity about the average for that quantity.	ξ	Two possible interpretations: <ol style="list-style-type: none"> 1. Within-domain (where a “domain” is an active item): “Distance” (metric still subject to definition) between two concepts or entities in an active corpus item 2. Cross-domain: “Distance” (metric again still TBD) between two active items (in A) within a corpus

4 The Free Energy in a Bistate System (The Ising Gas Model)

The free energy is defined by

$$F_{\Omega}[\{K_n\}] = -k_B T \log Z_{\Omega}$$

Equation 3

and the thermodynamic information on the system Ω is contained in the derivatives, e.g. $\partial F_{\Omega} / \partial K_n, \partial^2 F_{\Omega} / \partial K_n \partial K_m$, etc. These will include bulk effects, surface effects, and various finite-size effects. At this stage, with finite region Ω , there is *no* information about phase transitions or phases.

We allow the free energy per unit to be f (or f_b for bulk free energy).

From Hill, *Statistical Mechanics*⁴:

The basic equation from simple thermodynamics for the *Helmholtz Free Energy* is given as:

$$A = U - TS$$

where A is the Helmholtz free energy, U is the enthalpy, or energy associated with those units in an “active” state, T is the temperature, and S is the entropy.

In differential form

$$dA_n = -S_n dT + Hd\mathcal{F} + \mu_n dN$$

where H is an external magnetic field, or consistently maintained stimulus. (In our work, we will take this stimulus to be a search or query imposed on a corpus containing items that potentially respond to this stimulus by changing from an “inactive” state **A** into an “active” state **B**.)

Since A (the *free energy*) and other terms are extensive quantities, we create the term A_n to refer to the Helmholtz energy per unit, or to create an intensive quantity, and similarly for the other variables. (Note that this corresponds to f of the immediately preceding Goldenfeld notation.)

\mathcal{F} is an external parameter (which replaces the volume in ordinary thermodynamics, and comparable to intensity of magnetization, or *strength of input stimulus*) and is an extensive quantity. (In our application, this can be related to corpus size.) We use H to represent the external, consistently maintained stimulus. This can be a magnetic field, when considering a ferromagnetic system, or a sustained “search” or “query” activation, for our application. (Note that if presenting the query does not change our analog to “system volume,” then this $Hd\mathcal{F}$ term goes to zero.)

Finally, μ_n is normally the chemical potential; here we treat it as the energy that can be associated with a unit in its activated state, and N is the total number of units ($\mathbf{A} + \mathbf{B} = N$) in the system.

We note that as $H \rightarrow \infty$, $\mathcal{F} \rightarrow N$, or that as the external stimulus becomes very large, the total number of units in the “activated” state **A** approaches the total number of units N . The reverse, as $H \rightarrow -\infty$, is also true.

5 The Ising Model

We consider the nearest-neighbor Ising model Hamiltonian

⁴Hill, T.L. (1956), *Statistical Mechanics* (McGraw-Hill). Section 41, pgs 288 ff.

See also: http://en.wikipedia.org/wiki/Helmholtz_free_energy, http://en.wikipedia.org/wiki/Gibbs_free_energy, <http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/helmholtz.html>

$$-H_{\Omega} = H \sum_{i=1}^{N(\Omega)} S_i + J \sum_{\langle ij \rangle} S_i S_j$$

Equation 4

where we assume a uniform magnetic field H , and the notation $\langle ij \rangle$ means that “ i and j are nearest neighbor sites”. S_i refers to the spin on a site; in the Ising model, we allow for two spins, resulting in two possible states, **A** or **B**. (Spin up or down, or active / non-active, etc.)

In this model, the only interaction between spins is the *nearest-neighbor interaction*, denoted by J .

6 Analytic Properties; Computing the Entropy

While the free energy F_{Ω} is an *extensive* property, the local free energy f is *intensive*. We can define the principle analytic properties of f as:

1. $f < 0$.
2. $f(H, J, T, \dots)$ is continuous.
3. $\partial f / \partial T, \partial f / \partial H, \dots$ exist almost everywhere, and right and left derivatives exist everywhere and are almost equal everywhere.
4. The entropy per site $S \stackrel{\text{def}}{=} \partial f / \partial T \geq 0$ almost everywhere.
5. $\partial f / \partial T$ is monotonically non-increasing with T . Thus,

$$\frac{\partial^2 f}{\partial T^2} \leq 0,$$

which implies that the specific heat at constant magnetic field $C_H \geq 0$:

$$C_H \stackrel{\text{def}}{=} T \frac{\partial S}{\partial T} \Big|_H = - \frac{\partial^2 F}{\partial T^2} \Big|_H \geq 0.$$

Equation 5

We will find the specific heat useful later when we consider the possibility of phase transitions; we will of course subsume the temperature T , but it will be implicitly involved in our definition for H_{Ω} .

For the moment, we use (4) to express the *entropy* as

$$S = - \frac{\partial F}{\partial T} = k_b \log \text{Tr} e^{-\beta H_{\Omega}} + k_b \cdot \frac{1}{k_b T^2} \cdot \frac{\text{Tr} H_{\Omega} e^{-\beta H_{\Omega}}}{\text{Tr} e^{-\beta H_{\Omega}}}$$

$$\begin{aligned}
 &= k_b \left[\log Z_\Omega + \frac{\text{Tr} \beta H_\Omega e^{-\beta H_\Omega}}{Z_\Omega} \right] \\
 &= k_b \text{Tr}(\rho_n \log \rho_n)
 \end{aligned}$$

Equation 6

where

$$\rho_n \stackrel{\text{def}}{=} \frac{\exp(-\beta H_\Omega)}{\text{Tr} e^{-\beta H_\Omega}}$$

Equation 7

7 Free Energy

When a system is at equilibrium, the free energy is at a minimum. Systems can inhabit metastable states corresponding to local free energy minima. Thus, as we seek to use a free energy (or “energy landscape”) approach for modeling systems, we need to characterize the free energy equation, and identify how various terms interact when creating free energy minima. Only then can we ascertain the usefulness of any particular formalism.

7.1 Limitations of Simple Statistical Thermodynamic Methods

Previous efforts to apply statistical thermodynamics, in a meaningful way, to large-scale neural architectures have failed, largely because the behavior of the most commonly-used equations was insufficient to meet modeling needs. That is, a simple bistate system is most often treated as a “spin glass,” modeled by the Ising equations, which provide a Helmholtz Free Energy⁵. The simple equation for this situation, again using a bistate system wherein the fraction of units in an “activated state” is x , and the remaining fraction, $1-x$, is in an “inactive state” is given as:

$$A = U - TS$$

Equation 8

where A is the Helmholtz free energy, U is the enthalpy, or energy associated with those units in an “active” state, T is the temperature, and S is the entropy.

7.2 The Role of Temperature and the Enthalpy Term

When we look at a non-reduced free energy equation, we see that raising the temperature T causes the entropy term ($-TS$) to become a deeper concave curve. (Entropy itself is maximum when $x=0.5$ for the case where activation and interaction parameters, or enthalpy, are zero.)

⁵http://en.wikipedia.org/wiki/Helmholtz_free_energy, http://en.wikipedia.org/wiki/Gibbs_free_energy, <http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/helmholtz.html>

This means that increasing temperature drives the system minimum to be more governed by entropy.

The first RHS term in Equation 8 is the enthalpy term, U , given as:

$$U = e_1x + \frac{e_2}{2}x^2$$

Equation 9

The reduced version is divided through by T , giving:

$$\bar{U} = \frac{U}{T} = \varepsilon_1x + \frac{\varepsilon_2}{2}x^2$$

Equation 10

Before engaging in the detailed equations, we offer some notes about the key parameters, ε_1 and ε_2 . The first parameter, ε_1 , deals with the increase in activation energy of the “active fraction” of nodes relative to the inactive ones.

When we create a reduced free energy equation, the early parameters for e_1 and e_2 are now divided by T , resulting in the parameters ε_1 and ε_2 . An increase in T actually reduces both ε_1 and ε_2 .

The first parameter, ε_1 , deals with the increase in activation energy of the “active fraction” of nodes relative to the inactive ones. Thus, increasing T is the same as reducing e_1 , or the energy difference between an active node and a non-active one. Conversely, increasing ε_1 is equivalent to either reducing T *or* to increasing the energy difference between active and non-active nodes.

Either way, increasing ε_1 shifts the free energy minimum (at least, for simple versions of the free energy equation) to states where the equilibrium state requires fewer active nodes.

This only carries us so far. Systems with only activation energy, and no interaction energy, are not very interesting. In the simple Ising model (with simple state distribution entropy, not considering the effect of cluster distributions), there is just a single minimum when there is no interaction energy. State transitions are smooth, and not particularly interesting. This is not a useful model.

Things become a bit more interesting when we introduce the pairwise interaction energy term – both for simple and complex energy terms. We typically assign a negative value to the interaction energy; ε_2 is negative. The physical meaning of this is that an interaction between

similar terms (between, e.g., two active nodes) reduces the overall free energy of the system. That means that the interaction between two neighboring active nodes is a stabilizing force for equilibrium.

This further means that as we increase the (negative) value of ε_2 , we get a more pronounced difference in the effect of having nodes in the active versus nonactive states. Even for the simple-entropy version, we get a rather complex phase diagram. For our work with the more complex entropy, we shall simply keep in mind that increasing the (negative) interaction energy promotes formation of clusters, because it *precisely* this interaction energy that causes clusters to persist.

8 The Full Free Energy Equation

We divide *Equation 8* through by T and the various entropy coefficients associated, and substitute in terms. to obtain a reduced free energy expression:

$$\bar{A} = \varepsilon_1 x + \frac{\varepsilon_2 x^2}{2} - \overline{\ln \Omega} = \varepsilon_1 x + \frac{\varepsilon_2 x^2}{2} + [x \ln x + (1 - x) \ln(1 - x)].$$

Equation 11

In this equation, the two epsilon terms refer to the energy associated with the active units (ε_1) and the interaction energy (where we have used $\varepsilon_2 / 2$ as the interaction energy term for simplicity, given how the following equation resolves). The term on the far right is the (reduced) Canonical Ensemble, which will give us a set of simpler terms in the following equation. Various coefficients have been absorbed into the “reduced” free energy \bar{A} .

In nature, all systems tend towards a minimal free energy state. To compute this, we take the derivative of the previous equation with respect to x , the fraction of “active” units, and set it equal to zero. This gives us:

$$\frac{\partial \bar{A}}{\partial x} = \varepsilon_1 + \varepsilon_2 x + \frac{\partial}{\partial x} [x \ln x + (1 - x) \ln(1 - x)] = 0$$

Equation 12

When we examine the phase diagram (parameter space of solutions) for the previous equation, we find that there is nothing of use in modeling the large-scale distribution of items. (This discussion is carried out in greater depth in the *Applications White Paper, TR 2009-002*.)

The deficiency with the approach described in the previous section is that it has too simplistic a representation for entropy. The entropy term of the previous equations, based on the classic Ising model, represents only the fraction of units in an active state.

A new formulation is needed. This is presented in a succeeding *Technical Report*.