Non-equilibrium thermodynamics: foundations, scope, and extension to the meso-scale

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References

• S.R. de Groot and P. Mazur, Non-equilibrium Thermodynamics, Dover, New York, 1984
• J.M. Vilar and J.M. Rubi, PNAS (2001)
• J.M. Rubi, Scientific American, November (2008)
Thermodynamics

- Heat, work and energy in large-scale systems
- Thermodynamic limit:
  \[ N \to \infty \quad V \to \infty \]
  \[ \rho = \frac{N}{V} \text{ finite} \]
- It only characterizes equilibrium states

\[ 1 \to 2 \]
process

- States are represented by a reduced number of quantities. Gas: P, V, T; (related through eq of state)
- Time plays no role; states are quiescent
Why a non-equilibrium thermodynamics?

Thermodynamics describes changes in systems that are in equilibrium.

\[ TdS = dU + pdV - \mu dN \]

How to deal with systems outside equilibrium?
Non-equilibrium systems

• Properties are not uniform: $T(x,t)$; presence of gradients
• Systems evolve in time
• How to describe the evolution?
• In thermodynamics the evolution is dictated by the second law
• How the second law applies? Task of NET
Non-equilibrium thermodynamics

- **Local equilibrium**: the system is globally outside equilibrium but is locally in equilibrium.
- **Consequence**: thermodynamics is valid locally; the small volume elements are thermodynamics systems.
- **Requirement**: the small volume elements must contain enough particles; the system can be treated as a continuum medium.
Continuum hypothesis

I: large fluctuations
II: deterministic regime
III: inhomogeneities

If fluctuations are negligible then region I is very small and we can consistently define

$$\rho = \lim_{\Delta V \to 0} \frac{\Delta M}{\Delta V}$$

$$\rho = \frac{dm}{dV}$$
Temperature gradient

Gradient: $a/L$
Temperature differences: $a/N$

Size L

: volume elements; small thermodynamic systems
From devices to industrial plants

NET: ‘universal’
Reason: system → continuum medium

Scaling up
An example: Hydrodynamics

Scaling of the Navier-Stokes equation

\[
\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} = -\nabla p + \nu \nabla^2 \vec{v}
\]

\[
\lambda^{2h-1} \left( \frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) = -\lambda^{-1} \nabla p + \lambda^{h-2} \nu \nabla^2 \vec{v}
\]

\[
Re = \frac{UL}{\nu} \rightarrow \frac{\lambda^{h} U \lambda L}{\nu} = \frac{UL}{\nu}
\]

\[
t, \tilde{r}, \tilde{v} \rightarrow \lambda^{1-h} t, \lambda \tilde{r}, \lambda^h \tilde{v}
\]

\[
h = -1
\]

invariant!
Scales

- Macroscopic: objects
- Microscopic: molecules
- Mesoscopic: meso-structures (clusters, aggregates, proteins, DNA,...)
Protein

Atomistic

Mesoscopic
Diffusion

Fick

\[ \vec{J} = -D \nabla \rho \]

Description in terms of average values

\[ \frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{J} \]

i) Large scales
ii) Long times
NET of diffusion

\[ Tds = -\mu d\rho \]

Gibbs; local equilibrium

\[ \sigma = -\frac{1}{T} J \frac{\partial \mu}{\partial x} \]

\[ J = -\frac{L \partial \mu}{T \partial x}; \quad D = \frac{L}{T} \]

\[ \frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \frac{D \partial \rho}{\partial x} \]
Ion pumping

Active transport

Onsager relation:

$$J = - \frac{l_{rr}}{T} \Delta G - \frac{l_{rd}}{T} \left[ \mu^o_{Ca} - \mu^i_{Ca} \right]$$

$$J^o_{Ca} = - \frac{l_{dr}}{T} \Delta G - l_{dd} \left[ \mu^o_{Ca} - \mu^i_{Ca} \right]$$

Carrier proteins are used in active transport to pick up ions or molecules from near the cell membrane, carry them across the membrane, and release them on the other side. Active transport requires energy.
a) Forward

\[ C_{Ca}^0 \]

[ATP] \rightarrow \[ J_{Ca}^{2+} \] 

ADP,P

b) Reverse

\[ C_{Ca}^i \]

ATP

ADP,P

[\[ J_{Ca}^{2+} \] \rightarrow \[ C_{Ca}^i \]]
Efficiency-(ies)

First law efficiency:
\[ \eta_I = \frac{W}{Q + W} \]

Second law efficiency:
\[ \eta_{II} = \frac{W_{\text{ideal}}}{W} \]

\[ W_{\text{lost}} = W - W_{\text{ideal}} = T \Delta S_{\text{tot}} = T \left( \int \sigma dV \right) \Delta t \]

Ex. Aluminium electrolysis:
\[ \eta_I = 0.50 \]
\[ \eta_{II} = 0.42 \]

Fuel cells:
\[ \eta_{II} = 0.60 \]
From devices to nanosystems

At short scales matter cannot be considered as a continuum
Assumption: fluid is a continuum; ignoring molecular scales

Langevin forces: not considered by NET
Langevin ‘force’

Random walk

$\Delta x$

$\langle (\Delta x)^2 \rangle = 2Dt^\alpha$
Langevin equation:

\[ m \frac{dv}{dt} = -\zeta v + F_R \]

i) \( <F_R(t)> = 0 \)

\( ii) <F_R(t)F_R(t')> = 2kT\zeta\delta(t-t') \)

Diffusion: molecular nature

\[ <E> = \frac{1}{2}kT \]
Motion of a particle through a liquid

\[ m \frac{d\vec{v}}{dt} = \vec{F} \]

\[ TdS = dE_p = -d \left( \frac{1}{2} mv^2 \right) \]

\[ \sigma = -\frac{1}{T} m \vec{v} \cdot \frac{d\vec{v}}{dt} = -\frac{1}{T} \vec{v} \cdot \vec{F} \]

\[ \vec{v} = -\frac{L}{T} \vec{F} \]

\[ \vec{F} = -\zeta \vec{v} \]

\[ b = L / T = \zeta^{-1} \]

\[ \vec{v} = \vec{v}_0 \exp \left( -\frac{\zeta}{m} t \right) \]
Failure of NET: Chemical reactions

\[ \sigma = -\frac{1}{T} JA \]

\[ J = -\frac{L}{T} A = -\frac{L}{T} (\mu_2 - \mu_1) \]

Law of mass action

\[ J = -D \left( \frac{\mu_2}{e^{kT}} - \frac{\mu_1}{e^{kT}} \right) = -D (1 - e^{-\frac{A}{kT}}) \approx -\frac{L}{T} A \]

Conclusion: NET only accounts for the linear regime
Activation over a single barrier

- Basic relaxation mechanism:

  Overcoming of a single barrier

\[
\text{Free Energy} \\
\text{Reaction coordinate } Q
\]
Is thermodynamics applicable to small-scale systems outside equilibrium?

- How small is ‘small’?
  Extensivity validates thermodynamics

- What is the actual meaning of ‘being far away from equilibrium’?
  Mesoscale local equilibrium validates a mesoscopic non-equilibrium thermodynamics
Small-scale systems

Peculiar features:

1. Free energy contains more contributions

\[ G = N \mu(T, P) + N^3 h(T, P) \]

\( N \to \infty; \quad G \to N \mu \)  

Surface contribution
Snapshots of the proteins

- **myoglobin**
  (controls the oxygen transport)

- **Ca-ATPase 1SU4**
  (controls the active transport)

- **GFP**

- **Ca-ATPase 1KJU**

Catalytic cycle

E1 → E2
Checking the extensivity
Heat capacity of proteins

It is dominated, about 80% of the total by intramolecular contributions (stretching, bending and internal rotations)

Hydration contribution about 15%

\[ C_V \approx N \]

\[ H, G, \ldots \approx N \]

<table>
<thead>
<tr>
<th>Protein</th>
<th>This work</th>
<th>Experiments</th>
<th>Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myoglobin</td>
<td>27±9</td>
<td>24.2</td>
<td>17</td>
</tr>
<tr>
<td>GFP</td>
<td>47±10</td>
<td>–</td>
<td>24</td>
</tr>
<tr>
<td>Ca^{2+}-ATPase (1SU4)</td>
<td>180±35</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ca^{2+}-ATPase (1KJU)</td>
<td>180±30</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
2. Fluctuations are important

\[ A = \langle A \rangle + \delta A \]

thermodynamic value

fluctuation

Macroscopic: continuum

\[ A \approx \langle A \rangle \quad \rightarrow \quad \frac{\delta A}{\langle A \rangle} \ll 1 \]
Temperature relaxation

\[ \exp(-t/\tau) \]

\( \tau \sim 10 - 20 \text{ ps} \)

\( T_i = 350K \)

\( T_f = 250K \)

T, p are fast variables; related to collisions (many)
Density slower; related to rearrangements

---: Model

Protein

Water

---: Model

Temperature / K

\( 400 \)

\( 375 \)

\( 350 \)

\( 325 \)

\( 300 \)

\( 275 \)

time/ps

0

25

50

75
Heat transfer model

Thermal conductivity

\[ \kappa = \frac{\rho c_p R^2}{\tau} = \frac{3C_p}{4\pi R \tau} \]

\[ \tau = \frac{R^2}{D_T} \]

\[ D_T = \frac{\kappa}{(\rho c_p)} \]
Can we define a temperature?

Myoglobin

Gaussian distribution

Temperature
3. Entropy; Boltzmann versus Gibbs

\[ \Delta S_B (\alpha) = k_B \ln P(\alpha) \]

\[ \Delta S_G = -k_B \int P(\alpha_0, \alpha; t) \ln \frac{P(\alpha_0, \alpha; t)}{P_0} \, d\alpha \]

**Macroscopic limit:**

In the macroscopic limit Boltzmann and Gibbs entropies provide the same description:

\[ \frac{\partial}{\partial t} \langle \Delta S_B \rangle_{\alpha_0} \geq 0 \]

\[ \frac{\partial}{\partial t} \langle \Delta S_B \rangle_{\alpha_0} \leq 0 \]

Second law; macroscopic limit always:

\[ \frac{\partial}{\partial t} \langle \Delta S_G \rangle_{\alpha_0} \geq 0 \]
Unstable substance

Naked-eye: Sudden jump

Progressive molecular changes

Activation

Final product

Watching closely

Diffusion
Translocation of ions (through a membrane or protein channel)

Biological membrane

short time scale: local equilibrium along the coordinate

biological pumps, chemical and biochemical reactions

Local, linear $\rightarrow$ Global, non-linear

Arrhenius, Butler-Volmer, Law of mass action
Activated process

viewed as a diffusion process along a reaction coordinate

\[
\sigma(\gamma) \rightarrow J = -\frac{L}{T} \frac{\partial \mu}{\partial \gamma} = -\frac{kL}{P} e^{\frac{-\Phi}{kT}} \frac{\partial}{\partial \gamma} e^{\frac{\mu}{kT}} \equiv -D e^{\frac{-\Phi}{kT}} \frac{\partial}{\partial \gamma} e^{\frac{\mu}{kT}}
\]

From local to global:

\[
\gamma \rightarrow \int d\gamma...
\]

\[
\int_1^2 d\gamma Je^{\frac{\Phi}{kT}} = -D \int_1^2 d\gamma \frac{\partial}{\partial \gamma} e^{\frac{\mu}{kT}}
\]

\[
J = -\tilde{D} \left( e^{\frac{\mu_2}{kT}} - e^{\frac{\mu_1}{kT}} \right) \equiv -\tilde{D}(z_2 - z_1)
\]
Molecular changes: diffusion through a mesoscopic coordinate

\( \gamma : \text{mesoscopic coordinate} \)

\( P(\gamma, t) : \text{probability} \)

\[
\frac{\partial}{\partial t} \rho(\gamma, t) = - \frac{\partial}{\partial \gamma} J(\gamma, t)
\]

Second law


\[
\delta S = -k_B \int \delta \rho(\Gamma, t) \ln \frac{\rho(\Gamma, t)}{\rho_{eq.}(\Gamma)} d\Gamma
\]

\[
\delta s = -\frac{1}{T} \int \mu(\gamma, t) \delta \rho(\gamma, t) d\gamma
\]

\[
\mu(\gamma, t) = k_B T \ln \rho(\gamma, t) + \Phi(\gamma)
\]
Single molecule

\( x: \) center of mass

\( \Theta: \) size, others

Local equilibrium:

\[
T \, ds(x) = -\mu(x) \, d\rho(x) - F \, d\Theta(x)
\]

Mesoscale local equilibrium:

\[
\Theta(x) = \int \theta \, P(x, \theta) \, d\theta
\]

\[
T \, ds(x, \theta) = -\mu(x, \theta) \, dP(x, \theta)
\]
Meso-scale entropy production

\[ \sigma = -\frac{1}{T} \int J(\gamma, t) \frac{\partial}{\partial \gamma} \mu(\gamma, t) \, d\gamma \]

\[ J(\gamma, t) = -\frac{1}{T} \int L(\gamma, \gamma') \frac{\partial}{\partial \gamma'} \mu(\gamma', t) \, d\gamma' \]

\[ D = k_B L / \rho \]

\[ \frac{\partial}{\partial t} \rho(\gamma, t) = \frac{\partial}{\partial \gamma} D \left( \frac{\partial}{\partial \gamma} \rho(\gamma, t) + \frac{\rho(\gamma, t)}{k_B T} \frac{\partial}{\partial \gamma} \Phi(\gamma) \right) \]
The noise is the signal

Gaussian noise and time-reversal symmetry

\[ D = \frac{kT}{\gamma} \]

\[ V' = -kT \frac{d}{dx} \ln P_0 \]

\[ \frac{\partial}{\partial t} P(x,t) = \frac{\partial}{\partial x} \left( \frac{1}{\gamma} V'(x,t) P(x,t) + D \frac{\partial}{\partial x} P(x,t) \right) \]

Thermodynamics likes Gaussian stuff
RNA unfolding under tension

\[ \dot{\rho}_n(t) = -j_n + j_{n-1} \]

MNET

\[ j_n = -k_c(n+1,f)\rho_{n+1} + k_o(n+1)\rho_n \]

Master equation

\[ \dot{\rho}_n(t) = -[k_o(n+1) + k_c(n,f)]\rho_n + k_o(n)\rho_{n-1} + k_c(n+1,f)\rho_{n+1} \]

\[ \frac{\rho_{n+1,\text{st}}}{\rho_{n,\text{st}}} = \exp\left(-\Delta G(n,f)/k_B T\right) \]

Protein folding

Intermediate configurations, same as for chemical reactions
Muscular contraction

Energy transduction,
Molecular motors
Heat exchange at the nanoscale

Failure of the FDT at small distance $d$

$L. Lapas, A. Perez, JMR, PRL (2009)$

$$G(\omega, T_0) = \frac{k_B \hbar}{4\tau^*(\omega)} \left( \frac{\hbar \omega / k_B T_0}{\sinh(\hbar \omega / 2k_B T_0)} \right)^2$$
Nucleation

Basic scenario:

Metastable phase

Cluster at rest: $x \rightarrow n$

Cluster in a bath: $x \rightarrow (n, v, \omega)$
Conclusions

• Many systems we call ‘small’ still contain many particles and behave thermodynamically
• NET is not able to describe the activation kinetics but a proper interpretation of the concept of local equilibrium at the mesoscale can do it.
• This interpretation can be used in chemical and biochemical reactions, transport in confined systems (ion channels, zeolites), single molecules, heat exchange at the nanoscale, nucleation,...