On the principle of equipartition of kinetic energy: classical versus quantum

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Outline

1. Equipartition of energy in classical systems
2. Quantum systems: harmonic oscillator in Gibbs canonical state
3. Quantum Brownian particle
4. Fluctuation-dissipation relation
5. Partition energy theorem for a free quantum Brownian particle
6. Conclusions

Classical systems

Classical system described by the Hamiltonian:

$$H = H(\mathbf{x}, \mathbf{p}) = \sum_i \frac{p_i^2}{2m_i} + \sum_i U(x_i) + \sum_{i,k} V(x_i, x_k)$$

In thermodynamic equilibrium of temperature T and for Gibbs states $P(\mathbf{x}, \mathbf{p}) \sim e^{-H/k_B T}$ (k_B - Boltzmann constant) the averaged kinetic energy per one degree of freedom is:

$$E_k = \frac{1}{2m_j}\langle p_j^2 \rangle = \int_{-\infty}^{\infty} \mathbf{dp} \int_{-\infty}^{\infty} \mathbf{dx} \, \frac{p_j^2}{2m_j} \, exp\{-H(\mathbf{x}, \mathbf{p})/k_B T\}$$

Integration yields:

$$E_k = \frac{1}{2m_j}\langle p_j^2 \rangle = \frac{1}{2} k_B T$$

E_k does not depend on $U(x_i)$ and $V(x_i, x_k)$!!

Quantum systems: harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{m\omega_0^2 x^2}{2}$$

In thermodynamic equilibrium (density operator $\rho \sim e^{-H/k_B T}$):

$$\mathcal{E}_k(\omega_0) = \frac{1}{2m}\langle p^2 \rangle = \frac{\hbar\omega_0}{4} \coth \frac{\hbar\omega_0}{2k_B T}$$

$\mathcal{E}_k$ depends on the potential via ω_0!!

In the limit $\omega_0 \to 0$ corresponding to a free particle:

$$\mathcal{E}_k = \frac{1}{2} k_B T$$

the same as in the classical case

Quantum Brownian particle

Hamiltonian of the System (Brownian particle) + Environment (thermostat):

$$H = \frac{p^2}{2M} + U(x) + \sum_i \left[\frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} \left(q_i - \frac{c_i}{m_i \omega_i^2} x \right)^2 \right]$$

From Heisenberg equations: Generalized Langevin Equation

$$M\ddot{x}(t) + \int_0^t \gamma(t-s)\dot{x}(s)\, ds = -U'(x(t)) - \gamma(t)x(0) + F(t)$$

$$\gamma(t-s) = \sum_i \frac{c_i^2}{m_i \omega_i^2} \cos[\omega_i (t-s)]$$

$$F(t) = \sum_i c_i \left[q_i(0) \cos(\omega_i t) + \frac{p_i(0)}{m_i \omega_i} \sin(\omega_i t) \right]$$

Initial state of the total system

Initial state of the total system: $\rho(0) = \rho_S \otimes \rho_E$, where ρ_S is an arbitrary state of the Brownian particle and ρ_E is an equilibrium canonical state of the environment (thermostat) of temperature T,

$$\rho_E = \exp(-H_E/k_B T)/\mathrm{Tr}[\exp(-H_E/k_B T)]$$

where:

$$H_E = \sum_i \left[\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 q_i^2 \right]$$

is the Hamiltonian of the thermostat. Random force:

$$F(t) = \sum_i c_i \left[q_i \cos(\omega_i t) + \frac{p_i}{m_i \omega_i} \sin(\omega_i t) \right]$$

Statistics of Gaussian random force $F(t)$

$$F(t) = \sum_i c_i \left[q_i \cos(\omega_i t) + \frac{p_i}{m_i \omega_i} \sin(\omega_i t) \right]$$

Its mean value is zero,

$$\langle F(t) \rangle \equiv \mathrm{Tr}\left[F(t) \rho_T \right] = 0$$

and the symmetrized correlation function:

$$C(t_1, t_2) = \frac{1}{2} \langle F(t_1) F(t_2) + F(t_2) F(t_1) \rangle$$

takes the form:

$$C(t_1, t_2) = C(t_1 - t_2) = \sum_i \frac{\hbar c_i^2}{2 m_i \omega_i} \coth\left(\frac{\hbar \omega_i}{2 k_B T} \right) \cos[\omega_i (t_1 - t_2)]$$

Spectral function $J(\omega)$

$$\gamma(t-s) \quad = \sum_i \frac{c_i^2}{m_i\omega_i^2}\cos[\omega_i(t-s)], \quad J(\omega) = \sum_i \frac{c_i^2}{m_i\omega_i^2}\delta(\omega-\omega_i)$$

Damping kernel:

$$\gamma(\tau) = \int_0^\infty d\omega J(\omega)\cos\omega\tau = \int_0^\infty d\omega\,\hat{\gamma}(\omega)\cos\omega\tau$$

Correlation function:

$$C(\tau) = \int_0^\infty d\omega\,\frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2k_BT}\right)J(\omega)\cos\omega\tau = \int_0^\infty d\omega\,\hat{C}(\omega)\cos\omega\tau$$

Fluctuation-dissipation relation

$$\hat{C}(\omega) = \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2k_BT}\right)\,\hat{\gamma}(\omega)$$

$$M\ddot{x}(t) + \int_0^t \gamma(t-s)\dot{x}(s)\,ds = -\gamma(t)x(0) + F(t)$$

Momentum of Brownian particle

$$\dot{p}(t) + \frac{1}{M}\int_0^t \gamma(t-s)p(s)\,ds = -\gamma(t)x(0) + F(t)$$

Solution via the response function $R(t)$:

$$p(t) = R(t)p(0) - \int_0^t du\; R(t-u)\gamma(u)x(0) + \int_0^t du\; R(t-u)\eta(u).$$

Its Laplace transform:

$$\hat{R}_L(z) = \int_0^\infty dt\; \mathrm{e}^{-zt}R(t) = \frac{M}{Mz + \hat{\gamma}_L(z)}$$

Partition energy theorem for a free Brownian particle

$$E_k = \lim_{t\to\infty} \frac{1}{2M}\langle p^2(t)\rangle = \int_0^\infty d\omega\, \mathcal{E}_k(\omega)\, \mathbb{P}(\omega)$$

E_k - mean kinetic energy of Brownian particle

$\mathcal{E}_k = \frac{\hbar\omega}{4} \coth\left(\frac{\hbar\omega}{2k_B T}\right)$ - mean thermal kinetic energy of thermostat oscillator of eigenfrequency ω

$\mathbb{P}(\omega)$ - probability distribution of thermostat oscillators frequencies:

$$\mathbb{P}(\omega) = \frac{1}{\pi}\left[\hat{R}_L(i\omega) + \hat{R}_L(-i\omega)\right] = \frac{2}{\pi}\int_0^\infty dt\, R(t)\cos(\omega t)$$

$$\mathbb{P}(\omega) \geq 0, \qquad \int_0^\infty \mathbb{P}(\omega) d\omega = 1, \quad \hat{R}_L(z) = \frac{M}{Mz + \hat{\gamma}_L(z)}$$

Drude model of dissipation

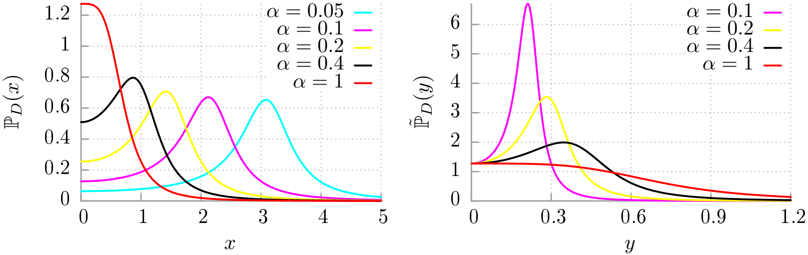

Figure : Drude model $\gamma_D(t) = (\gamma_0/2\tau_c)e^{-t/\tau_c}$. Probability distributions $\mathbb{P}_D(x)$ and $\tilde{\mathbb{P}}_D(y)$ in two different scalings for selected values of the dimensionless parameter $\alpha = \tau_v/\tau_c$. In the left panel τ_c is fixed and $\tau_v = M/\gamma_0$ is changed. In the right panel τ_v is fixed and τ_c is changed.

Debye model of dissipation

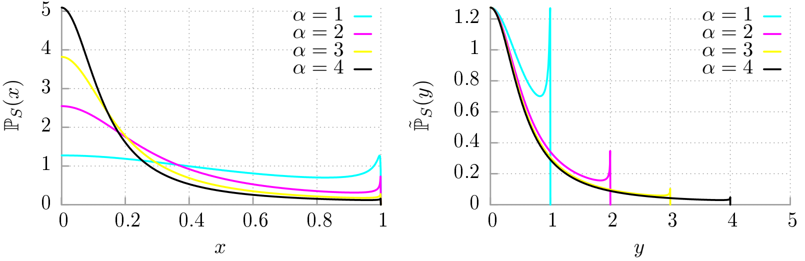

Figure : $\mathbb{P}_S(x)$ for the oscillatory decay $\gamma_S(t) = \frac{\gamma_0 \sin(t/\tau_c)}{\pi t}$ (the Debye type model) and selected $\alpha = \tau_v/\tau_c$. In the left panel τ_c is fixed and $\tau_v = M/\gamma_0$ is changed. In the right panel τ_v is fixed and τ_c is changed.

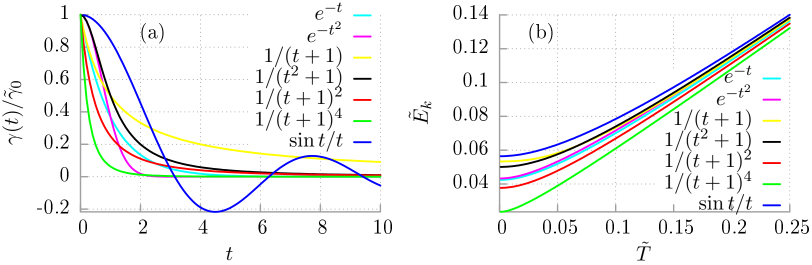

Figure : Panel (a): The normalized memory functions $\gamma(t)/\tilde{\gamma}_0$ representing various dissipation mechanisms. Panel (b): The dimensionless kinetic energy $\tilde{E}_k = \tau_c E_k/\hbar$ vs. dimensionless temperature $\tilde{T} = \tau_c k_B T/\hbar$ and various forms of $\gamma(t)$.

Selected regimes

1. High temperature regime: $E_k = \frac{1}{2} k_B T$
2. Low temperature regime (fluctuations of vacuum at $T = 0$) :

$$E_0 = \frac{1}{4} \int_0^\infty d\omega \; \hbar\omega \, \mathbb{P}(\omega) = \frac{\hbar}{4} \langle \xi \rangle$$

3. The first correction for small temperature $T > 0$

$$E_1(T) = \frac{1}{2} \int_0^\infty d\omega \; \hbar\omega \, \mathbb{P}(\omega) \exp\left[-\frac{\hbar\omega}{k_B T} \right]$$

4. For Drude model, when $\tau_c >> \hbar / k_B T$,

$$E_k = \frac{1}{4} \hbar\Omega \coth\left(\frac{\hbar\Omega}{2 k_B T} \right), \quad \Omega^2 = \frac{\gamma_0}{M\tau_c}$$

Conclusions

1. The mean kinetic energy E_k of the Brownian particle equals the thermally-averaged kinetic energy $\mathcal{E}_k$ per one degree of freedom of thermostat oscillators, additionally averaged over randomly-distributed oscillator frequencies.

$$E_k = \langle \mathcal{E}_k \rangle = \int_0^\infty \mathcal{E}_k(\omega)\, \mathbb{P}(\omega)\, d\omega \to \frac{1}{2} k_B T \quad \text{for} \quad T \to \infty$$

2. The mean kinetic energy depends on "everything" : the system-thermostat coupling strength and dissipation mechanism (correlation time of thermal noise)
3. At zero temperature, $T = 0$, the mean kinetic energy is non-zero

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