Microscopic Legendre Transform and Canonical Ensemble

Ramandeep S. Johal

Indian Institute of Science Education and Research Mohali

10th Indian Statistical Physics Community Meeting
April 23-25, 2025

April 24, 2025

Overview

What is a Legendre Transform?

- A Legendre transform switches from one set of variables to another—especially useful when the new variables are more natural to work with.
- Common in physics when changing from quantities like velocity to momentum, or entropy to temperature.

Mathematical Definition

The Legendre-Fenchel transform:

$$f^*(p) = \inf_x \left(px - f(x)\right).$$

If $f(x)$ is concave and differentiable:

$$f^*(p) = px - f(x), \quad \text{where } p = \frac{df}{dx}$$

- It replaces variable x with $p = \frac{df}{dx}$

Known simply as Legendre transform in physics.

Legendre-Fenchel transforms in a nutshell, by Hugo Touchette

Legendre Transform in Thermodynamics

- Internal energy: $U(S,V)$
- Temperature: $T = \left(\frac{\partial U}{\partial S}\right)_V$
- Helmholtz free energy: $S \to T$.

$$F(T,V) = U(S,V) - TS$$

Legendre Transform of entropy:

$$\beta F(\beta, V) = \beta U - S(U,V).$$

Inverse Legendre Transform:

$$S(U,V) = \beta U - \beta F(\beta, V).$$

Canonical ensemble

The system is in thermal equilibrium with the heat reservoir:

$$p_i^* = \frac{e^{-\beta\varepsilon_i}}{\sum_{i=1}^{W} e^{-\beta\varepsilon_i}},$$

The equilibrium free energy:

$$\beta F(\beta) = -\ln \sum_{i=1}^{W} e^{-\beta\varepsilon_i}.$$

Canonical ensemble

Mean energy:

$$U^* = \frac{\partial}{\partial \beta}(\beta F) = \sum_{i=1}^{W} p_i^* \varepsilon_i$$

Entropy:

$$\begin{aligned} S(U^*) &= \beta U^* - \beta F(\beta) \\ &= -\sum_{i=1}^{W} p_i^* \ln p_i^* \equiv \mathcal{S}^* \end{aligned}$$

Thermodynamic entropy is equal to the Shannon entropy of the equilibrium distribution.

Jaynes' Maximum Entropy Principle

Statement

Given a set of constraints, the most unbiased estimate of a probability distribution is the one that maximizes the Shannon entropy:

$$S = -\sum_i p_i \ln p_i$$

subject to:

$$\sum_i p_i = 1 \quad \text{(normalization)}$$

$$\sum_i p_i f_i = \langle f \rangle \quad \text{(constraint on mean value)}$$

Mathematical Solution

- Use the method of Lagrange multipliers to incorporate constraints:

$$\mathcal{L} = -\sum_i p_i \ln p_i - \alpha \left(\sum_i p_i - 1 \right) - \lambda \left(\sum_i p_i f_i - \langle f \rangle \right)$$

- Solving this ($\delta \mathcal{L} = 0$) gives:

$$p_i = \frac{e^{-\lambda f_i}}{Z}, \quad Z = \sum_i e^{-\lambda f_i}$$

The Maxent principle

Constraints: $k = 1, ..., m$

$$\langle f_k(x) \rangle = \sum_{i=1}^{n} p_i f_k(x_i) = F_k$$

Solution:

$$p_i = \exp[-\lambda_0 - \sum_{j=1}^{m} \lambda_j f_j(x_i)]$$

$$\lambda_0 = \ln Z = \ln \sum_{i=1}^{n} \exp[-\sum_{j=1}^{m} \lambda_j f_j(x_i)].$$

$$F_k = -\frac{\partial}{\partial \lambda_k} \ln Z.$$

$$S(F_1, ..., F_m) = \sum_{k=1}^{m} \lambda_k F_k + \ln Z(\lambda_1, ..., \lambda_m).$$

Example: Canonical Ensemble

- Maximize entropy with given average energy ($\sum_i p_i E_i = U$):
- Variational condition:

$$\sum_{i=1}^{W} (\beta\varepsilon_i + 1 + \ln p_i + \alpha) dp_i = 0.$$

- Resulting distribution:

$$p_i = \frac{e^{-\beta E_i}}{Z}, \quad Z = \sum_i e^{-\beta E_i}$$

- Legendre Transform structure:

$$S(U) = \beta U + \ln Z(\beta).$$

Interpretation

$$\text{Canonical entropy} \Longleftrightarrow \text{Shannon entropy}$$

- Equilibrium free energy is related to thermodynamic entropy via Legendre transform
- Thermodynamic entropy may be related to Shannon entropy via Jaynes' principle.

Can the equilibrium free energy be directly related to Shannon entropy via an optimization procedure?

Microscopic Legendre Transform ($\mathscr{L}_{\mathscr{M}}$)

$$\beta F(\beta, V, N) = \underset{U}{\mathrm{Min}} \{\beta U - S(U, V, N)\}.$$

$$\beta U = \beta \textstyle\sum_{i=1}^{W} p_i \varepsilon_i \rightarrow \sum_{i=1}^{W} p_i.(\beta \varepsilon_i)$$

$$\beta F(\beta\varepsilon_1, ..., \beta\varepsilon_W) = \underset{p_1,\dots,p_W}{\mathrm{Min}} \left\{ \sum_{i=1}^{W} p_i.(\beta\varepsilon_i) - \tilde{\mathcal{S}}(p_1, ..., p_W) \right\}$$

$$\tilde{\mathcal{S}}(p_1, ..., p_W) = -\sum_{i=1}^{W} p_i \ln p_i - \alpha \left(\sum_{i=1}^{W} p_i - 1 \right)$$

Optimum condition:

$$\left. \frac{\partial \tilde{\mathcal{S}}}{\partial p_i} \right|_{p_i = p_i^*} = \beta \varepsilon_i.$$

Exact differential of entropy

$$\tilde{\mathcal{S}} = -\sum_{i=1}^{W} p_i \ln p_i - \alpha \left(\sum_{i=1}^{W} p_i - 1 \right)$$

$$d\tilde{\mathcal{S}} = \sum_{i=1}^{W} \frac{\partial \tilde{\mathcal{S}}}{\partial p_i} dp_i,$$

where

$$\frac{\partial \tilde{\mathcal{S}}}{\partial p_i} = -(1 + \ln p_i + \alpha).$$

At the optimal point $(p_i = p_i^*)$:

$$\frac{\partial \tilde{\mathcal{S}}}{\partial p_i} = \beta \varepsilon_i.$$

$$\beta \varepsilon_i + 1 + \ln p_i^* + \alpha = 0 \quad \Longrightarrow \quad p_i^* = e^{-(1+\alpha)} \cdot e^{-\beta \varepsilon_i}$$

Definition of heat

$$đQ = \sum_{i=1}^{W} \varepsilon_i dp_i$$

$$d\tilde{\mathcal{S}} = \sum_{i=1}^{W} \frac{\partial \tilde{\mathcal{S}}}{\partial p_i} dp_i.$$

At equilibrium,

$$\frac{\partial \tilde{\mathcal{S}}}{\partial p_i} = \beta \varepsilon_i.$$

$$\therefore \qquad d\tilde{\mathcal{S}}^* = \beta \sum_{i=1}^{W} \varepsilon_i dp_i^*.$$

MLT and Jaynes' approach

Consider a system in equilibrium with the heat reservoir.
A reversible process,

$$d\tilde{\mathcal{S}} + dS_{\mathrm{R}} = 0.$$

$$d\tilde{\mathcal{S}} = -\sum_{i=1}^{W}(1 + \ln p_i + \alpha)dp_i.$$

$$đQ = \sum_{i=1}^{W} \varepsilon_i dp_i.$$

Since this heat is exchanged with the heat reservoir, so the change in the entropy of the latter is $dS_{\mathrm{R}} = -\beta\, đQ$.

$$\sum_{i=1}^{W}(\beta\varepsilon_i + 1 + \ln p_i + \alpha)dp_i = 0.$$

Conclusion

- The microscopic Legendre transform offers a novel perspective on the relationship between Shannon entropy and Helmholtz free energy.
- It provides an alternative derivation of the canonical ensemble and underscores the connection between information-theoretic and thermodynamic entropy.
- Future applications: Non-equilibrium processes. Generalized entropies.

Foundations of Physics (2025) 55:12
https://doi.org/10.1007/s10701-025-00824-7

RESEARCH

Microscopic Legendre Transform, Canonical Ensemble and Jaynes' Maximum Entropy Principle

Ramandeep S. Johal[1]

Received: 21 June 2024 / Accepted: 10 January 2025

Thank You

for your attention