Linear Irreversible Thermodynamics for Periodically Modulated Systems

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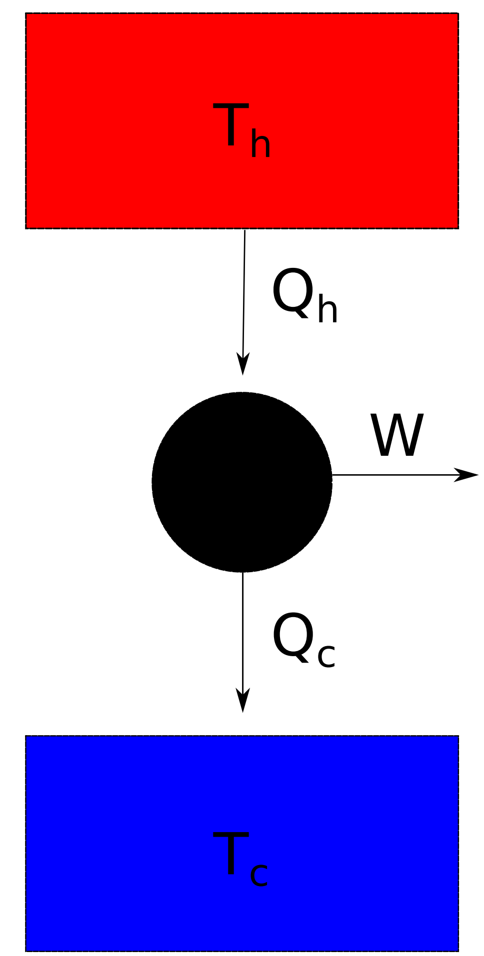
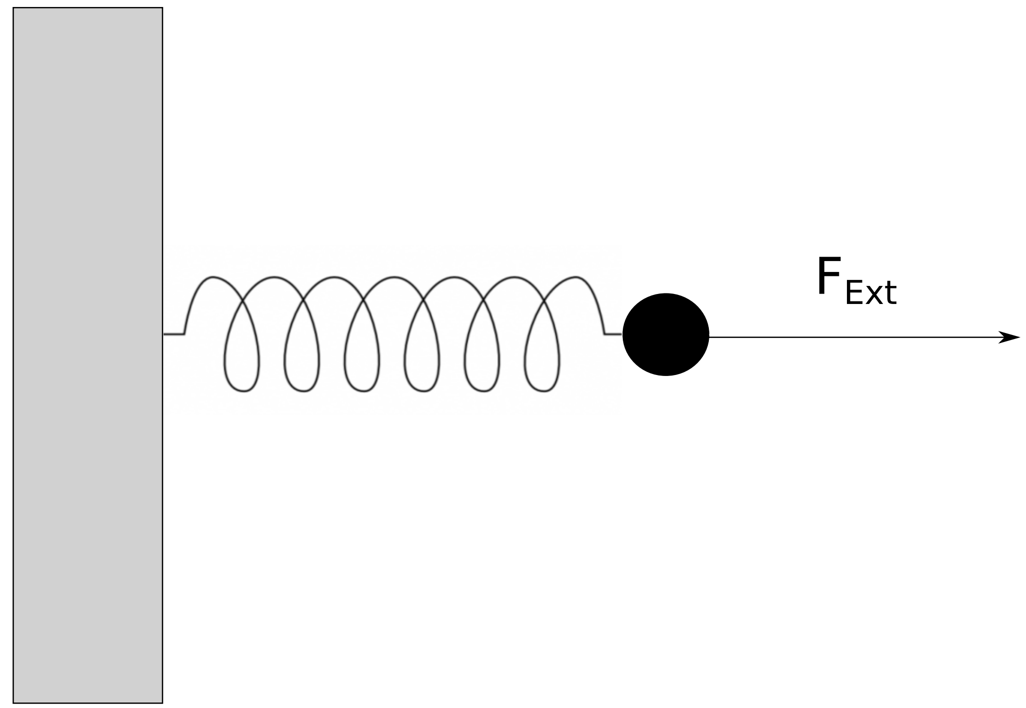
Introduction

- Linear irreversible thermodynamics
- Time-dependent systems
- Work to work conversion



System



$$F_{\mathrm{Tot}}(t) = F_{\mathrm{Fric}}(t) + F_{\mathrm{Spring}}(t) + F_{\mathrm{Ext}}(t)$$
$$F_{\mathrm{Fric}}(t) = -\gamma \dot{x}(t)$$
$$F_{\mathrm{Spring}}(t) = -kx(t)$$

$$m\ddot{x}(t) = -\gamma \dot{x}(t) - kx(t) + F_{\mathrm{Ext}}(t)$$

$$= 0$$

(Overdamped Limit)

Work and Heat

Overdamped E.O.M.: $\gamma \dot{x}(t) = -kx(t) + F_{\mathrm{Ext}}(t)$

Solution: $x(t) = \dfrac{1}{\gamma}\displaystyle\int_0^\infty d\tau\, e^{-\frac{k\tau}{\gamma}} F_{\mathrm{Ext}}(t-\tau)$

Thermodynamics:

$$\dot{E}(t) = -F_{\mathrm{Spring}}(t)\dot{x}(t)$$
$$\dot{W}(t) = -F_{\mathrm{Ext}}(t)\dot{x}(t)$$
$$\dot{Q}(t) = \dot{E} - \dot{W} = \gamma \dot{x}(t)^2 \geq 0$$

Cyclic process

Periodic driving: $$F_{\mathrm{Ext}}(t+\mathcal{T}) = F_{\mathrm{Ext}}(t)$$

Steady state:

$$\begin{aligned} x(t+\mathcal{T}) &= x(t) \\ \Rightarrow \qquad \dot{\bar{E}} &= \frac{1}{\mathcal{T}}\int_0^{\mathcal{T}} dt\, \dot{E}(t) = 0 \\ \Rightarrow \qquad \dot{\bar{W}} &= -\dot{\bar{Q}} \leq 0 \end{aligned}$$

Kelvin statement of the second law:

‚There is no process whose only effect is to accept heat from a single heat reservoir and transform it entirely into work.'

Entropy

Definition: $$\dot{\bar{S}} = \frac{\dot{\bar{Q}}}{T} \geq 0$$

Quasi-static limit: $$\dot{\bar{S}} = 0 \Leftrightarrow \dot{x}(t) = 0, \quad \forall t$$

Forces and fluxes: $$\dot{\bar{S}} = \sum_i \mathcal{F}_i J_i$$

Linear regime: $$J_i = \sum_j L_{ij} \mathcal{F}_j \Rightarrow \dot{\bar{S}} = \sum_{i,j} \mathcal{F}_i L_{ij} \mathcal{F}_j$$

Thermodynamic forces and fluxes

Thermodynamic Force: $F_{\text{Ext}}(t) = \mathcal{F} g(t)$

Thermodynamic Flux:

$$\dot{\bar{S}} = \mathcal{F} J = \frac{\mathcal{F}}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, g(t) \dot{x}(t)$$

$$\begin{aligned} \Rightarrow J &= \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, g(t) \dot{x}(t) \\ &= \frac{1}{\mathcal{T}\gamma} \int_0^{\mathcal{T}} dt \int_0^{\infty} d\tau\, g(t) \dot{g}(t-\tau) e^{-\frac{k\tau}{\gamma}} \mathcal{F} \end{aligned}$$

Work to work conversion

Two work-sources: $F_{\rm Ext}(t) = F_{\rm Ext,1}(t) + F_{\rm Ext,2}(t)$

$$W_1 = \int dt F_{\rm Ext,1}(t)\dot{x}(t) = T\mathcal{F}_1 J_1 \qquad W_2 = \int dt F_{\rm Ext,2}(t)\dot{x}(t) = T\mathcal{F}_2 J_2$$

Working regime: $W_1 > 0, \quad W_2 < 0$

Efficiency:

$$\dot{\bar{S}} = \mathcal{F}_1 J_1 + \mathcal{F}_2 J_2 \longrightarrow \bar{\eta} = -\frac{W_2}{W_1} = -\frac{\mathcal{F}_2 J_2}{\mathcal{F}_1 J_1} \leq 1$$

The Onsager Matrix

Thermodynamic fluxes:

$$
\begin{aligned}
J_1 &= \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt\, g_1(t) \dot{x}(t) \\
&= \frac{1}{\mathcal{T}\gamma} \int_0^{\mathcal{T}} dt \int_0^{\infty} d\tau\, g_1(t) \left(\mathcal{F}_1 \dot{g}_1(t-\tau) + \mathcal{F}_2 \dot{g}_2(t-\tau) \right) e^{-\frac{k\tau}{\gamma}}
\end{aligned}
$$

Onsager matrix:

$$
L = \begin{bmatrix} \frac{1}{T\mathcal{T}\gamma} \int_0^{\mathcal{T}} dt \int_0^{\infty} d\tau\, g_1(t) \dot{g}_1(t-\tau) e^{-\frac{k\tau}{\gamma}} & \frac{1}{T\mathcal{T}\gamma} \int_0^{\mathcal{T}} dt \int_0^{\infty} d\tau\, g_1(t) \dot{g}_2(t-\tau) e^{-\frac{k\tau}{\gamma}} \\ \frac{1}{T\mathcal{T}\gamma} \int_0^{\mathcal{T}} dt \int_0^{\infty} d\tau\, g_2(t) \dot{g}_1(t-\tau) e^{-\frac{k\tau}{\gamma}} & \frac{1}{T\mathcal{T}\gamma} \int_0^{\mathcal{T}} dt \int_0^{\infty} d\tau\, g_2(t) \dot{g}_2(t-\tau) e^{-\frac{k\tau}{\gamma}} \end{bmatrix}
$$

Onsager-Casimir symmetry

Time-reversal:

$$F_{\mathrm{Ext},i}(t), g_i(t) \to \tilde{F}_{\mathrm{Ext},i}(t) = F_{\mathrm{Ext},i}(-t), \tilde{g}_i(t) = g_i(-t)$$

Onsager coefficients:

$$\begin{aligned}
\tilde{L}_{ij} &= \frac{1}{\mathcal{T}\gamma}\int_0^{\mathcal{T}} dt \int_{-\infty}^{0} d\tau\, g_i(-t)\dot{g}_j(-t+\tau)e^{\frac{k\tau}{\gamma}} \\
&= \frac{1}{\mathcal{T}\gamma}\int_0^{\mathcal{T}} dt \int_{-\infty}^{0} d\tau\, g_j(t)\dot{g}_i(t-\tau)e^{\frac{k\tau}{\gamma}} \\
&= L_{ji}
\end{aligned}$$

Time-symmetric driving: $L_{ij} = L_{ji}$

Conclusions

- Linear irreversible thermodynamics can describe time-dependent systems.
- A generalized Onsager-Casimir relation is found.

Karel Proesmans and Christian Van den Broeck. "Onsager coefficients in periodically driven systems." *Physical review letters* 115.9 (2015): 090601.