

# Thermodynamics & Statistical Physics

## Chapter 10. Fluctuation

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# Table of contents

## 1 §10. Fluctuation

- 10.1 Quasi-thermodynamics of fluctuation
- 10.5 Brownian motion
- 10.6 Diffusion and temporal correlation of Brownian particle's momentum
- 10.7 Examples of Brownian motion

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- Fluctuation of thermal parameters:  $N, V, E; S, T$ .  
For  $S$  (or  $T$ ), means  $\overline{[S(N, V, E) - S(\overline{N}, \overline{V}, \overline{E})]^2}$ .

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$$E = \bar{E} + \left(\frac{\partial E}{\partial S}\right)_0 \Delta S + \left(\frac{\partial E}{\partial V}\right)_0 \Delta V + \frac{1}{2} \left[ \left(\frac{\partial^2 E}{\partial S^2}\right)_0 (\Delta S)^2 + 2 \left(\frac{\partial^2 E}{\partial S \partial V}\right)_0 \Delta S \Delta V + \left(\frac{\partial^2 E}{\partial V^2}\right)_0 (\Delta V)^2 \right].$$

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$$W \propto e^{-\frac{\Delta E - T\Delta S + p\Delta V}{kT}}$$

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$$E = \bar{E} + T\Delta S - p\Delta V + \frac{1}{2} \left[ \frac{\partial}{\partial S} \left( \frac{\partial E}{\partial S} \right) (\Delta S)^2 + \frac{\partial}{\partial S} \left( \frac{\partial E}{\partial V} \right) \Delta S \Delta V + \frac{\partial}{\partial V} \left( \frac{\partial E}{\partial S} \right) \Delta S \Delta V + \frac{\partial}{\partial V} \left( \frac{\partial E}{\partial V} \right) (\Delta V)^2 \right]$$

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 &= \bar{E} + T\Delta S - p\Delta V + \frac{1}{2} (\Delta T \Delta S - \Delta p \Delta V).
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# Table of contents

## 1 §10. Fluctuation

- 10.1 Quasi-thermodynamics of fluctuation
- 10.5 Brownian motion
- 10.6 Diffusion and temporal correlation of Brownian particle's momentum
- 10.7 Examples of Brownian motion

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# Table of contents

## 1 §10. Fluctuation

- 10.1 Quasi-thermodynamics of fluctuation
- 10.5 Brownian motion
- 10.6 Diffusion and temporal correlation of Brownian particle's momentum
- 10.7 Examples of Brownian motion

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- Before to get  $\bar{p}$ , turn to the temporal correlation function:  $\overline{F(t)F(t+\tau)} \equiv \frac{1}{N} \sum_{i=1}^N F_i(t)F_i(t+\tau)$ .
- If the duration ( $\tau_c$ ) of the fluctuating force is short enough,  $\overline{F(t)F(t+\tau)} = 2D_p\delta(\tau)$ ; and  $2D_p = \overline{F^2(t)}$ .

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In equilibrium,  $\frac{\overline{p^2}}{2m} = \frac{1}{2}kT$ ,  $\therefore D_p = m\gamma kT = \alpha kT$ .

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- The combination:  $\overline{p(t)p(t')} = \frac{D_p}{\gamma} [e^{-\gamma|t-t'|} - e^{-\gamma(t+t')}]$ .

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# Table of contents

## 1 §10. Fluctuation

- 10.1 Quasi-thermodynamics of fluctuation
- 10.5 Brownian motion
- 10.6 Diffusion and temporal correlation of Brownian particle's momentum
- 10.7 Examples of Brownian motion

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- $m \frac{dv}{dt} = \mathcal{F} - \alpha v + F(t)$ , Langevin's equation.  
 $L \leftrightarrow m, i \leftrightarrow v, \mathcal{V} \leftrightarrow \mathcal{F}, R \leftrightarrow \alpha, \text{ and } V \leftrightarrow F$ .

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 where  $\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega' - \omega)t} dt = \delta(\omega - \omega')$ .

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# Table of contents

## 1 §10. Fluctuation

- 10.1 Quasi-thermodynamics of fluctuation
- 10.5 Brownian motion
- 10.6 Diffusion and temporal correlation of Brownian particle's momentum
- 10.7 Examples of Brownian motion