

Introduction to Nonequilibrium Thermodynamics

Onsager's variational principle

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Context

- Stand-alone lecture on (phenomenological) **non-equilibrium thermodynamics** in the form of **Onsager's variational principle** resulting in kinetic equations of **gradient dynamics** form
- Given in the context of a lecture course *Introduction to the Theory of Phase Transitions* (ITPT)
- **Introductory lecture** tailored for Bachelor/Master students, possibly also useful for beginning PhD
- Assumed is some knowledge of equilibrium thermodynamics (aka “Thermostatistics”)

Aims

- **Develop:** Basic concepts how to go from **Thermostatistics** to **Thermodynamics**
- **Understand:** Nonequilibrium Thermodynamics as Gradient Dynamics
- **Derive:** Simple kinetic equations

Bibliography and Further Reading

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Introduction

- Up to here you considered **Thermostatics** equivalent to **Equilibrium Thermodynamics** where “processes” are quasi-static and reversible (e.g., Carnot process, see bachelor physics course)
- Real processes are normally **irreversible**, then **in isolated and closed systems¹ entropy S increases in time**
 $dS > 0$
- Entropy can only decrease in open systems if

$$dS_{\text{intrinsic}} + dS_{\text{influx}} < dS_{\text{outflux}}$$

as then

$$dS_{\text{total}} = dS_{\text{intrinsic}} + dS_{\text{influx}} - dS_{\text{outflux}} < 0 \quad (1)$$

¹“abgeschlossene & geschlossene Systeme”

Single variable - general

- Variable a shall be the only relevant macroscopic thermodynamic (scalar) quantity characterising a particular system, called **state variable**
- $U(a)$ inner energy, constant for isolated system
- Entropy $S(a)$
- Helmholtz free energy $F = U - TS$ with $T \dots$ Temperature²

²Proper td potential for closed system, i.e., T is controlled (not U).

- Consider change in time

$$\frac{dS}{dt} = \frac{dS}{da} \frac{da}{dt} \quad \text{or} \quad \frac{dF}{dt} = \frac{dF}{da} \frac{da}{dt} \quad (2)$$

- At equilibrium $\frac{dS}{da} = 0$ as S maximal; $\frac{dF}{da} = 0$ as F minimal
- For small deviation from equilibrium, we expect

$$\frac{da}{dt} = M \frac{dS}{da} \quad \text{or} \quad \frac{da}{dt} = -\tilde{M} \frac{dF}{da} \quad (3)$$

with mobilities $M, \tilde{M} > 0$ (in simplest case constants)

- With other words dS/da or dF/da represents a **thermodynamic force** that drives evolution of state variable a

- At equilibrium $a = a_0$
- Expand $S(a)$ about a_0 :

$$S(a) = S(a_0) + \underbrace{(a - a_0) \frac{dS}{da}}_{=0} \Big|_{a_0} + \frac{(a - a_0)^2}{2} \frac{d^2S}{da^2} \Big|_{a_0} \quad (4)$$

with $\frac{d^2S}{da^2} \Big|_{a_0} < 0$

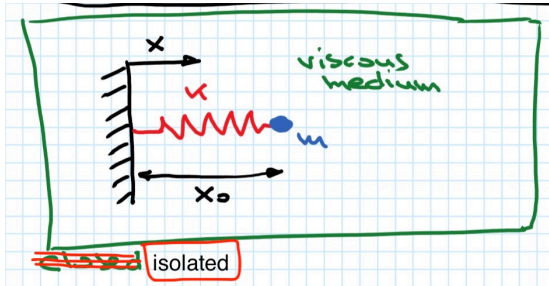
- With Eq. (3) get

$$\frac{da}{dt} = M \frac{d^2S}{da^2} \Big|_{a_0} (a - a_0) \quad (5)$$

resulting in exponential relaxation towards a_0 .

- analog for F

Elastically bound mass point in viscous medium



- Mass point bound by spring to wall, all immersed in viscous medium (sketch)
- Potential $\Phi(x) = \frac{k}{2}x^2$
- Position x represents state variable
- Medium with known entropy $S(U, V)$
- Total energy U_0 fixed \rightarrow energy of medium $U = U_0 - \Phi(x)$
 $\rightarrow S = S(U_0 - \Phi(x), V)$

- For $\Phi(x) \ll U_0$ Taylor-expand:

$$S(x) \approx S(U_0, V) - \left(\frac{\partial S}{\partial U} \right)_V \Phi(x) = S_0 - \frac{1}{T} \Phi(x) \quad (6)$$

- Then

$$\frac{\partial S}{\partial x} = -\frac{1}{T} \frac{\partial \Phi}{\partial x} \quad (7)$$

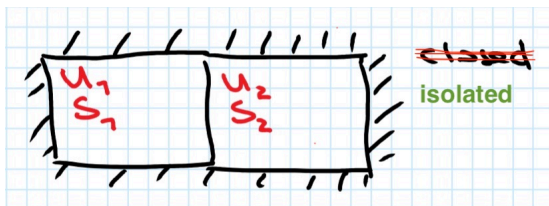
- Linear ansatz corresponds here to

$$\frac{dx}{dt} = -\frac{M}{T} \frac{\partial \Phi}{\partial x} = -\zeta x \quad \text{with friction coefficient } \zeta = \frac{Mk}{T}, \quad (8)$$

i.e., overdamped Newtonian equation of motion (strong friction limit)

- Solution $x(t) = x_{\text{initial}} \exp(-\zeta t)$

Heat exchange between two reservoirs



- $U = U_1 + U_2$ constant (with equilibrium values U_{1e}, U_{2e}), and V constant
- Small deviation from equilibrium $U_1 = U_{1e} + u$,
 $U_2 = U_{2e} - u$, with $u \ll U_{1e}, U_{2e}$ being the state variable

- Entropy $S = S_1(U_{1e} + u) + S_2(U_{2e} - u)$
- Taylor-expand to

$$S \approx [S_1(U_{1e}) + S_2(U_{2e})] + u \left(\left. \frac{\partial S_1}{\partial U_1} \right|_{\text{eq}} - \left. \frac{\partial S_2}{\partial U_2} \right|_{\text{eq}} \right) + \frac{u^2}{2} \left(\left. \frac{\partial^2 S_1}{\partial U_1^2} \right|_{\text{eq}} + \left. \frac{\partial^2 S_2}{\partial U_2^2} \right|_{\text{eq}} \right) \quad (9)$$

- At equilibrium ($u = 0$, U_1 control parameter; $U_2 = U - U_1$)

$$0 = \frac{\partial S}{\partial U_1} = \frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} \quad \text{i.e.} \quad \left. \frac{\partial S_1}{\partial U_1} \right|_{\text{eq}} = \left. \frac{\partial S_2}{\partial U_2} \right|_{\text{eq}} = \frac{1}{T_{\text{eq}}} \quad (10)$$

- Time derivative of (9) [only 3rd term of r.h.s. remains]

$$\frac{dS}{dt} = u \frac{du}{dt} \left(\left. \frac{\partial^2 S_1}{\partial U_1^2} + \frac{\partial^2 S_2}{\partial U_2^2} \right)_{\text{eq}} \quad (11)$$

- **Out of equilibrium** ($u \neq 0$)

$$\frac{1}{T_1} = \left. \frac{\partial S_1}{\partial U_1} \right|_{U_1 = U_1^e + u} = \frac{1}{T_{\text{eq}}} + u \left. \frac{\partial^2 S_1}{\partial U_1^2} \right|_{\text{eq}} \quad \text{dito} \quad \frac{1}{T_2} = \frac{1}{T_{\text{eq}}} - u \left. \frac{\partial^2 S_2}{\partial U_2^2} \right|_{\text{eq}} \quad (12)$$

- Gives with (11)

$$\frac{dS}{dt} = \frac{du}{dt} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{du}{dt} \frac{dS}{du} \quad (13)$$

- Linearer ansatz (3) ($\frac{da}{dt} = M \frac{dS}{da}$) corresponds to

$$\frac{du}{dt} = \frac{M}{T_1 T_2} (T_2 - T_1) \quad (14)$$

where M may also depend on T

→ energy flux proportional to ΔT

Onsager reciprocity relations

- Up to here we considered one state variable
- Now consider n **state variables** $\{a_1, a_2, \dots, a_n\}$ with equilibrium values $a_j^0 = 0$
- $S(a_1, \dots, a_n)$ is entropy of closed system with increase

$$\frac{dS}{dt} = \sum_j \frac{\partial S}{\partial a_j} \frac{da_j}{dt} \quad (15)$$

Again consider $\partial S / \partial a_j$ as **thermodynamic forces**

- For small deviations from equilibrium, i.e., $a_j \ll 1$ linear ansatz

$$\frac{da_j}{dt} = \sum_k A_{jk} \frac{\partial S}{\partial a_k} \quad \text{for} \quad j = 1 \dots n \quad (16)$$

Here, the A_{jk} are **kinetic coefficients** to be experimentally determined

- Eq. (15) with (16) gives

$$\frac{dS}{dt} = \sum_{j,k} \frac{\partial S}{\partial a_j} A_{jk} \frac{\partial S}{\partial a_k} > 0 \quad (17)$$

where we used the second law of thermodynamics

- I.e., the quadratic form has to be always positive → Matrix **A** positive (semi-)definite
- And **Onsager's symmetry relations** hold

$$A_{jk} = A_{kj} \quad (18)$$

- Sometimes called the “4th law of thermodynamics”. Onsager showed within Statistical Physics that they result from time reversibility of microscopic dynamics (microscopic reversibility)

- **Examples:**

- Exchange of heat and particles between two reservoirs [Thermophoresis or (Ludwig-)Soret effect]¹ paragraph 91
- Coupling of electrical current and temperature gradient [Thermoelectrical effects or Peletier and Seebeck effects]¹ paragraph 94 & 95

Onsager variational principle - the Rayleighian

- For closed systems ($U = \text{const}$), i.e., with $F = U - TS$ we have

$$\frac{dF}{dt} = -T \frac{dS}{dt} \quad (19)$$

i.e., all relations above apply in principle also to free energy $F(a_1, a_2, \dots, a_n)$

- Eqs. (16) and (17) become

$$\frac{da_j}{dt} = - \sum_k L_{jk} \frac{\partial F}{\partial a_k} \quad (20)$$

and

$$\frac{dF}{dt} = - \sum_{j,k} \frac{\partial F}{\partial a_j} L_{jk} \frac{\partial F}{\partial a_k} < 0, \quad (21)$$

respectively, where L_{jk} are the kinetic coefficients that again form a symmetric, positive definite matrix

- Introduce **Rayleighian**³

$$R = \frac{dF}{dt} + \Phi = \sum_j \frac{\partial F}{\partial a_j} \frac{da_j}{dt} + \frac{1}{2} \sum_{j,k} \zeta_{jk} \frac{da_j}{dt} \frac{da_k}{dt} \quad (22)$$

- $\frac{dF}{dt}$... Rate of change of the free energy of the system
- Φ ... **Dissipation function**, e.g., simplest a quadratic form in velocities or rates
- Friction coefficient matrix** $\underline{\zeta}$ – a positive definite symmetric matrix

- Onsager's variational principle** applies to irreversible transport processes (that are close enough to equilibrium):
- For isothermal systems, **kinetic equations** are obtained by **minimizing the Rayleighian (22) with respect to the rates of change of state variables** $\frac{da_1}{dt}, \dots, \frac{da_n}{dt}$.

$$\frac{\partial R}{\partial \dot{a}_j} = 0 \quad \rightarrow \quad - \frac{\partial F}{\partial a_j} = \sum_k \zeta_{jk} \frac{da_k}{dt}, \quad \text{for } j = 1 \dots n \quad (23)$$

- Expresses a balance of reversible force $-\partial F/\partial a_j$ and friction force $\sum_k \zeta_{jk} \frac{da_k}{dt}$. Inverting (23), one obtains (20), i.e., $\zeta_{jk}^{-1} = L_{jk}$.
- Also note, that substitution of (23) into (22) shows that for realised kinetics

$$\dot{F} = -2\Phi, \quad \text{i.e. } R = -\Phi \quad (24)$$

Application of Onsager variational principle summarized

- Choose appropriate state variables a_1, \dots, a_n .
- Construct the free energy function $F = F(a_1, \dots, a_n)$.
- Construct the energy dissipation function Φ .
- Obtain the Rayleighian $R = \dot{F} + \Phi$.
- Obtain the time evolution of the state variables a_j (kinetic equations) by minimizing R with respect to the rates $\frac{da_j}{dt}$.
- Additional constraints may apply

Derive diffusion equation with Onsager principle

- Diffusion of Brownian particle (mass m , size a) in viscous fluid (dynamic viscosity η) and potential U
- Microscopic description by Langevin equation $m \frac{dv}{dt} = -\zeta v - \frac{\partial U}{\partial x} + F_{\text{fluc}}(t)$ for particle velocity $v(t)$ with friction constant $\zeta = 6\pi\eta a$ for spherical particles (Stokes drag); neglect inertia term for overdamped motion
- Corresponding Smoluchovski equation for dynamics of probability density $\rho(x, t)$ of finding a particle at x at t (Fokker-Planck eq.)

$$\frac{\partial \rho}{\partial t} = D \frac{\partial}{\partial x} \left[\frac{\partial \rho}{\partial x} + \frac{\rho}{k_B T} \frac{\partial U}{\partial x} \right] \quad (25)$$

For derivation from Langevin equation see³ appendix F. Here $D = k_B T / \zeta$ (Einstein relation) and (25) is also called **diffusion equation**.

- Here, derive via Onsager principle. Consider particle density $\rho(x, t)$ as infinite set of state variables ρ_i (particle numbers in bins of size Δx at x_i with $\Delta x \rightarrow 0$)
- Describes non-equilibrium state of diffusing particles
- Instead of writing Rayleighian (22) in terms of $\partial \rho / \partial t$, use $v(x, t)$, the average velocity of particles at x
- Relation of $\partial \rho / \partial t$ and $v(x, t)$ is continuity equation (conservation law)

$$\frac{\partial \rho}{\partial t} = - \frac{\partial}{\partial x} (v \rho) \quad (26)$$

where $v \rho$ is the particle flux

- Energy dissipation functional

$$\Phi = \frac{1}{2} \int dx \zeta \rho v^2 \quad (27)$$

- Free energy has entropic part and external potential part (no particle interaction yet)

$$F[\rho] = \int dx [k_B T \rho \log \rho + \rho U(x)] \quad (28)$$

i.e.,

$$\frac{dF}{dt} = \int dx [k_B T (\log \rho + 1) + U(x)] \frac{\partial \rho}{\partial t} \quad (29)$$

- With (26) and integration by parts we have

$$\frac{dF}{dt} = \int dx \left[k_B T \frac{\partial \rho}{\partial x} + \rho \frac{\partial U}{\partial x} \right] v \quad (30)$$

- Collect and obtain Rayleighian

$$R = \int dx \left[\frac{1}{2} \zeta \rho v^2 + k_B T v \frac{\partial \rho}{\partial x} + \rho v \frac{\partial U}{\partial x} \right] \quad (31)$$

- Minimize R , i.e., determine $\delta R / \delta v = 0$

$$v = - \frac{1}{\zeta \rho} \left[k_B T \frac{\partial \rho}{\partial x} + \rho \frac{\partial U}{\partial x} \right] \quad (32)$$

- With continuity (26) get **diffusion equation** in external potential

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left\{ D \left[\frac{\partial \rho}{\partial x} + \frac{\rho}{k_B T} \frac{\partial U}{\partial x} \right] \right\} \quad (33)$$

where we used Einstein's relation

Derive gradient-dynamics equations with Onsager principle – Conserved scalar order parameter

- Diffusion equation [(33) without U] is simplest example of wider class
- **Evolution equation for single conserved order parameter field ψ** (sometimes called Cahn-Hilliard-type (CH) equations)
- Need to have form of continuity equation (conservation law)

$$\frac{\partial \psi}{\partial t} = -\frac{\partial j_c}{\partial x} \quad (34)$$

where j_c is the ψ -conserving flux

- General energy functional $F[\psi]$ with

$$\frac{dF}{dt} = \int dx \frac{\delta F}{\delta \psi} \frac{\partial \psi}{\partial t} \quad (35)$$

- Dissipation functional

$$\Phi = \frac{1}{2} \int dx \zeta j_c^2 \quad (36)$$

- Collect and obtain Rayleighian, use (34) and integration by parts

$$R = \int dx \left[\frac{1}{2} \zeta j_c^2 + \frac{\delta F}{\delta \psi} \frac{\partial \psi}{\partial t} \right] = \int dx \left[\frac{1}{2} \zeta j_c^2 + \left(\frac{\partial}{\partial x} \frac{\delta F}{\delta \psi} \right) j_c \right] \quad (37)$$

- Minimize R , i.e., determine $\delta R / \delta j_c = 0$

$$j_c = -\frac{1}{\zeta} \frac{\partial}{\partial x} \frac{\delta F}{\delta \psi} \quad (38)$$

- With continuity (34) get **evolution equation for single conserved scalar order parameter field ψ** (here 2d)

$$\partial_t \psi = \nabla \cdot \left\{ Q_c(\psi) \nabla \frac{\delta F[\psi]}{\delta \psi} \right\} \quad (39)$$

with free energy functional $F[\psi]$ and mobility function $Q_c(\psi) = 1/\zeta \geq 0$.

- Difficult to find a general argument regarding the ψ -dependence of $\zeta = 1/Q$. Q can be obtained from underlying 'microscopic' model, but is not known on the level of phenomenological thermodynamics.
- However, experience shows that Q is often proportional to ψ^n with $n = 0, 1, 2, 3$, so one could Taylor-expand a general Q and discuss the physical meaning of each term.

Deriving gradient-dynamics equations with Onsager principle – Nonconserved scalar order parameter

- Analogue: **evolution equation for single non-conserved order parameter field ψ** (sometimes called Allen-Cahn-type (AC) equations)
- No continuity equation needed, instead define non-conserving flux (creation/deposition/condensation rate)

$$\frac{\partial \psi}{\partial t} = j_{nc} \quad (40)$$

- Dissipation functional

$$\Phi = \frac{1}{2} \int dx \zeta_{nc} j_{nc}^2 \quad (41)$$

- Variation of R w.r.t. j_{nc} gives (CHECK YOURSELF!)

$$\partial_t \psi = -Q_{nc} \frac{\delta F[\psi]}{\delta \psi} \quad (42)$$

where mobility $Q_{nc}(\psi) = 1/\zeta_{nc} \geq 0$

Deriving gradient-dynamics equations with Onsager principle – Mixed dynamics

- Analogue: **evolution equation for single order parameter field with mixed dynamics**
- Form is general balance equation

$$\frac{\partial \psi}{\partial t} = -\frac{\partial j_c}{\partial x} + j_{nc} \quad (43)$$

- Dissipation functional with two contributions

$$\Phi = \frac{1}{2} \int dx \left(\zeta_c j_c^2 + \zeta_{nc} j_{nc}^2 \right) \quad (44)$$

- Variation of R w.r.t. j_c and j_{nc} , use of (43) gives (CHECK YOURSELF!)

$$\partial_t \psi = \nabla \cdot \left(Q_c(\psi) \nabla \frac{\delta F[\psi]}{\delta \psi} \right) - Q_{nc} \frac{\delta F[\psi]}{\delta \psi} \quad (45)$$

with mobilities as above

Generalisation to n coupled scalar order parameter fields

Now, n fields ψ_1, \dots, ψ_n with conserved and/or non-conserved dynamics

$$\partial_t \psi_\alpha = \sum_\beta \nabla \cdot \left[Q_{\alpha\beta}^c(\psi_1, \dots, \psi_n) \nabla \frac{\delta F}{\delta \psi_\beta} \right] - \sum_\beta Q_{\alpha\beta}^{nc}(\psi_1, \dots, \psi_n) \frac{\delta F}{\delta \psi_\beta} \quad (46)$$

where \mathbf{Q}^c and $\mathbf{Q}^{nc} \dots$ are symmetric, positive-definite matrices of mobility functions for conserved and nonconserved dynamics, respectively

Summary & conclusion

- Considered a simple approach to nonequilibrium thermodynamics out of equilibrium but “close to it”
- Linear nonequilibrium thermodynamics: relation between thermodynamic fluxes and forces linear, not the resulting equations (related to linear response theory)
- Onsager reciprocity relations, crosscoupling, e.g., thermoelectrical effects
- Onsager variational principle: Minimisation of Rayleighian w.r.t. fluxes gives kinetic equations
- Gradient dynamics for (non)conserved scalar fields
- More general approach: GENERIC³
- Also see nonequilibrium statistical physics

³*General Equation for the Nonequilibrium Reversible-Irreversible Coupling*