Beyond the Second Law of Thermodynamics

Dissipation: The Phase-Space Perspective

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The Second Law of Thermodynamics

There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work.

William Thomson
(Lord Kelvin)

There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir.

Rudolf Clausius
**Entropy and the Second Law**

- **Isolated Systems**
  - No exchange of energy or matter between the system and the environment is allowed.

- **Closed Systems**
  - Energy exchange is allowed but not matter exchange.

\[ \Delta S \geq 0 \]

\[ \Delta S \geq \frac{Q}{T} \]

\[ Q \]

\[ T \]

**Second Law**  \( \rightarrow \)  **Time's Arrow!**
“The law that entropy always increases holds, I think, the supreme position among the laws of nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equation – then so much the worse for Maxwell's equations ... but if your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.” (1928)

“...The second law of thermodynamics is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of the basic concepts, it will never be overthrown.” (1949)
Why is the second law an inequality?

\[ \Delta S - \frac{Q}{T} = \geq 0 \]

Holy Grail of Statistical Mechanics

\[ S = S_r + S_i \]

reversible entropy change \[ \Delta S_r = \frac{Q}{T} \]

irreversible entropy production \[ \Delta S_i \geq 0 \]

Ludwig E. Boltzmann (1844-1906)
Second Law with Work

\[ \Delta U = W + Q \]  \hspace{1cm} \text{(First Law of Thermodynamics)}

\[ \Delta F = \Delta U - T \Delta S \]  \hspace{1cm} \text{(Helmholtz Free Energy)}

\[ W - \Delta F = T \Delta S - Q = \text{Holy Grail} \geq 0 \]

\[ W = W_{\text{rev}} + W_{\text{dis}} \]

reversible work \hspace{1cm} W_{\text{rev}} = \Delta F

dissipative work \hspace{1cm} W_{\text{dis}} \geq 0
\[ \langle W \rangle - \Delta F = k_B T \int \rho_F(q, p, t) \ln \frac{\rho_F(q, p, t)}{\rho_B(q, -p, t)} \, dq \, dp \]
\[ = k_B T D(\rho_F \| \rho_B) \]
A Non-Equilibrium Process: Time-Dependent Hamiltonian

Forward Process

\[ H(q, p; \lambda_0) \rightarrow H(q, p; \lambda(t)) \rightarrow H(q, p; \lambda_1) \]

Backward Process

\[ H(q, p; \lambda_1) \rightarrow H(q, p; \lambda(t)) \rightarrow H(q, p; \lambda_0) \]

Equilibrium

\[ T \]

\[ Q' \]

\[ W' \]
Example

\[ 0 < \Delta F < W \]

Forward

Non-Equilibrium

Backward

\[ -\Delta F < W < 0 \]
Phase Space Trajectory and Density

6N-dimensional phase space

\[ q(t), p(t) \]

\( q = (q_1, q_2, \ldots, q_{3N}) \) position

\( p = (p_1, p_2, \ldots, p_{3N}) \) momentum

\[ [q(t), p(t)] = \text{phase trajectory} \]

\[ \rho(q, p, t) = \text{probability density} \]

Liouville Theorem

\[ \rho(q_0, p_0, t) = \rho(q(t), p(t), t) = \rho(q_1, p_1, t_1) \]

Microscopic Time Reversibility

\[ (q_0, p_0) \rightarrow (q_1, p_1) \]

\[ (q_1, -p_1) \rightarrow (q_0, -p_0) \]

Joseph Liouville (1809-1882)
Thermal Equilibrium and Gibbs Entropy

Equilibrium Density

\[ \rho_{eq}(q, p) = \frac{1}{Z} \exp[-\beta H(q, p)] \]

\[ Z = \int \exp[-\beta H(q, p)] dq dp \] (partition function)

\[ \rho_{eq}(q, p) = \rho_{eq}(q - p) \] (detailed balance)

\[ H(q, p) = -k_B T \ln Z - k_B T \ln \rho_{eq}(q, p) \]

Gibbs Entropy

\[ S = -k_B \int \rho(q, p) \ln \rho(q, p) dq dp \]

\[ S(t_0) = S(t) = S(t_1) \]

J. Willard Gibbs (1839-1903)
Definition of Work

\[ W(q_0, p_0) = H(q_1, p_1; \lambda_1) - H(q_0, p_0; \lambda_0) \]

Statistical Average

\[ \langle W \rangle = \int \rho(q_0, p_0; t_0) W(q_0, p_0) \, dq_0 \, dp_0 \]
\[ = \int \rho(q_0, p_0; t_0) [H(q_1, p_1; \lambda_1) - H(q_0, p_0; \lambda_0)] \]
Proof

\[ \langle W \rangle = \int \rho(q_0, p_0; t_0) \left[ H(q_1, p_1; \lambda_1) - H(q_0, p_0; \lambda_0) \right] \]

\[ = -kT \int \rho_F(q_1, p_1, t_1) \ln \rho_B(q_1, -p_1, t_1) dq_1 dp_1 \]

\[ + kT \int \rho_F(q_0, p_0, t_0) \ln \rho_F(q_0, p_0, t_0) dq_0 dp_0 \]

\[ + kT \ln \left( \frac{Z_0}{Z_1} \right) \]

\[ = -kT \int \rho_F(q, p, t) \ln \rho_B(q, -p, t) dq dp \]

\[ + kT \int \rho_F(q, p, t) \ln \rho_F(q, p, t) dq dp \]

\[ + \Delta F \]

\[ \langle W \rangle - \Delta F = kT \int \rho_F(q, p, t) \ln \left[ \frac{\rho_F(q, p, t)}{\rho_B(q, -p, t)} \right] dq dp = kT D(\rho_F \| \rho_B) \]
Relative Entropy (Kullback-Leibler distance)

\[
D(\rho\|\eta) = \int \rho(x) \ln \frac{\rho(x)}{\eta(x)} \, dx
\]

\[\rho(x) \geq 0, \eta(x) \geq 0 ; \int \rho(x) \, dx = \int \eta(x) \, dx = 1\]

\(D(\rho\|\eta)\) is a `distance` between two densities.

\[D(\rho\|\eta) \geq 0, \quad D(\rho\|\eta) = 0 \text{ iff } \rho(x) = \eta(x)\]

\[\exp[-D(\rho\|\eta)]\] is a measure of the difficulty to statistically distinguish two densities. (Stein's lemma)

\[D(\rho\|\eta) \geq D(\tilde{\rho}\|\tilde{\eta})\]

if \(\tilde{\rho}\) and \(\tilde{\eta}\) have less information than \(\rho\) and \(\eta\)
Relative Entropy: Exercise with Dice

\[
\text{normal:} \quad p_1 = \frac{1}{6}, \quad p_2 = \frac{1}{6}, \quad p_3 = \frac{1}{6}, \quad p_4 = \frac{1}{6}, \quad p_5 = \frac{1}{6}, \quad p_6 = \frac{1}{6} \\
\text{biased:} \quad q_1 = \frac{1}{3}, \quad q_2 = \frac{1}{12}, \quad q_3 = \frac{1}{12}, \quad q_4 = \frac{1}{12}, \quad q_5 = \frac{1}{6}, \quad q_6 = \frac{1}{4}
\]

\[
D(p\|q) = \sum_{i=1}^{6} p_i \ln \frac{p_i}{q_i} = 0.163\ldots
\]

Find which dice you have by rolling it \( N \) times.

If you guess it is the normal one the probability that you are wrong is

\[
P_{\text{err}}(N) = e^{-ND(p\|q)}, \quad P_{\text{err}}(10) = 0.196, \quad P_{\text{err}}(20) = 0.04, \quad P_{\text{err}}(50) = 0.00028
\]
Relative Entropy and Reduced Information

normal dice \[ \tilde{p}_{\text{odd}} = p_1 + p_3 + p_5 = \frac{1}{2}, \quad \tilde{p}_{\text{even}} = p_2 + p_4 + p_6 = \frac{1}{2} \]

biased dice \[ \tilde{q}_{\text{odd}} = q_1 + q_3 + q_5 = \frac{7}{12}, \quad \tilde{q}_{\text{even}} = q_2 + q_4 + q_6 = \frac{5}{12} \]

\[ D(\tilde{p} \parallel \tilde{q}) = \tilde{p}_{\text{odd}} \ln \frac{\tilde{p}_{\text{odd}}}{\tilde{q}_{\text{odd}}} + \tilde{p}_{\text{even}} \ln \frac{\tilde{p}_{\text{even}}}{\tilde{q}_{\text{even}}} = 0.014 \]

\[ D(p \parallel q) > D(\tilde{p} \parallel \tilde{q}) \]
Dissipation and Time's Arrow

\[
\left\langle W \right\rangle - \Delta F = kT \int \rho_F(q, p, t) \ln \frac{\rho_F(q, p, t)}{\rho_B(q, -p, t)} \, dq \, dp = kT D(\rho_F \| \rho_B)
\]

\[D(\rho_F \| \rho_B) \geq 0 \rightarrow \text{Second Law}\]

If \( \rho_F = \rho_B \), \( D(\rho_F \| \rho_B) = 0 \) \rightarrow \text{No Dissipation}\n
Dissipation is a quantitative measure of Irreversibility (time's arrow)!
Slow Expansion

Forward
$(q_0, p_0)$

$t=0$

$t=\tau/2$

$(q_1, p_1)$

$t=\tau$

Backward
$(q_0, -p_0)$

$t=0$

$t=\tau/2$

$(q_1, -p_1)$

$t=\tau$

No Dissipation
Forward

$(q_0, p_0)$

$t = 0$

$t = \tau / 2$

$(q_1, p_1)$

$t = \tau$

Backward

$(q_0, -p_0)$

$t = 0$

$t = \tau / 2$

$(q_1, -p_1)$

$t = \tau$
Which direction is the triangle moving?
Jarzinski equality and Crooks Theorem

\[
\langle W_{\text{dis}} \rangle = kT \int \rho_F(q,p,t) \ln \left( \frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)} \right) dq \, dp
\]

Work at a phase point

\[ W_{\text{dis}}(q,p,t) = kT \ln \frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)} \]
(can be negative)

Crooks theorem

\[ \exp[-\beta W_{\text{dis}}(q,p,t)] = \frac{\rho_B(q,-p,t)}{\rho_F(q,p,t)} \]

Jarzynski equality

\[ \langle \exp[-\beta W_{\text{dis}}] \rangle = \int \rho_F(q,p,t) \exp[-\beta W_{\text{dis}}(q,p,t)] dq \, dp = 1 \]
Coarse Graining

Devide the whole phase space into $N$ subsets $\chi_j$ ($j=1\cdots N$)

\[
\rho^j_F(t) = \int_{\chi_j} \rho_F(q, p, t) dq dp; \quad \rho^j_B(t) = \int_{\bar{\chi}_j} \rho_B(q, p, t) dq dp
\]

\[
\langle W \rangle_j - \Delta F \geq kT \ln \frac{\rho^j_F}{\rho^j_B}
\]
\[ \langle W \rangle - \Delta F \geq kT D(\rho_F^j \| \rho_B^j) \]

where \( D(\rho_F^j \| \rho_B^j) = \sum_{j=1}^{N} \rho_F^j \ln \frac{\rho_F^j}{\rho_B^j} \)

Since we don't have full information of the phase densities, we can have only a lower bound.

If we have no information at all (N=1), then

\[ D(\rho_F \| \rho_B) = 0 \rightarrow \langle W \rangle \geq \Delta F \quad \text{2nd law!} \]
**Overdamped Brownian Particle in a Harmonic Potential**

\[
\rho(x, t) = \int \rho(x, p, x_1, p_1, x_2, p_2, \ldots, t) \, dp \, dx_1 \, dp_1 \ldots
\]

\[
\langle W \rangle - \Delta F \geq D(\rho_F(x, t) \| \rho_B(x, t))
\]
Application: Physics and Information

Szilard found a relation between physics and information.

\[ 1 \text{ bit} = k_B \log 2 \]

Landauer principle

The erasure of one bit of information is necessarily accompanied by a dissipation of at least \( k_B T \log 2 \) heat. Information can be obtained without dissipation of heat.

\[ Q \geq k_B T \log 2 \]
$Q \rightarrow W = k_B T \ln 2$

Contradiction to 2\textsuperscript{nd} Law?
Brownian Engine (Backward Process)

\[ W = -kT \ln 2 \]
Brownian Computer (Forward Process)

$W = + kT \ln 2$

Erasure

Restore-to-One Procedure: $d \rightarrow a \rightarrow b \rightarrow c \rightarrow d$
Coarse Grained Measurement

\[ W \geq \ln \left[ \frac{P_F(R)}{P_B(R)} \right] = k_B T \ln 2 + k_B T \ln (1 - \epsilon) \]
For quantum systems

von Neumann Entropy: \( S = -k \text{Tr} \hat{\rho} \ln \hat{\rho} \)

\[ \langle W_{\text{dis}} \rangle = kT \left[ \text{Tr} \hat{\rho}_F \ln \hat{\rho}_F - \text{Tr} \hat{\rho}_F \ln (\theta \hat{\rho}_B \tilde{\theta}) \right] \]
An exact expression of dissipation is obtained. Now the second law of thermodynamics is an equality!

Dissipation is a direct measure of irreversibility (time's arrow).

Even when full information is not available, the formula provides a lower bound of the dissipation.

The relation between information and physical processes is unambiguously formulated. The Landauer principle is proven.

\[
\langle W \rangle - \Delta F = k_B T \int \rho_F(q, p, t) \ln \frac{\rho_F(q, p, t)}{\rho_B(q, -p, t)} dq \, dp \\
= k_B T D(\rho_F \| \rho_B)
\]