Stochastic Thermodynamics: All fudge or theory

<u>Peter Hänggi</u> and Peter Talkner

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Open system trajectories specify fluctuating work but not heat

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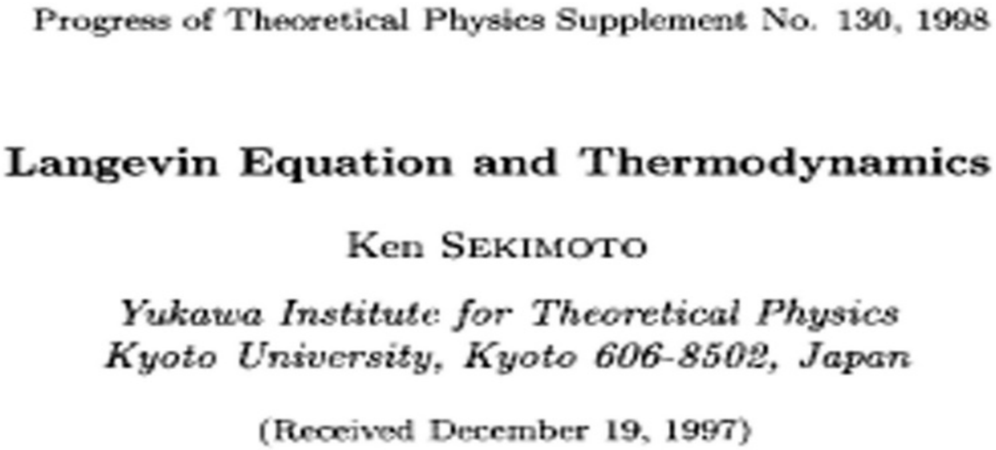
Based on the explicit knowledge of a Hamiltonian of mean force, the classical statistical mechanics and equilibrium thermodynamics of open systems in contact with a thermal environment at arbitrary interaction strength can be formulated. Yet, even though the Hamiltonian of mean force uniquely determines the equilibrium phase space probability density of a strongly coupled open system, the knowledge of this probability density alone is insufficient to determine the Hamiltonian of mean force, needed in constructing the underlying statistical mechanics and thermodynamics. We demonstrate that under the assumption that the Hamiltonian of mean force is known, an extension of thermodynamic structures from the level of averaged quantities to fluctuating objects (i.e., a stochastic thermodynamics) is possible. However, such a construction undesirably also involves a vast ambiguity. This situation is rooted in the eminent lack of a physical guiding principle allowing us to distinguish a physically meaningful theory out of a multitude of other equally conceivable ones.



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Langevin Equation and Thermodynamics

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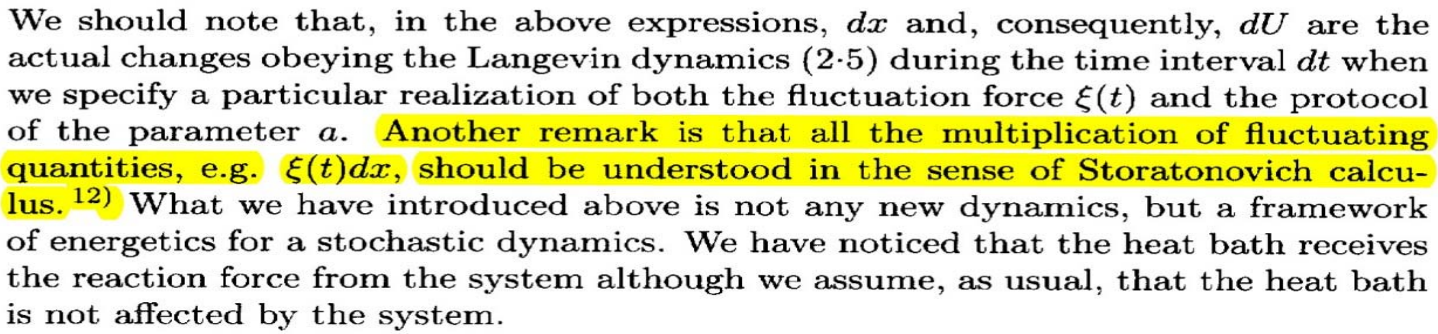
(Received December 19, 1997)

$$\gamma\frac{dx}{dt} = -\frac{dU}{dx} + \xi(t).$$

$$0 = -\left(-\gamma\frac{dx}{dt} + \xi(t)\right)dx + \frac{dU}{dx}dx$$

heat

$$dQ \equiv -\left(-\gamma\frac{dx}{dt} + \xi(t)\right)dx$$



We should note that, in the above expressions, dx and, consequently, dU are the actual changes obeying the Langevin dynamics (2·5) during the time interval dt when we specify a particular realization of both the fluctuation force $\xi(t)$ and the protocol of the parameter a. Another remark is that all the multiplication of fluctuating quantities, e.g. $\xi(t)dx$, should be understood in the sense of Storatonovich calculus.[12] What we have introduced above is not any new dynamics, but a framework of energetics for a stochastic dynamics. We have noticed that the heat bath receives the reaction force from the system although we assume, as usual, that the heat bath is not affected by the system.

First Law – ~~Energy Conservation~~

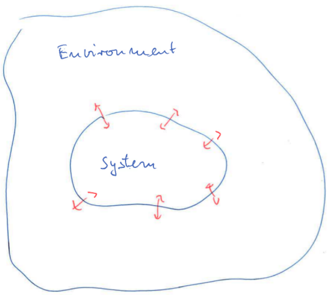
$$\Delta U = \Delta Q + \Delta W$$

ΔU	change in internal energy
ΔQ	heat added on the system
ΔW	work done on the system

H. von Helmholtz: “Über die Erhaltung der Kraft” (1847)

$$\Delta U = (T\Delta S)_{\text{quasi-static}} - (p\Delta V)_{\text{quasi-static}}$$

Weakly coupled systems



$E_{\text{interaction}} \ll E_{\text{system}}$

System $\oplus$ Environment in thermal equilibrium at total energy E_{tot}

$$p_\beta(\mathbf{x}) = Z^{-1} e^{-\beta H_S(\mathbf{x})}$$

$$Z = \int d\Gamma_S e^{-\beta H_S(\mathbf{x})}$$

$\mathbf{x} \in \Gamma_S$: phase space of system

$$d\Gamma_s = \frac{d^{3N}\mathbf{q} d^{3N}\mathbf{p}}{h^{3N}}$$: volume element

$$\beta = k_B^{-1} \frac{\partial S_{\text{tot}}}{\partial E_{\text{tot}}}$$: inverse temperature

Standard form of canonical equilibrium of a subsystem holds for large systems with short-range interactions:

$$E_{\text{interaction}} \propto V_S^{2/3}\,, \quad E_{\text{system}} \propto V_S$$

canonical ensemble

$$\rho^T = \delta(E^T - H^T(\xi,Z))/\omega^T(E^T,Z) \Rightarrow P(E^S|E^T,Z) = \frac{\omega^S(E^S)\,\omega^B(E^T-E^S)}{\omega_T(E^T)}$$

$$E^T = E^S + E^B$$

$$= \frac{\omega^S(E^S)}{\varepsilon\,\omega^T(E^T)} \exp\left[\frac{S_B^B(\overbrace{E^T-E^S}^{E^B})}{k_B}\right]$$

NEXT: $$S_B^B(E^T-E^S) = S_B^B(\bar{E}^B) + \frac{1}{T_B^B(\bar{E}_B)}(E^T - E^S - \bar{E}^B) + \dots,$$

$$\rightsquigarrow = \frac{\omega^S(E^S)}{\varepsilon\,\omega^T(E^T)} \exp\left[\frac{S_B^B(\bar{E}^B)}{k_B} + \frac{(E^T-\bar{E}^B)-E^S}{k_B T_B^B(\bar{E}^B)} + \dots\right]$$

with $+\dots \to 0$! $(\partial^2 S_B^B/\partial^2 E^B) = -1/T_B^2 C_B^B)$

$$\Rightarrow P(E^S|E^T,Z) = \frac{\omega^S(E^S)}{Z_{can}} \exp\left[-\frac{E^S}{k_B T_B^B(\bar{E}^B)}\right]$$

note: $T_B^B(\bar{E}_B) \overset{?}{=} T_B^B(E^T)$; IF "normal": $T_B^B = T_G^B = T_G^S = T_G^T$

$$F_S = -\beta^{-1} \ln Z \ : \qquad \text{free energy}$$

$$U_S = -\frac{\partial}{\partial \beta} \ln Z = \langle H_S \rangle_S \ : \qquad \text{internal energy}$$

$$S_S = k_B \ln Z_S - k_B \beta \frac{\partial}{\partial \beta} \ln Z_S = -k_B \langle \ln p_\beta \rangle_S \ : \qquad \text{entropy}$$

yielding

$$F_S = U_S - TS_S \tag{1}$$

$$U_S = \frac{\partial}{\partial \beta} (\beta F_S) \tag{2}$$

$$S_S = k_B \beta^2 \frac{\partial}{\partial \beta} F_S \tag{3}$$

Any pair of the three equations (1 – 3) implies the third one. Potentials F_s, U_S and S_S satisfying (1 –3) are THERMODYNAMICALLY CONSISTENT.

Strongly coupled systems

$H_{\text{tot}}(\mathbf{x}, \mathbf{y}) = H_S(\mathbf{x}) + H_i(\mathbf{x}, \mathbf{y}) + H_B(\mathbf{y})$: total system's Hamiltonian

$\mathbf{x} \in \Gamma_S$, Γ_S phase space of system

$\mathbf{y} \in \Gamma_B$, Γ_B phase space of environment

Let the total system stay in a canonical equilibrium state at inverse temperature β:

$$\rho_\beta(\mathbf{x}, \mathbf{y}) = Z_{\text{tot}}^{-1} e^{-\beta H_{\text{tot}}(\mathbf{x}, \mathbf{y})}$$

$$Z_{\text{tot}} = \int d\Gamma_S d\Gamma_B e^{-\beta H_{\text{tot}}(\mathbf{x}, \mathbf{y})}$$

Then the system is in the state

$$p_\beta(\mathbf{x}) = \int d\Gamma_B \rho_\beta(\mathbf{x}, \mathbf{y})$$

The reduced state $p_\beta(\mathbf{x})$ in general differs from the Gibbs state $Z_S^{-1} e^{-\beta H(\mathbf{x})}$ of a weakly coupled system. To write $p_\beta(\mathbf{x})$ in the form of a Gibbs state one introduces the HAMILTONIAN OF MEAN FORCE $H^*(\mathbf{x})$ defined by

$$
\begin{aligned}
e^{-\beta H^*(\mathbf{x})} &= \langle e^{-\beta(H_S(\mathbf{x})+H_i(\mathbf{x},\mathbf{y}))} \rangle_B \\
&= Z_B^{-1} \int d\Gamma_B \, e^{-\beta(H_S(\mathbf{x})+H_i(\mathbf{x},\mathbf{y})+H_B(\mathbf{y}))} \\
Z_B &= \int d\Gamma_B \, e^{-\beta H_B(\mathbf{y})} \\
H^*(\mathbf{x}) &= H_S(\mathbf{x}) - \beta^{-1} \ln \langle e^{-\beta H_i(\mathbf{x},\mathbf{y})} \rangle_B \\
p_\beta(\mathbf{x}) &= Z_S^{-1} e^{-\beta H^*(\mathbf{x})} \\
Z_S &= \int d\Gamma_S \, e^{-\beta H^*(\mathbf{x})} = Z_{\mathrm{tot}} / Z_B
\end{aligned}
$$

The Hamiltonian of mean force in general depends on temperature, the parameters specifying the coupling of system and environment as well as on properties of the environment.

If $H_S(\mathbf{x}) = T(\mathbf{p}) + V(\mathbf{q})$ and $H_i(\mathbf{q}, \mathbf{y})$, $(\mathbf{x} \equiv (\mathbf{q}, \mathbf{p}))$ then

$$H^*(\mathbf{x}) = T(\mathbf{p}) + V^*(\mathbf{q})$$

$$V^*(\mathbf{q}) = V(\mathbf{q}) - \beta^{-1} \ln \langle e^{-\beta H_i(\mathbf{q},\mathbf{y})} \rangle_B \;:\; \text{potential of mean force}^*$$

In this case the reduced position pdf $p_\beta(\mathbf{q})$ is determined by the potential of mean force

$$p_\beta(\mathbf{q}) = e^{-\beta V^*(\mathbf{q})} / Z_S^{\text{conf}}$$

$$Z_S^{\text{conf}} = Z_S / \int d\mathbf{p} e^{-\beta T(\mathbf{p})}$$

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[*] J.G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

Warning

W1 Note that $\hat{H}^*$ $(H^*(\mathbf{x}))$ determines $\hat{p}_\beta$ $(p_\beta(\mathbf{x}))$ but not vice versa:

$$\ln p_\beta = -\beta H^* - \ln Z_S$$

In other words, H_S^* cannot be inferred from the intrinsic point of view of the open system, say in terms of tomography of the open system density matrix. Additional information from the environment in the form of $Z_S = Z_{\mathrm{tot}}/Z_B$ is required.

Thermodynamics

$$F_S = -\beta^{-1} \ln Z_s = F_{\text{tot}} - F_B$$

$$U_s = \frac{\partial}{\partial\beta}\beta F_S = U_{\text{tot}} - U_B$$

$$S_S = k_B\beta^2\frac{\partial}{\partial\beta}F_S = S_{\text{tot}} - S_B$$

$$C_S = -k_B\beta^2\frac{\partial^2}{\partial\beta^2}\beta F_S = C_{\text{tot}} - C_B$$

The potentials F_S, U_S and S_S are thermodynamically consistent because they follow from a partition function.

R.P. Feynman, F.L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963).
G.W. Ford, J.T. Lewis, R.F. O'Connell, Phys. Rev. Lett. **55**, 2273 (1985).
P. Hänggi, G.-L. Ingold, P. Talkner, New J. Phys. **10**, 115008 (2008).
G.-L. Ingold, P. Hänggi, P. Talkner, Phys. Rev. E **79**, 061105 (2009).

Further warnings

W2 INTERNAL ENERGY

$$U_S = -\frac{\partial}{\partial\beta}\ln Z_S = \langle\frac{\partial}{\partial\beta}\beta H^*\rangle_S = \langle H^*\rangle_S + \beta\langle\partial H^*/\partial\beta\rangle_s$$

$$\langle\cdot\rangle_S = Z_S^{-1}\int d\Gamma_S\cdot e^{-\beta H^*}$$

The internal energy in general does not agree with the average of the Hamiltonian of mean force. The temperature dependence of H^* entails an additional contribution.

W3 ENTROPY

$$S_S = -k_B\langle\ln p_\beta\rangle_S + k_B\beta^2\langle\partial H^*/\partial\beta\rangle_S$$

The entropy in general deviates from the Shannon-Gibbs (von Neumann) entropy due to the temperature dependence of the Hamiltonian of mean force.

(19) combined with (18) one gets

$$\begin{aligned} U_S &= -\frac{\partial}{\partial \beta} \ln Z_S \\ &= \langle H_S^* \rangle_S + \beta \langle \frac{\partial H_S^*}{\partial \beta} \rangle_S \end{aligned} \tag{22}$$

In other words, only if the Hamiltonian of mean force is temperature-independent the internal energy coincides with the mean value of the Hamiltonian of mean force; otherwise it has to be corrected by the mean value of the derivative of the Hamiltonian of mean force with respect to the inverse temperature.

Alternatively, one can express the internal energy of the total system by the mean value of the total Hamiltonian, $U_{SB} = \langle H \rangle_{SB}$, which can be split into its respective parts yielding [4]

$$\begin{aligned} U_S &= U_{SB} - U_B^0 \\ &= \langle H_S \rangle_S + \langle H_I \rangle_{SB} + \langle H_B \rangle_{SB} - \langle H_B \rangle_B^0 \end{aligned} \tag{23}$$

In general, only for weakly interacting systems the internal energy coincides with the mean value of the system Hamiltonian. Again, the ***classical*** Caldeira Leggett model provides an exception from this rule.

Thermodynamics with system trajectories?

Work supplied to a system by a change of a system's parameter:

$$\begin{aligned} w &= H_{\text{tot}}(\mathbf{Z}(\tau,\mathbf{z}),\lambda(\tau)) - H(\mathbf{z},\lambda(0)) \\ &= \int_0^\tau dt \frac{\partial H_s(\mathbf{X}(t,\mathbf{z}),\lambda(t))}{\partial \lambda(t)} \dot{\lambda}(t) \\ \dot{\mathbf{Z}} &= \{H(\mathbf{Z},\lambda),\mathbf{Z}\}\ , \quad \mathbf{Z}(0) = \mathbf{z} \equiv (\mathbf{x},\mathbf{y}) \\ \{f(\mathbf{z}),g(\mathbf{z})\} &= \sum_i \frac{\partial f}{\partial z_i^p}\frac{\partial g}{\partial z_i^q} - \frac{\partial f}{\partial z_i^q}\frac{\partial g}{\partial z_i^p} \ : \quad \text{Poisson bracket} \end{aligned}$$

Note that

$$\frac{\partial H_{\text{tot}}}{\partial \lambda} = \frac{\partial H_s}{\partial \lambda} = \frac{\partial H^*}{\partial \lambda}$$

For example, if

$$H_S(\mathbf{x},\lambda) = H_0(\mathbf{x}) + Q\lambda\,, \quad Q \;:\; \text{a coordinate of S}$$

the work done on the system by a parameter variation extending over the time span $(0,\tau)$ is given by

$$w = \int_0^\tau dt Q(t,\mathbf{z})\dot{\lambda}(t)$$

requiring to monitor the trajectory $Q(t,\mathbf{z})$ for $0 \leq t \leq \tau$. Provided an energy-expression $E(\mathbf{x},\lambda)$ exists that on average agrees with the internal energy

$$U_S = \langle E(\mathbf{x},\lambda)\rangle_S$$

then the first law-like energy balance

$$dE = \delta W + \delta Q$$

would define a fluctuating heat Q. Accordingly, the hypothetical $E(\mathbf{x},\lambda)$ may be denoted as a fluctuating internal energy.

Stochastic Energetics, Stochastic Thermodynamics

Starting point of STOCHASTIC ENERGETICS[1] and STOCHASTIC THERMODYNAMICS[2] is the overdamped dynamics of a particle with position q moving in a potential $U(q)$ under the influence of additive Gaussian white noise $\xi(t)$ caused by a heat bath at inverse temperature β:

$$\gamma\dot{q} = -U'(q,\lambda) + \sqrt{2\gamma/\beta}\xi(t)\,,\ \gamma\ :\ \text{friction constant}$$

$$\langle\xi(t)\rangle = 0\,,\quad \langle q(t)q(s)\rangle = \delta(t-s)$$

$$p_\beta(q) = e^{-\beta U(q,\lambda)} / \int dq\, e^{-\beta U(q,\lambda)}\ :\quad \text{thermal equilibrium}$$

provided that λ is constant and appropriate boundary conditions are satisfied.

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[1] K. Sekimoto, Prog. Theor. Phys. Supp. **130**, 17 (1998); K. Sekimoto, *Stochastic Energetics*, Lect. Notes in Physics **799**, (Springer, Berlin, 2010).

[2] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005); U. Seifert, AIP Conference Proceedings **1332**, 56 (2011); U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).

In stochastic energetics and stochastic thermodynamics a possible temperature dependence of the potential $U(q,\lambda)$ is disregarded and $U(q,\lambda)$ is assumed to represent the fluctuating internal energy. Recently, Seifert[1] reformulated stochastic thermodynamics on the basis of thermodynamics of open systems with the Hamiltonian of mean force as a central element. He postulates the form of the fluctuating internal energy as

$$E(\mathbf{x},\lambda) = \frac{\partial}{\partial\beta}\beta H^*(\mathbf{x})$$

Its thermal average yields the correct thermodynamic internal energy

$$\langle E(\mathbf{x},\lambda)\rangle_S = U_S$$

Note that in spite of its name, the fluctuating internal energy is a deterministic function of the phase-space variable $\mathbf{x}$. A randomness appears only through the stochasticity of the time-evolution of $\mathbf{x}$.

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[1] U. Seifert, Phys. Rev. Lett. **116**, 020601 (2016).

However, any other function

$$\tilde{E}(\mathbf{x},\lambda) = E(\mathbf{x},\lambda) + h_E(\mathbf{x},\lambda)$$

where $h_E(\mathbf{x},\lambda) \in \mathcal{N}_\beta = \{h(\mathbf{x}) | \int d\Gamma_S h(\mathbf{x}) p_\beta(\mathbf{x}) = 0\}$ equally has the required average $\langle \tilde{E}(\mathbf{x},\lambda)\rangle_S = U_S$.

Another form of $E(\mathbf{x},\lambda)$ can be given in terms of a conditional average over the environment

$$\begin{aligned} E(\mathbf{x},\lambda) &= \langle H_{\text{tot}} | \mathbf{x}\rangle - \langle H_B\rangle_B \\ \langle \cdot | \mathbf{x}\rangle &= d\Gamma_B \cdot w(\mathbf{y}|\mathbf{x}) \\ w(\mathbf{y}|\mathbf{x}) &= \frac{\rho_\beta(\mathbf{x},\mathbf{y})}{\int d\Gamma_B \rho_\beta(\mathbf{x},\mathbf{y})} \\ &= \frac{e^{-\beta(H_i(\mathbf{x},\mathbf{y})+H_B(\mathbf{y}))}}{\int d\Gamma_B e^{-\beta(H_i(\mathbf{x},\mathbf{y})+H_B(\mathbf{y}))}} \\ &= Z_B^{-1} e^{-\beta(H_{\text{tot}}-H^*(\mathbf{x}))} \end{aligned}$$

$w(\mathbf{y}|\mathbf{x})$: distribution of bath degrees of freedom $\mathbf{y}$ under the condition of a fixed system state $\mathbf{x}$. It defines the stationary preparation class[1] consisting of all microscopic initial phase-space distributions of the form $w(\mathbf{y}|\mathbf{x})p_0(\mathbf{x})$ with arbitrary $p_0(\mathbf{x})$.

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[1] H. Grabert, P. Talkner, P. Hänggi, Z. Phys. B **26** 389 (1977)

Once the fluctuating internal energy of the system is defined as $E(\mathbf{x}, \lambda)$ the remaining energy $G(\mathbf{x}, \mathbf{y})$ may be assigned to the environment

$$\begin{aligned} G(\mathbf{x}, \mathbf{y}) &= H_{\text{tot}}(\mathbf{x}, \mathbf{y}) - E(\mathbf{x}, \lambda) \\ &= \delta H_i(\mathbf{x}, \mathbf{y}) + \delta H_B(\mathbf{x}, \mathbf{y}) + \langle H_B \rangle_B \\ \delta H_i(\mathbf{x}, \mathbf{y}) &= H_i(\mathbf{x}, \mathbf{y}) - \langle H_i(\mathbf{x}, \mathbf{y}) | \mathbf{x} \rangle \\ \delta H_B(\mathbf{x}, \mathbf{y}) &= H_B(\mathbf{y}) - \langle H_B(\mathbf{y}) | \mathbf{x} \rangle \end{aligned}$$

This division though is not mandatory: a part of the interaction energy $\delta H_i(\mathbf{x}, \mathbf{y})$ could be attributed to the system, as well as an additional contribution from the null-space $\mathcal{N}_\beta$ yielding a truly fluctuating internal energy expression

$$e(\mathbf{x}, \mathbf{y}, \lambda) = E(\mathbf{x}, \lambda) + \alpha(\mathbf{x}) \delta H_i(\mathbf{x}, \mathbf{y}) + h_E(\mathbf{x}, \lambda)$$

which is a random field due to the dependence on the environmental coordinates $\mathbf{y}$ which are distributed according to $w(\mathbf{y}|\mathbf{x})$.

Fluctuating heat

Fluctuating internal energy with $\alpha(\mathbf{x}) = h_E(\mathbf{x}, \lambda) = 0$

$$E(\mathbf{x}, \lambda) = \frac{\partial}{\partial \beta} \left(\beta H^*(\mathbf{x}, \lambda) \right)$$

$$w = H_{\text{tot}}(\mathbf{Z}(\tau, \mathbf{z}), \lambda(\tau)) - H_{\text{tot}}(\mathbf{z}, \lambda(0)) \quad \text{work}$$

with $\Delta E = w + q$ yields for the fluctuating heat q:

$$\begin{aligned} q &= G(\mathbf{z}) - G(\mathbf{Z}(\tau, \mathbf{z})) \\ &= \delta H_i(\mathbf{z}) + \delta H_B(\mathbf{z}) - \delta H_i(\mathbf{Z}(\tau), \mathbf{z}) - \delta H_B(\mathbf{Z}(\tau, \mathbf{z})) \end{aligned}$$

[redacted]

[redacted]

Fluctuating entropy

Fluctuating entropy is a central notion of stochastic thermodynamics[1]. Usually it is assumed to be proportional to the logarithm of the system pdf

$$s_0^{\mathrm{sth}}(\mathbf{x}) = -k_B \ln p(\mathbf{x})$$

such that its average coincides with the Shannon entropy $-k_B \int d\Gamma_S p(\mathbf{x}) \ln p(\mathbf{x})$.
However, this violates W3: $\langle s_0^{\mathrm{sth}}(\mathbf{x}) \rangle_\beta \neq S_S$.
Recent attempt[2] to cure this deficit:

$$s^{\mathrm{sth}}(\mathbf{x}) = -k_B \ln p(\mathbf{x}) + k_B \beta^2 \frac{\partial}{\partial \beta} H^*(\mathbf{x}, \beta)$$

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[1] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005).

[2] U. Seifert Phys. Rev. Lett. **116**, 020601 (2016).

Non-equilibrium

One might think that the restriction to equilibrium leads to a specific complication of the consistency relations in terms of the derivatives with respect to temperature. This is not correct. Even though the initial pdf $p^0(\mathbf{x})$ of the open system may be independent of temperature, any further time-evolution imposes an interaction with the environment rendering the pdf $p^t(\mathbf{x})$ temperature dependent:

$$p^t(\mathbf{x}) = \int d\Gamma_B p^0(X(\mathbf{z},-t))\,\underbrace{w(\mathbf{Y}(\mathbf{z},-t)|\mathbf{X}(\mathbf{z},-t))}_{\beta-\text{dependent}}$$

$w(\mathbf{y}|\mathbf{x}) = \rho_\beta(\mathbf{x},\mathbf{y})/p_\beta(\mathbf{x})$: conditional pdf characterizing the stationary preparation class.

The conditions for thermodynamic consistency are of the same form as in equilibrium with $p_\beta(\mathbf{x})$ replaced by $p(\mathbf{x},\beta) \equiv p^t(\mathbf{x})$ and $h_F(\mathbf{x};\beta), h_S(\mathbf{x};\beta) \in \mathcal{N}^{\text{neq}}$, $\mathcal{N}^{\text{neq}} = \left\{h(\mathbf{x}) \middle| \int d\Gamma_S h(\mathbf{x}) p(\mathbf{x},\beta) = 0\right\}$.

Again, by means of a proper choice of $h_F(\mathbf{x};\beta)$ and $h_S(\mathbf{x};\beta)$ either fluctuating free energy or fluctuating entropy can be virtually arbitrarily assigned to a given fluctuating internal energy.
In principle, the functional dependence of the fluctuating internal energy need not necessarily be the same as in equilibrium.

Summary

- Equilibrium statistical mechanics and thermodynamics of open systems in strong contact with the environment
    - Hamiltonian of mean force $H^*(\mathbf{x})$ replaces H_S. It is defined in terms of a renormalized Boltzmann factor and hence, depends on temperature, in general.
    - W1: $H^*(\mathbf{x})$ cannot be determined from an intrinsic open system point of view
    - W2: $U_S = \langle H^* \rangle_S + \beta \langle \frac{\partial}{\partial \beta} H^* \rangle_S$
    - W3: Thermodynamic entropy may deviate from Shannon-Gibbs entropy
- Stochastic energetics and thermodynamics
    - Fluctuating internal energy must be DEFINED such that its equilibrium average equals the internal energy. There are no stringent arguments for a particular choice.
    - Fluctuating energy and fluctuating work can be used to define fluctuating heat by means of a first law-like balance requiring a closed total system. The ambiguity of the fluctuating internal energy is consequently inherited by the heat.

Summary (cont.)

- Thermodynamic consistency allows one to construct compatible families of fluctuating internal energy, fluctuating free energy and fluctuating entropy. For a given fluctuating internal energy one may choose virtually any second fluctuating thermodynamic potential with a matching third one.
- For other initial prepration classes than the stationary preparation class there is no obvious way of introducing a Hamiltonian of mean force.

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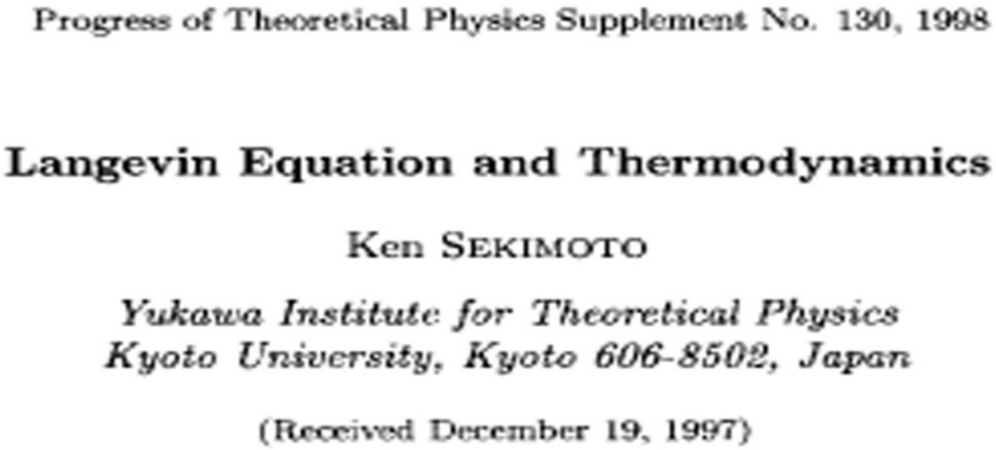

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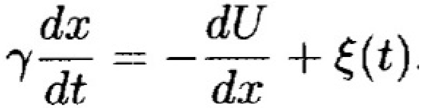
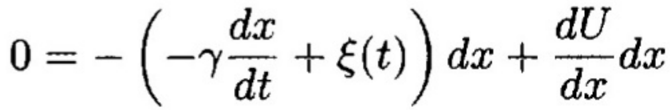
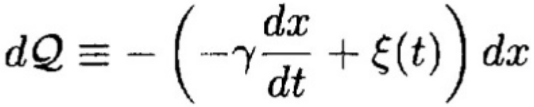


$$\gamma\frac{dx}{dt} = -\frac{dU}{dx} + \xi(t).$$

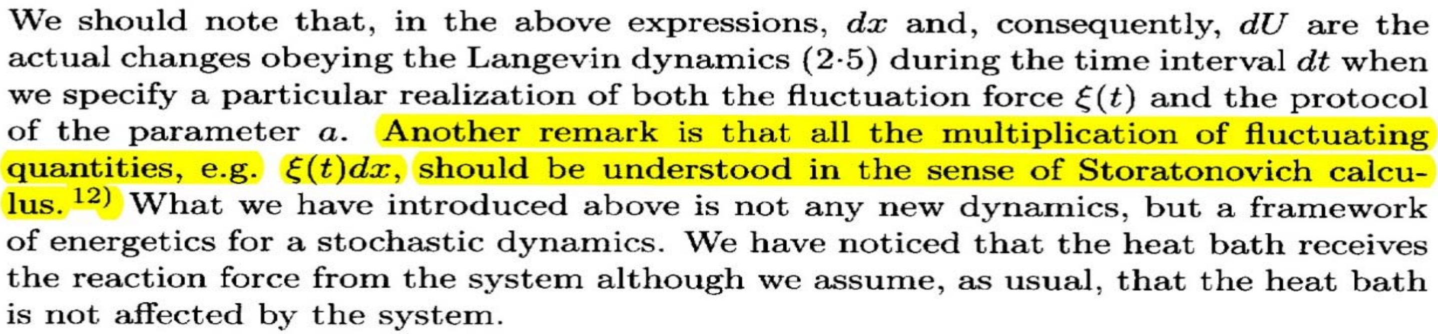


$$0 = -\left(-\gamma\frac{dx}{dt} + \xi(t)\right)dx + \frac{dU}{dx}dx$$

heat



$$dQ \equiv -\left(-\gamma\frac{dx}{dt} + \xi(t)\right)dx$$



We should note that, in the above expressions, dx and, consequently, dU are the actual changes obeying the Langevin dynamics (2·5) during the time interval dt when we specify a particular realization of both the fluctuation force $\xi(t)$ and the protocol of the parameter a. Another remark is that all the multiplication of fluctuating quantities, e.g. $\xi(t)dx$, should be understood in the sense of Storatonovich calculus.[12)] What we have introduced above is not any new dynamics, but a framework of energetics for a stochastic dynamics. We have noticed that the heat bath receives the reaction force from the system although we assume, as usual, that the heat bath is not affected by the system.

In contrast, the thermodynamic entropy of the open system can be expressed as

$$\begin{aligned} S_S &= k_B \frac{\partial T \ln Z_S}{\partial T} \\ &= k_B \left(\ln Z_S + T \frac{\partial \ln Z_S}{\partial T} \right) \\ &= k_B \left(\ln Z_S - (\beta / Z_S) \frac{\partial \mathrm{Tr}_S e^{-\beta H_S^*}}{\partial \beta} \right) \\ &= k_B \left(\ln Z_S + \beta \langle H_S^* \rangle_S + \beta^2 \langle \frac{\partial H_S^*}{\partial \beta} \rangle_S \right) \end{aligned} \tag{26}$$

Comparing with the expression for the von Neumann entropy we find

$$S_S = S_S^{\mathrm{vN}} + k_B \beta^2 \langle \frac{\partial H_S^*}{\partial \beta} \rangle \tag{27}$$

Hence the two entropy expressions agree only if the potential of mean force does not depend on temperature.

Examples

Jaynes Cummings model

$$\hat{H}_{\text{tot}} = \underbrace{\frac{\epsilon}{2}\sigma_z}_{\hat{H}_S} + \underbrace{\Omega\left(a^\dagger a + \frac{1}{2}\right)}_{\hat{H}_B} + \underbrace{\chi\sigma_z\left(a^\dagger a + \frac{1}{2}\right)}_{\hat{H}_i}$$

partition functions

$$Z_{\text{tot}} = q_+ + q_- \,, \quad q_\pm = \frac{e^{\beta\Omega/2} e^{\mp\beta(\epsilon+\chi)/2}}{1 - e^{-\beta(\Omega\pm\chi)}}$$

$$Z_B = \frac{1}{2\sinh(\beta\Omega/2)}$$

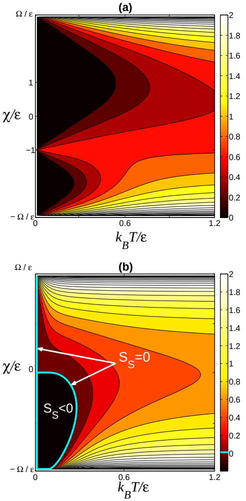
$$Z_S = 2(q_+ + q_-)\sinh(\beta\Omega/2)$$

Hamiltonian of mean force

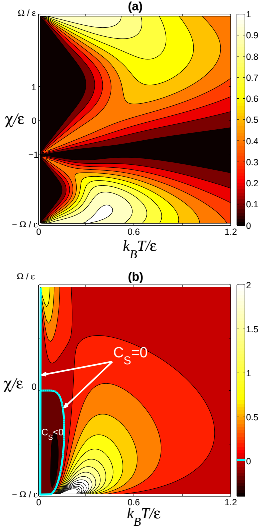
$$\hat{H}^* = \frac{\epsilon^*}{2}\sigma_z + \gamma$$

$$\epsilon^* = \epsilon + \chi + \frac{2}{\beta}\text{Arctanh}\left(\frac{e^{-\beta\Omega}\sinh(\beta\chi)}{1 - e^{-\beta\Omega}\cosh(\beta\chi)}\right)$$

$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$



Entropy



Specific heat

(a): $\Omega/\epsilon = 3$, (b): $\Omega/\epsilon = 1/3$

M. Campisi, P. Talkner, P. Hänggi, J. Phys. A **42**, 392002 (2009).

Quantum interlude

$$\begin{aligned} \Gamma_S \otimes \Gamma_B &\Rightarrow \mathcal{H}_S \otimes \mathcal{H}_B \\ \int d\Gamma_s \int d\Gamma_b &\Rightarrow \mathrm{Tr}_S \mathrm{Tr}_B \\ \rho(\mathbf{x}, \mathbf{y}) &\Rightarrow \hat{\rho} \\ H_{\mathrm{tot}} &\Rightarrow \hat{H}_{\mathrm{tot}} \end{aligned}$$

$$\begin{aligned} \hat{H}^* &= -\beta^{-1} \ln \mathrm{Tr}_B e^{-\beta \hat{H}_{\mathrm{tot}}} / \mathrm{Tr} e^{-\beta H_B} \\ \hat{p}_\beta &= Z_S^{-1} e^{-\beta \hat{H}^*} \\ Z_S &= Z_{\mathrm{tot}} / Z_B = \mathrm{Tr}_B \mathrm{Tr}_S e^{-\beta \hat{H}_{\mathrm{tot}}} / \mathrm{Tr}_B e^{-\beta \hat{H}_B} \end{aligned}$$

For quantum systems, the Hamiltonian of mean force ALWAYS depends on temperature.

For an environment consisting of harmonic oscillators (Magalinskii[1], Ullersma[2]) the Hamiltonian of mean force is independent of temperature.

For a system with a single degree of freedom that couples to a bath of harmonic oscillators à la Caldeira-Leggett[3] the Hamiltonian of mean force coincides with the bare system Hamiltonian. This though is an untypical exception.

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[2] V.B. Magalinskii, Sov. Phys. JETP **9**, 1381 (1959).

[2] P.Ullersma, Physica **32**, 27 (1966)

[3] A.O. Caldeira, A.J. Leggett, Physica A **121**, 587 (1983).

Note that

$$\langle e(\mathbf{x},\mathbf{y},\lambda)\rangle_{\rm spc} = \langle E(\mathbf{x},\lambda) + h_E(\mathbf{x},\alpha)\rangle_p$$

$$\langle f(\mathbf{x},\mathbf{y})\rangle_{\rm spc} = \int d\Gamma_B d\Gamma_S f(\mathbf{x},\mathbf{y}) w(\mathbf{y}|\mathbf{x}) p(\mathbf{x}) \ : \ \text{av. stat. prep. class}$$

$$\langle k(\mathbf{x})\rangle_p = \int d\Gamma_S k(\mathbf{x}) p(\mathbf{x}) \ : \ \text{average w.r.t. } p(\mathbf{x})$$

Then the environmental energy becomes

$$\begin{aligned} g(\mathbf{x},\mathbf{y}) &= H_{\rm tot}(\mathbf{x},\mathbf{y}) - e(\mathbf{x},\mathbf{y},\lambda) \\ &= (1-\alpha(\mathbf{x}))\delta H_i(\mathbf{x},\mathbf{y}) + \delta H_B(\mathbf{x},\mathbf{y}) + \langle H_B\rangle_B - h_E(\mathbf{x},\lambda) \end{aligned}$$

From the point of view of simplicity one could argue that
(1) $\alpha(\mathbf{x}) = 0$ to avoid randomness of the fluctuating internal energy at a fixed time, and
(2) $h_E(\mathbf{x},\lambda) = 0$ to avoid any $\mathbf{x}$-dependence of the environmental energy other than from the fluctuations $\delta H_i(\mathbf{x},\mathbf{y})$ and $\delta H_B(\mathbf{x},\mathbf{y})$.