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Theoretical Framework

Statistical Mechanics

"Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics." States of Matter (1975), by David L. Goodstein

Central problem of thermodynamics: characterize the actual state of equilibrium among all virtual states

Entropy postulate: there exist a function S of the extensive variables $(X_0, X_1...X_r)$ called entropy, that assumes the maximum value for a state of equilibrium among all vritual states and that possesses the following properties:

- Extensivity $S^{(1 \cup 2)} = S^1 + S^2$
- Convexity $S((1-\alpha)X^1 + \alpha X^2) \ge (1-\alpha)S(x^1) + \alpha S(X^2)$
- Monotonicity $\frac{\partial S}{\partial E}|_{X_1...X_r} = \frac{1}{T} > 0$

The equilibrium state corresponds to the maximum entropy compatible with the constrains

Concepts of statistical mechanics: entropy [1]

- Fundamental postulate of statistical mechanics $S = k_b \ln |\Gamma|$
- Where S is the thermodynamic entropy, k_b is Boltzmann constant and $|\Gamma|$ the volume in the phase space

$$S(X_{0},...,X_{r}) = k_{b} \ln \int_{\Gamma} dx = k_{b} \int dx \prod_{i=0}^{r} \left[\theta(X_{i}(x) - (X_{i} - \Delta X_{i}))\theta(X_{i} - X_{i}(x))\right]$$
(1)

- $(X_0, ..., X_r)$ are the extensive variables
- The θ functions assures that the integrand is not null only in the interval $X_i \Delta X_i \leq X_i(x) \leq X_i$

(2)

(3)

Concepts of statistical mechanics: micro-canonical ensamble

Lets focus on a particular observable A (extensive)

$$S(X; a) = k_b \ln \int_{\Gamma} dx \delta(A(x) - a)$$

$$J_{\Gamma}$$

$$S(X) = S(X; a*) > S(X; a)$$

$$\frac{|\Gamma(a)|}{|\Gamma|} = \frac{1}{|\Gamma|} \int_{\Gamma} dx \delta(A(x) - a)$$

$$= \exp\left\{\frac{1}{k_b}\left[S(X;a) - S(X;a^*)\right]\right\}$$

$$\simeq \exp\left\{\frac{1}{k_b} \left[\frac{\partial^2 S}{\partial A^2}|_{a^*} (a - a^*)^2\right]\right\}$$

 $a^* = \langle A(x) \rangle = \frac{1}{|\Gamma|} \int_{\Gamma} dx A(x)$

$$\frac{|\Gamma(a)|}{|\Gamma|} = \frac{1}{|\Gamma|} \int_{\Gamma} dx \delta(A(x) - a)$$

(4)

Concepts of statistical mechanics: canonical ensemble

$$a^* = \frac{1}{|\Gamma|} \int_{\Gamma} dx_s dx_R A(x_s) \tag{6}$$

$$\langle A(x) \rangle = \int dx_s dx_r A(x_s) \delta(H^{(s)})$$
 (7)

$$\langle A(x) \rangle = \frac{1}{|\Gamma|} \int dx_s dx_r A(x_s) \delta(H^S(x_s) + H^R(x_R) - H^S(x_S))$$
 (8)

$$\langle A(x) \rangle = \frac{1}{|\Gamma|} \int dx_s A(x_s) \times \int dx_r \delta(H^R(x_R) - (E - H^{(S)}(x_s)))$$
 (9)

$$\int dx_r \delta(H^R(x_R) - (E - H^{(S)}(x_S))) \simeq \exp\left\{\frac{1}{k_b} S^R(E - H^S)\right\} (10)$$

Concepts of statistical mechanics: canonical ensemble

$$\exp\left\{\frac{1}{k_b}S^R(E-H^S)\right\} \simeq \exp\left[\frac{1}{k_b}S^R(E)\right] \exp\left[-\frac{1}{k_b}\frac{\partial S^{(R)}}{\partial E}|_E H^{(S)}(x_S)\right]$$
(11)

$$\langle A(x) \rangle = \frac{1}{Z} \int dx_s A(x_s) exp \left[-\frac{H^{(S)}(x_s)}{k_b T} \right]$$
 (12)

$$Z = \int dx_s \exp\left[-\frac{H^S(x_s)}{k_L T}\right] \tag{13}$$

$$\langle A(x) \rangle = \frac{1}{Z} \int dE \int dx \delta(H(x) - E) A(x) \exp(-\frac{E}{k_B T})$$
 (14)

$$\langle A(x) \rangle = \frac{1}{Z} \int dE' a^*(E') exp \left[-\frac{E' - TS(E')}{k_B T} \right]$$
 (15)

Concepts of statistical mechanics: canonical ensemble[1]

$$Z \simeq \exp\left[-\frac{E*-TS(E*)}{k_bT}\right] = \exp\left(-\frac{F}{k_bT}\right)$$
 (16)

$$\frac{\partial \ln Z(\beta)}{\partial \beta} = -\frac{1}{Z} \int dx H(x) \exp\left[-\frac{H}{k_b T}\right] = -\langle H(x) \rangle = -E \quad (17)$$

$$\frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = \left\langle H(x)^2 \right\rangle - \left\langle H(x) \right\rangle^2 \tag{18}$$

$$\langle H(x)^2 \rangle - \langle H(x) \rangle^2 = -\frac{\partial E}{\partial (1/k_b T)} = k_b T^2 \frac{\partial E}{\partial T} = k_b T^2 C$$
 (19)

In this way a statistical quantity the variance has been connected to a thermodynamic quantity: the temperature.

Numerical simulations

"Never make a calculation until you know the answer. Make an estimate before every calculation, try a simple physical argument (symmetry! invariance! conservation!) before every derivation, guess the answer to every paradox and puzzle. Courage: No one else needs to know what the guess is. Therefore make it quickly, by instinct. A right guess reinforces this instinct. A wrong guess brings the refreshment of surprise. In either case life as a spacetime expert, however long, is more fun!" John Archibald Wheeler

Bibliography I



Luca Peliti. *Statistical mechanics in a nutshell*. Princeton University Press, 2011.

ROC and ϕ factor

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