

0.1 Non-equilibrium Statistical Physics

Fluctuations. 1. Equilibrium state: thermodynamic level/quantities (N, T, P) , 随机变量存在概率分布 \rightarrow 涨落 $N = N_0 + \delta N$;
2. Non-equilibrium state, thermodynamic level: 时空间不均匀, $T(x, t), n(x, t)$. 通过局域平衡假设分析. $\frac{\partial n}{\partial x} \rightarrow$ flux. Relaxation(弛豫); Transportation(输运). force-flux 关系.

0.1.1 Analyze Fluctuations

[Example] Classical nucleation theory: 若 $\mu_{\text{vapor}} > \mu_{\text{liquid}}$, 则凝结发生. Local fluctuation of density ρ : grow/decay.

$G = -\alpha |\Delta\mu| \overset{\uparrow}{R^3} + \beta \sigma \cdot \overset{\downarrow}{R^2}$. 需要足够大的凝结核.

0.1.1.1 Static Thermodynamic Analysis

研究发生 $\overset{\text{equilibrium}}{f_0} \rightarrow \overset{\text{fluctuated}}{f_0 + \delta f}$ 的概率.

令系统 1 和系统 2 状态分别为 $(E_1, V_1), (E_2, V_2)$, 且满足 $E_1 \ll E_2, V_1 \ll V_2$; $\begin{cases} E_1 + E_2 = E \\ V_1 + V_2 = V \end{cases}$.

设平衡态熵为 S_0 , 涨落态熵为 S_f . 熵变 $\Delta S = S_f - S_0$. 处于涨落态的概率 $P \propto e^{\Delta S/k_B}$, 可近似 $P_2 \simeq P_0, T_2 \simeq T_0$, 得

$$\Delta S = \Delta S_1 + \Delta S_2 = \Delta S_1 + \int_0^f \frac{dE_2 + P_2 dV_2}{T_2} \begin{cases} \Delta E_2 = -\Delta E_1 \\ \Delta V_2 = -\Delta V_1 \end{cases} \simeq \Delta S_1 - \frac{\Delta E_1 + P_0 \Delta V_1}{T_0}$$

于是迁移概率为 $P_1 \propto \exp\left(-\frac{\Delta E - T \Delta S + p \Delta V}{k_B T}\right)$. 因此涨落态可用 $(\Delta E, \Delta S, \Delta V)$ 描述. 将 ΔE 在平衡态附近展开:

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

$$\text{将展开式代入分子: } \Delta E - T \Delta S + p \Delta V = \frac{1}{2} \left[\Delta \left(\frac{\partial E}{\partial S} \right)_0 \Delta S + \Delta \left(\frac{\partial E}{\partial V} \right)_0 \Delta V \right] = \frac{1}{2} [\Delta T \Delta S - \Delta p \Delta V],$$

于是得到 $P \propto \exp\left(-\frac{\Delta T \Delta S - \Delta p \Delta V}{2k_B T}\right)$, 即三个 Δ 中只有两个独立. 类似的关系还有:

$$1. \Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V = \frac{C_v}{T} \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V;$$

$$2. \Delta P = \left(\frac{\partial P}{\partial T}\right)_V \Delta T + \left(\frac{\partial P}{\partial V}\right)_T \Delta V = \left(\frac{\partial P}{\partial T}\right)_V \Delta T - \frac{1}{\kappa_T V} \Delta V, \text{ 其中等温压缩率 } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T.$$

使用 Maxwell Relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, 迁移概率化为 $P \propto \exp\left[-\frac{C_v}{2k_B T^2} (\Delta T)^2 - \frac{1}{2k_B \kappa_T T V} (\Delta V)^2\right]$.

$$\text{计算涨落: } \langle (\Delta T)^2 \rangle = \frac{\int (\Delta T)^2 P(\Delta T, \Delta V) d(\Delta T)}{\int P(\Delta T, \Delta V) d(\Delta T)} = \frac{k_B T^2}{C_v} \propto \frac{1}{V}, \quad \langle (\Delta V)^2 \rangle = k_B T \kappa_T V \propto V$$

定义相对涨落为 $\frac{\sqrt{\langle (\Delta A)^2 \rangle}}{\langle A \rangle}$. $(\Delta E)^2 = \left[\left(\frac{\partial E}{\partial T}\right)_{VN} \Delta T + \left(\frac{\partial E}{\partial V}\right)_{TN} \Delta V \right]^2$, 等式两边同取期望值 $\langle \cdot \rangle$, 忽略交叉项:

$$\langle (\Delta E)^2 \rangle = \langle (C_v \Delta T)^2 \rangle + \left\langle \left[\left(\frac{\partial E}{\partial V}\right)_{TN} \Delta V \right]^2 \right\rangle + \overset{\text{cross terms} \rightarrow 0}{\dots} \overset{\text{fluctuation of particle numbers}}{\text{canonical}} = C_v k_B T^2 + k_B T \kappa_T V \left(\frac{\partial E}{\partial V}\right)_{TN}^2.$$

[Discussion] 令 internal energy per particle $\tilde{\epsilon}$ 与 volume per particle v .

$$k_B T \kappa_T V \left(\frac{\partial E}{\partial V}\right)_{TN}^2 = k_B T \kappa_T N v \left(\frac{\partial \tilde{\epsilon}}{\partial v}\right)_T^2 = k_B T \kappa_T N n^3 \left(\frac{\partial \tilde{\epsilon}}{\partial n}\right)_T^2, \text{ 其中粒子数密度 } n = \frac{N}{V} = \frac{1}{v}.$$

回忆巨正则系综: $\langle (\Delta E)^2 \rangle = k_B T^2 C_v$, 即 canonical 项. 将其和粒子数涨落项 $\langle (\Delta N)^2 \rangle$ 分离, 从而写作

$$\langle (\Delta E)^2 \rangle = \langle (\Delta E)^2 \rangle_{\text{canonical}} + \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{TV}^2 \langle (\Delta N)^2 \rangle, \text{ 其中 } \langle (\Delta N)^2 \rangle = \frac{\langle N \rangle^2 k_B T \kappa_T}{V}$$

观察相对涨落与体积 V 关系为 $\frac{\sqrt{\langle (\Delta T)^2 \rangle}}{\langle T \rangle} \sim \frac{1}{\sqrt{V}}, \quad \frac{\sqrt{\langle (\Delta V)^2 \rangle}}{\langle V \rangle} \propto \frac{1}{\sqrt{V}}$. 因此 MFT 难以用于小尺度系统.

0.1.1.2 Time Analysis of Fluctuations

$x_0 \rightarrow x_f(t)$. 视涨落为含时信号 $A(t)$. 时间平均 $\langle A \rangle = \frac{1}{T} \int_0^T A(t) dt$; 定义时间关联函数 $\phi(t) = \frac{1}{T} \int_0^T \delta A(u) \delta A(u+t) du$.

假定 ergodic(各态历经), 时间平均化为系综平均: $\phi(t_1, t_2) = \langle \delta A(t_1) \delta A(t_2) \rangle^{\text{ensemble}}$. 时间平移不变性: $\phi(t_1, t_2) \rightarrow \phi(t_2 - t_1)$.

时间平移不变性 in Joint probability $P_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n) = P_n(x_1, t_1 + \Delta t; x_2, t_2 + \Delta t; \dots; x_n, t_n + \Delta t)$

[Discussion] Correlation & Macroscopic properties.

1. 空间关联函数 $g_{ij} \xrightarrow{\text{in equilibrium}}$ Response χ ;

2. 时间关联函数 $\phi(t) \xrightarrow{\text{out of equilibrium}}$ conductivity, viscosity(粘度).

[Example] 测量 k_B . 分光出点光源, 凸透镜聚焦后散射至垂吊镜面, 相机收集其反射光. 镜子受空气撞击即布朗运动(视为热浴). 热平衡下 $\frac{1}{2} L \langle \theta^2 \rangle = \frac{1}{2} k_B T \Rightarrow \langle \theta^2 \rangle = \frac{k_B T}{L}$. (能均分定理: Hamiltonian \propto 自由度平方) 分别在 1 atom 和 10^{-4} mmHg 进行实验. 前者相比后者的偏转产生频率高得多. 但只要温度一样, 仅凭 $\langle \theta^2 \rangle$ 无法区分. 类比于价格/股票的含时变化.

0.1.1.2.1 Spectral Analysis [Discussion] 使用三棱镜分光, 实际上就是一种频谱分析.

$$\tilde{x}(\omega) = \int_{-\infty}^{+\infty} x(t) e^{i\omega t} dt, \quad x(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{x}(\omega) e^{-i\omega t} d\omega$$

对 statistically stationary signal(稳态信号), 关联函数 $\phi(t' - t) = \langle x(t') x(t) \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \langle \tilde{x}(\omega) \tilde{x}(\omega') \rangle e^{-i(\omega t + \omega' t')} d\omega d\omega'$,

可推断频域内关联函数为 $\langle \tilde{x}(\omega) \tilde{x}(\omega') \rangle = 2\pi [\tilde{x}^2(\omega)] \delta(\omega - \omega')$, 那么变换回时域形式: $\phi(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{x}^2(\omega) e^{-i\omega t} d\omega$,

其中 $\tilde{x}^2(\omega)$ 是 $x^2(t)$ 的傅里叶变换. 令 $\tilde{x}^2(\omega)$ 对频域积分并归一化, 得到

$\phi(0) = \langle x^2(t) \rangle = \int_{-\infty}^{+\infty} \tilde{x}^2(\omega) \frac{d\omega}{2\pi} = 2 \int_0^{+\infty} \tilde{x}^2(\omega) \frac{d\omega}{2\pi}$, 即得出 **Wiener-Khinchin theorem**(for random process & statistically stationary signal).

[Example] $\phi(t) = \langle x(0)x(t) \rangle = \langle x(0)^2 \rangle e^{-\lambda|t|}$. $\tilde{x}^2(\omega) = \langle x(0)^2 \rangle \frac{2\lambda}{\omega^2 + \lambda^2}$, $\langle x^2(t) \rangle = \left\langle 2 \int_0^{+\infty} \tilde{x}^2(\omega) \frac{d\omega}{2\pi} \right\rangle$,

$$\int_0^{+\infty} \frac{\lambda}{\omega^2 + \lambda^2} d\omega = \int_0^{+\infty} \frac{1}{\omega'^2 + 1} d\omega' = \frac{\pi}{2} \Rightarrow \langle x^2(t) \rangle = \langle x^2(0) \rangle.$$

0.1.2 Relaxation of Weakly Non-equilibrium State

形如 $\frac{dx(t)}{dt} = -\lambda x(t) \Rightarrow x(t) = x(0)e^{-\lambda t}$ 的(描述性) Relaxation equation. 物质输运和热量输运是耦合的, 则

$$\langle x_i(t) \rangle \Rightarrow \frac{dx_i(t)}{dt} = - \sum_k \lambda_{ik} x_k(t). \text{ 延拓 } \phi_{ik}(t' - t) = \langle x_i(t') x_k(t) \rangle = \langle x_k(t) x_i(t') \rangle = \phi_{ki}(t - t') \Rightarrow \boxed{\phi_{ik}(t) = \phi_{ki}(-t)}.$$

若 $x_i(-t) = x_i(t)$, $\phi_{ik}(t' - t) = \langle x_i(t') x_k(t) \rangle = \langle x_i(-t') x_k(-t) \rangle = \phi_{ik}[-t' - (-t)] = \phi_{ik}(t - t') \Rightarrow \phi_{ik}(t) = \phi_{ik}(-t)$

因此时间反演对称下, 有 $\boxed{\phi_{ik}(t) = \phi_{ki}(t)}$

0.1.2.1 Flux & Force

求和约定: $\dot{x}_i(t) = -\lambda_{ik} x_k(t)$, 定义共轭量 $X_i = \frac{\partial S}{\partial x_i}$ 以引入熵 $S(x_1, x_2, \dots, x_n)$. $\dot{x}_i(t), X_i(t)$ 分别为 flux 和 force.

Taylor 展开: $S(x_i) = S(0) + \left(\frac{\partial S}{\partial x_i} \right)_{x_i=0} x_i + \frac{1}{2} \left(\frac{\partial^2 S}{\partial x_i \partial x_j} \right)_{x_i=x_j=0} x_i x_j + \dots = S(0) - \frac{1}{2} \beta_{ij} x_i x_j$, 其中 $\beta_{ij} = \beta_{ji}$.

代入展开式: $X_i = \frac{\partial S}{\partial x_i} = \frac{\partial}{\partial x_i} \left[S(0) - \frac{1}{2} \beta_{jk} x_j x_k \right] = -\frac{\beta_{jk}}{2} \frac{\partial}{\partial x_i} (x_j x_k) = -\frac{\beta_{jk}}{2} (\delta_{ij} x_k + x_j \delta_{ik}) = -\beta_{ik} x_k$.

于是 Force $X_i = -\beta_{ik} x_k$, 从而得到 **Force-Flux** 关系 $\boxed{\dot{x}_i = \gamma_{ik} X_k}$, 其中 $\gamma_{ik} = \lambda_{il} (\beta^{-1})_{lk}$ 是 **Kinetic Coefficient**.

比如写作二阶形式的 $\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \end{bmatrix} = \begin{bmatrix} \gamma_{11} & \gamma_{12} \\ \gamma_{21} & \gamma_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix}$. 若常数项 $S(0) = 0$, 则熵可写作共轭量乘积: $S = \frac{1}{2} X_i x_i$,

变化率为 $\frac{dS}{dt} = \frac{1}{2} (\dot{X}_i x_i + X_i \dot{x}_i)$. 利用 force-flux 关系处理 $x_i \dot{X}_i = x_i (-\beta_{ik} \dot{x}_k) = x_i (-\beta_{ki} \dot{x}_k) = X_k \dot{x}_k$,

因此 $\dot{S} = X_i \dot{x}_i = \frac{\partial S}{\partial x_i} \dot{x}_i$, 显然就是链式求导规则.

[Example] 考虑铜棒, 忽略体积变化($dV = 0$). 存在热流 \vec{J}_h . Internal energy per volume: $u(x, y, z, t)$. 则有

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_h = 0 \xrightarrow{du=TdS} \frac{\partial S}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_h \Rightarrow \frac{\partial S}{\partial t} + \nabla \cdot \left(\frac{\vec{J}_h}{T} \right) = -\frac{1}{T^2} \vec{J}_h \cdot \nabla T.$$

等式右边为 rate of entropy production ($\neq 0$ 时为非平衡过程), 即为 0 时形成对 S 的连续性方程.

0.1.2.2 Onsager's Reciprocal Relation

$$\text{平衡态时, } \langle \dot{x}_i \rangle = 0, \langle x_i \rangle = \tilde{x}_i. \langle x_i X_j \rangle = \text{Tr}_{x_i} [x_i X_j A e^{\Delta S(x_1, x_2, \dots, x_n)/k_B}] = \text{Tr}_{x_i} [x_i X_j A e^{\frac{1}{2k_B} \beta_{ij} (x_i - \tilde{x}_i)(x_j - \tilde{x}_j)}]$$

$$\frac{\partial \langle x_i \rangle}{\partial \tilde{x}_j} = \delta_{ij} = \frac{\partial}{\partial \tilde{x}_j} \text{Tr}_{x_i} [x_i A e^{-\frac{1}{2k_B} \beta_{ij} (x_i - \tilde{x}_i)(x_j - \tilde{x}_j)}] = \text{Tr}_{x_i} \left[x_i \frac{\partial}{\partial \tilde{x}_j} A e^{-\frac{1}{2k_B} \beta_{ij} (x_i - \tilde{x}_i)(x_j - \tilde{x}_j)} \right] = -\frac{1}{k_B} \langle x_i X_j \rangle.$$

$$\text{于是得到关系 } \langle x_i X_j \rangle = -k_B \delta_{ij}.$$

$$\text{Time reversal symmetry of } x_i: \langle x_i(0) x_j(t) \rangle = \langle x_i(t) x_j(0) \rangle \xrightarrow{t=0} \langle x_i(0) \dot{x}_j(0) \rangle = \langle \dot{x}_i(0) x_j(0) \rangle.$$

$$\text{等式两边分别代入 force-flux 关系: } \begin{cases} \langle x_i(0) \gamma_{jl} X_l(0) \rangle = -k_B \gamma_{jl} \delta_{il} = -k_B \gamma_{ji} \\ \langle \gamma_{il} X_l(0) x_j(0) \rangle = -k_B \gamma_{il} \delta_{jl} = -k_B \gamma_{ij} \end{cases}, \text{ 联立即得 } \boxed{\gamma_{ij} = \gamma_{ji}}.$$

$$\text{若将 } \dot{x}_i = \gamma_{ij} X_j \text{ 定义为 } \frac{\partial f}{\partial X_i}, \text{ 则有 } f = \frac{1}{2} \gamma_{ij} X_i X_j. \text{ 熵变化率可表述为 } \frac{dS}{dt} = X_i \dot{x}_i = X_i \frac{\partial f}{\partial X_i} = 2f$$

[Discussion] Dynamics of fluctuation $x_i = 0 \rightarrow x_i \neq 0$. 若过程可表述为 $\dot{x}_i = -\Gamma_{ik} x_k$;

1. 且 Γ_{ik} 可对角化, 则可进一步写作 decay $\dot{x}'_i = -\lambda_i x'_i$;

2. 且 Γ_{ik} antisymmetric (特征值纯虚数), 即 $\dot{x}_i = -\lambda_{ik}^A x_k$, 则动力学为 oscillatory (振荡).

0.1.2.3 Fluctuation Phenomena

0.1.2.3.1 XY Model Hamiltonian $H = -\frac{1}{2} J \sum_{\langle i, j \rangle} \langle \vec{S}_i \cdot \vec{S}_j \rangle$, 其中自旋形式为 $\vec{S}_i = (\cos \theta_i, \sin \theta_i)$.

相比一般的 Ising model 多了 θ 进行控制. 选定 \vec{R} 处一格点, 设 θ 足够小. 则 Hamiltonian 为 $\lim_{\theta \rightarrow 0} H = \frac{J}{4} \sum_{\vec{R}} \sum_{\vec{a}} [\theta(\vec{R}) - \theta(\vec{R} + \vec{a})]^2$; 使用 Fourier 变换 $\theta_{\vec{k}} = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \theta(\vec{R}) e^{-i\vec{k} \cdot \vec{R}}$,

将 Hamiltonian 写作动量 \vec{k} 形式 $H = \frac{1}{2} \sum_{\vec{k}} J_{\vec{k}} |\theta_{\vec{k}}|^2$, 其中 $J_{\vec{k}} = 2J \sum_{\vec{a}} [1 - \cos(\vec{k} \cdot \vec{a})]$.

$$\langle \vec{S}(\vec{R}) \cdot \vec{S}(\vec{0}) \rangle = \begin{cases} \exp(-\frac{T}{\alpha} \frac{R}{a}), & d=1, \text{ short range order} \\ (R/a)^{-\frac{T}{2\pi\alpha}}, & d=2, \text{ quasi-long-range order} \\ \exp[-\frac{T k_D a}{\pi^2 \alpha}] \left(1 + \frac{\pi}{4k_D R}\right), & d=3, \text{ long range order} \end{cases}$$

0.1.2.3.2 Topological Defects 拓扑缺陷: vortex. 通过矢量场分析(汇源, winding number).

[Example] 二维点电荷电场, 点电荷所在位置即 defect core. 沿着圆周电场矢量方向旋转 360 度(规定旋转方向和圆周旋转方向相同为+, 反之为-). 则 winding number 为 +1. 匀强电场则为 0. 即 $\oint d\theta = 2\pi k, k \in \mathbb{Z}$.

根据 $H \sim \int (\nabla \theta)^2$ 可知, 拓扑缺陷的激发需要能量, 并且和角度梯度有关. 设 $\frac{\partial \theta}{\partial r} = 0 \Rightarrow \nabla \theta = \frac{1}{r} \frac{\partial \theta}{\partial \phi} \hat{e}_\phi + \frac{\partial \theta}{\partial r} \hat{e}_r$,

$$\oint d\theta = \oint \nabla \theta \cdot d\vec{l} = \frac{1}{r} \frac{\partial \theta}{\partial \phi} 2\pi r = 2\pi k \Rightarrow \frac{\partial \theta}{\partial \phi} = k \Rightarrow \theta = k\phi + c_0, c_0 \text{ 使得全局相位偏移.}$$

对 $H \sim \int (\nabla \theta)^2$ 使用变分法, 即 $\delta H = 0 \Rightarrow \nabla^2 \theta = 0$

$$1. \text{ One defect: } E = \varepsilon_0(a) + \frac{K}{2} \int (\nabla \theta)^2 d^2 \vec{x} \stackrel{\theta=k\phi}{=} \varepsilon_0(a) + \pi K k^2 \ln \left(\frac{R}{a} \right)$$

2. Two defects. r 为两缺陷间距, $E_{\text{int}} = 2\pi k_1 k_2 K \ln \left(\frac{R}{r} \right)$, 可类比二维形式的 Coulomb 势能(但不完全等效), k_1, k_2 acts as charge. 温度从 0K 升高, 涨落变强, 激发出结构.

[Discussion] KPZ 方程(fluctuation/growth of interfaces). $h(\vec{x}, t)$ 为界面厚度.

$$\frac{\partial h(\vec{x}, t)}{\partial t} = \nu \nabla^2 h + \lambda (\nabla h)^2 + \eta(\vec{x}, t), \quad \eta = \text{white noise} \quad \langle \eta(\vec{x}, t) \rangle = 0$$

0.1.3 Brownian Motion

[Discussion] 墨滴在水中的扩散并不完全是布朗运动, 较大的影响因素是 flux. Brownian motion 本质是可以写出 Hamiltonian 的, 应当是一个完全确定系统. 随机性的来源: 观察的时间间隔 Δt . 散点连线后是完全无规律的. 长链分子(Polymer) 的空间结构也可类比于布朗运动, 但不完全相同(需要考虑之前分子所占体积, 亦即 Self Avoidance); 特征是 $\sqrt{\langle \vec{R}^2 \rangle} \sim L^{\frac{1}{2} + \delta}$, 其中 δ 为分子自身体积产生的.

0.1.3.1 Random walk model

$$\langle r^2 \rangle \propto t.$$

0.1.3.1.1 n steps on 1D lattice n 步后处于第 m 格的概率为

$$P_n(m) = C_n^{\frac{n+m}{2}} \left(\frac{1}{2}\right)^{\frac{n+m}{2}} \left(\frac{1}{2}\right)^{\frac{n-m}{2}}, \text{ 设 } k = \frac{n+m}{2} \text{ 检验归一化: } \sum_{m=-n}^n P_n(m) = \sum_{k=0}^n C_n^k P_L^k P_R^{n-k} = 1.$$

$$\langle m \rangle = \sum_{m=-n}^n m P_n(m) = 0, \quad \langle m^2 \rangle = \sum_{m=-n}^n m^2 P_n(m) = n \rightarrow \langle x^2 \rangle \propto t.$$

极限下取高斯分布 $\lim_{n \rightarrow \infty} P_n(m) = \frac{1}{\sqrt{2\pi n}} \exp\left(-\frac{m^2}{2n}\right)$. 使用 $\begin{cases} x = ml \\ t = n\tau \end{cases}$ 连续化为 $P(x, t)dx = \frac{dx}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$, 其中扩散系数 $D = \frac{l^2}{2t}$, 在气体中约 $(10^{-6}, 10^{-5})$ m²/s, 在液体中约 $(10^{-10}, 10^{-9})$ m²/s.

[Discussion] 从单粒子到粒子群. 设 N particles, 且均为 $\delta(x, 0)$ 分布. 经过时段 t_1 后, 则有分布函数 $P(x, t_1)dx \rightarrow n(\vec{x}, t) d\vec{x}$. 这就是扩散现象.

$$\text{连续性方程 } \frac{\partial n(\vec{x}, t)}{\partial t} = -\nabla \cdot \vec{j}(\vec{x}, t), \text{ Fick's law } \vec{j}(\vec{x}, t) = -D \nabla n(\vec{x}, t), \text{ 从而导出扩散方程 } \frac{\partial n(\vec{x}, t)}{\partial t} = D \nabla^2 n(\vec{x}, t).$$

$$\text{一维扩散方程解为 } n(\vec{x}, t) = \frac{N}{(4\pi Dt)^{d/2}} \exp\left(-\frac{|\vec{x}|^2}{4Dt}\right).$$

$$\langle x \rangle = 0, \langle x^2 \rangle = \frac{1}{N} \int_{-\infty}^{+\infty} x^2 n(\vec{x}, t) d^d \vec{x} = \boxed{2dDt}, \text{ 可见各轴分量独立.}$$

$$\langle (\Delta x)^2 \rangle \sim Dt, \text{ 纯粹依靠扩散作用在空气中传播 1m 需耗时 } t \sim \frac{\langle (\Delta x)^2 \rangle}{D} \sim 10^6 \text{ s} \approx 11 \text{ days}.$$

$$[\text{Discussion}] \sqrt{\langle (\Delta x)^2 \rangle} \sim t^\gamma. \gamma > \frac{1}{2}: \text{super diffusion}; \gamma < \frac{1}{2}: \text{sub diffusion. e.g. cloud size: } \gamma \approx \frac{3}{2}.$$

一种解释 $\gamma \neq \frac{1}{2}$ 非 normal diffusion 的思路: Levy flight(令步长为概率分布).

Galton Board. 每层都是 $X_i = \pm 1$ 的离散随机变量. 最后位置 $S_n = \sum_{i=1}^n X_i$, 处于 k 的概率 $P(S = k) = C_n^k p^k (1-p)^{n-k}$.

一般性地, 步长期望 $\langle X_i \rangle = (+l) \times p + (-l) \times (1-p) = l(2p-1)$, 最后位置期望为 $\langle S_n \rangle = \sum_{i=1}^n \langle X_i \rangle = nl(2p-1)$.

$$\langle S_n^2 \rangle = \left\langle \sum_{ij} X_i X_j \right\rangle = \sum_i \langle X_i^2 \rangle + \sum_{i \neq j} \langle X_i X_j \rangle = [l^2 p + l^2 (1-p)] n + \sum_{i \neq j} \langle X_i \rangle \langle X_j \rangle = nl^2 + n(n-1)(2p-1)^2 l^2$$

0.1.3.1.2 d -Dim Off-Lattice Random Walk 将位矢 \vec{r} 展开为基矢形式 $\vec{r} = \sum_{\alpha=1}^d x_\alpha \hat{e}_\alpha$, 其中 $x_\alpha = \sum_{i=1}^N \vec{a}_i \cdot \vec{e}_\alpha = a_i \sum_{i=1}^N \cos \theta_i$.

$$\text{根据独立性有 } \langle r^2 \rangle = \sum_{\alpha=1}^d \langle x_\alpha^2 \rangle, \text{ 各轴 } \langle x_\alpha^2 \rangle = a^2 \sum_{i=1}^N \langle \cos^2 \theta_i \rangle + a^2 \sum_{i \neq j} \langle \cos \theta_i \cos \theta_j \rangle = Na^2 \langle \cos^2 \theta \rangle.$$

对2维球面 $d\Omega = \sin \theta d\theta d\phi$, 推广至 $(d-1)$ 维球面: $d\Omega = \sin^{d-2} \theta_1 \sin^{d-3} \theta_2 \cdots \sin^1 \theta_{d-2} d\theta_1 d\theta_2 \cdots d\theta_{d-1} d\phi$.

于是归一化条件 $\int P(\{\theta\})d\Omega = 1$ 应写为

$$\int P_0(\sin \theta_1)^{d-2}(\sin \theta_2)^{d-3} \cdots (\sin \theta_{d-2})^1 d\theta_1 d\theta_2 \cdots d\theta_{d-1} = \left[\int P_0(\sin \theta_1)^{d-1} d\theta_1 \right] \times \Omega'(\theta_2, \theta_3, \cdots, \theta_{d-1}) = 1.$$

计算 $\langle \cos^2 \theta_1 \rangle = \int \cos^2 \theta_1 P_0 d\Omega = \Omega' \int_0^\pi P_0 \cos^2 \theta_1 \sin^{d-2} \theta_1 d\theta_1 = \frac{1}{d}$, 于是 $\langle r^2 \rangle = \sum_{\alpha=1}^d N a^2 \langle \cos^2 \theta \rangle = N a^2 \sum_{\alpha=1}^d \frac{1}{d} = N a^2$.

即极高 d 维下, 矢量集中在球面的 "赤道" 上, 这是因为高维下赤道附近的 "面积" 更集中. 最后所得 $\langle r^2 \rangle$ 与维数无关.

[Discussion] Random unit vector \vec{n} in n -dim space. $\vec{n} = \sum_{\alpha=1}^d n_\alpha \hat{e}_\alpha$, $\langle n_\alpha^2 \rangle = \sum_{\alpha=1}^d \langle n_\alpha^2 \rangle = d \langle n_1^2 \rangle = d \langle \cos^2 \theta \rangle = 1 \Rightarrow \langle n_1^2 \rangle = \frac{1}{d}$

0.1.3.2 Stochastic process

Static continuous random variable $X_i: \{x_0\} \xrightarrow{t_0} [x_1, x_1 + dx] \xrightarrow{t_1} [x_2, x_2 + dx] \rightarrow \cdots$

令 $P_1(x, t) = \text{Prob}[x < x(t) < x + dx]$ 为 t 时刻 $x \in (x, x + dx)$ 的概率,

$P_n(x_0, t_0; x_1, t_1; \cdots; x_{n-1}, t_{n-1}) dx_0 \cdots dx_{n-1} = \text{Prob}[x_0 < x(t_0) < x_0 + dx_0, \cdots, x_{n-1} < x(t_{n-1}) < x_{n-1} + dx_{n-1}]$

定义 **Transition Probability**: $\text{Prob}[(x_0, t_0) \rightarrow (x_1, t_1)] dx_1 = \frac{P_2(x_0, t_0; x_1, t_1) dx_1}{P_1(x_0, t_0)}$.

该语言下的关联函数为 $\langle x_0(t_0) x_1(t_1) \rangle = \int x_0(t_0) x_1(t_1) P_n(x_0, t_0; x_1, t_1, \cdots) \prod_{k=0}^{n-1} dx_k$.

0.1.3.3 Smoluchowski's Approach

从 x_0 出发, 经过 n 步后到达 x 的概率为 $\text{Prob}(x_0 \xrightarrow{n \text{ steps}} x) = P_n(x_0|x)$, 可写作递推形式 ($n \geq 1$) $\sum_{z=-\infty}^{+\infty} P_{n-1}(x_0|z) P_1(z|x)$,

即从 x_0 出发, 经过 $n-1$ 步到达任意位置 z , 再经过 1 步到达 x . 对于位置 z , 要求

$$P_1(z|x) = \frac{1}{2} (\delta_{z, x+1} + \delta_{z, x-1}), P_0(z|x) = \delta_{z, x}, \text{代入递推得 } P_n(x_0|x) = \frac{1}{2} P_{n-1}(x_0|x-1) + \frac{1}{2} P_{n-1}(x_0|x+1).$$

构造辅助函数 $Q_n(\xi) \equiv \sum_{x=-\infty}^{+\infty} P_n(x_0|x) \xi^{x-x_0}$, 将其递推化:

$$Q_n(\xi) = \sum_{x=-\infty}^{+\infty} \left[\frac{1}{2} P_n(x_0|x-1) \xi^{x-x_0} + \frac{1}{2} P_n(x_0|x+1) \xi^{x-x_0} \right] = \frac{1}{2} \xi Q_{n-1}(\xi) + \frac{1}{2} \xi^{-1} Q_{n-1}(\xi) = \frac{1}{2} (\xi + \xi^{-1}) Q_{n-1}(\xi)$$

代入初始条件 $Q_0(\xi) = 1$ 解得 $Q_n(\xi) = \left(\frac{1}{2}\right)^n \sum_{|x-x_0| \leq n} C_n^{[n+(x-x_0)]/2} \xi^{x-x_0}$.

通过同构可知 $P_n(x_0|x) = \left(\frac{1}{2}\right)^n C_n^{[n+(x-x_0)]/2}$, 其中 $|x-x_0| \leq n$.

0.1.3.4 State of System(Markov Procss, History-Independent)

态: $n = 1, 2, 3, \cdots, M$; 态为 n 的概率: $y(n)$; 时间: $t = s\tau, s = 0, 1, 2, \cdots$ 系统在 $t = s\tau$ 时刻处于状态 n 的概率: $P(n, s)$.

Markov Chain: $P(n, s) \rightarrow P(n, s+1) \rightarrow P(n, s+2) \rightarrow \cdots$, 即依赖于前一时刻的状态, 和历史无关.

前文所谈则是 history-dependent $P(n, s) = f[P(n, s-1), P(n, s-2), \cdots, P(n, 0)]$.

定义 **Conditional Prob**: $P(n_1, s_1|n_2, s_2)$. 则从 s_0 时刻的状态 n_0 迁移至 (s_0+1) 时刻的状态 n 的概率为

$$P(n_0, s_0|n, s+1) = \sum_{m=1}^M P(n_0, s_0|m, s) P(m, s|n, s+1) = \sum_{m=1}^M P(n_0, s_0|m, s) Q_{mn}(s).$$

那么系统在 s 时刻处于状态 n 的概率为 $P(n, s) = \sum_{m=1}^M P(m, s-1) P(m, s-1|n, s)$, 重复该递推直至化为形式:

$$\begin{aligned} P(n, s) &= \sum_{m, m_1, m_2, \cdots, m_{s-1}} P(m, 0) P(m, 0|m_1, 1) P(m_1, 1|m_2, 2) \cdots P(m_{s-1}, s-1|n, s) \\ &= \sum_{m, m_1, m_2, \cdots, m_{s-1}} P(m, 0) Q_{mm_1}(1) Q_{m_1 m_2}(2) \cdots Q_{m_{s-1} n}(s-1) = \sum_m P(m, 0) (Q^S)_{mn}, P(m, s_0|n, s) = (Q^{s-s_0})_{mn} \end{aligned}$$

其中运用了类似于矩阵乘法 $\sum_j A_{ij} B_{jk} = (AB)_{ik}$.

[Example] N -ring $[P(N+1) \equiv P(1)]$. 将 Random Walk 近似为 Markov Process. $Q_{n,n+1} = Q_{n+1,n} = \frac{1}{2}, n \in \mathbb{N}$.

$$P(n, s) = P(n-1, s-1)Q_{n-1,n} + P(n+1, s-1)Q_{n+1,n} = \frac{1}{2} [P(n-1, s-1) + P(n+1, s-1)]$$

$$\text{Define } \delta P(n, s) \equiv P(n, s) - P(n, s-1) = P(n-1, s-1)Q_{n-1,n} + P(n+1, s-1)Q_{n+1,n} - P(n, s-1) \\ = \frac{1}{2} [P(n-1, s-1) + P(n+1, s-1) - 2P(n, s-1)]$$

Let t be continuous: $\tau \frac{dP_n(t)}{dt} = \frac{1}{2} [P_{n-1}(t) + P_{n+1}(t) - 2P_n(t)]$; Then let n be continuous:

$$\tau \frac{dP_n(t)}{dt} = \frac{a^2}{2} \frac{P_{n-1}(t) + P_{n+1}(t) - 2P_n(t)}{a^2} \Rightarrow \frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}, \quad D \sim \frac{a^2}{2\tau}. \text{ 正是 Feynmann Kac formula.}$$

0.1.3.5 Langevin's Theory

忽略粒子间关联(flux). Based on force & dynamics, equation of motion. $x(t + \delta t) - x(t) = f(t)\delta t \Rightarrow \dot{x}(t) = f$, random force.

$$\text{介观(mesosopic) level: } M \frac{d\vec{v}}{dt} = -\frac{\vec{v}}{B} + \vec{F}(t) \cdot f_{\text{stokes}} = f\left(\frac{\text{半径}}{a}, \frac{\text{粘度}}{\eta}, \frac{\text{速度}}{v}, \frac{\text{质量}}{m}\right) = 6\pi\eta a v \Rightarrow B = \frac{1}{6\pi\eta a}$$

$$\text{随机力满足 } \langle F(t) \rangle = 0, \quad \langle \vec{F}(t) \vec{F}(t') \rangle = C_1 \delta(t - t').$$

[Discussion] 回忆 Ideal gas: $\langle \delta n(x) \delta n(x') \rangle = c \delta(x - x')$, 形式与随机力的二阶矩相似.

只有一阶矩和二阶矩非零, 则可使用 Gaussian distribution 描述.

$$[\text{Example}] \text{ Irregular part(noise) of collective electron motion in circuit. } L \frac{dI}{dt} = -RI + V(t)$$

两边同乘 \vec{v} 且求期望 $\langle \cdot \rangle$, 有 $\frac{d}{dt} \left(\frac{1}{2} M \langle v(t)^2 \rangle \right) + M\tau^{-1} \langle v(t)^2 \rangle = \langle v(t)F(t) \rangle$, 即得到动能形式的 Langevin 方程.

$$\frac{dK(t)}{dt} = \langle v(t)F(t) \rangle - \frac{2}{\tau} K(t). \text{ 其中 } \tau = MB. \text{ 平衡态: } \frac{dK(t)}{dt} = 0 \Rightarrow \langle v(t)F(t) \rangle = \frac{2}{\tau} K_0 = \frac{2}{\tau} \cdot \frac{d}{2} k_B T, d \text{ 为维数.}$$

$$\text{在 } d=1 \text{ 情况下, 定义 } v(t) = e^{-t/\tau} u(t), \text{ 其中 } \tau = MB. \text{ 将其代入方程后解得 } v(t) = \frac{1}{M} \int_0^t dt' e^{-(t-t')/\tau} F(t').$$

$$\text{那么 } \langle v(t)F(t) \rangle = \frac{C_1}{2M}, \text{ 其中 } C_1 \text{ 来自于 } \langle \vec{F}(t) \vec{F}(t') \rangle = C_1 \delta(t - t').$$

$$\text{平衡态: } \frac{C_1}{2M} = \frac{2}{\tau} \cdot \frac{1}{2} k_B T \Rightarrow C_1 = \frac{2k_B T}{B}, \text{ Fluctuation-Dissipation Theorem(涨落耗散定理).}$$

0.1.3.5.1 Analysis of Particle Postion 检查 Langevin 语言下的 $\langle r^2(t) \rangle = 2dDt$ 是否仍然满足.

$$\text{方程写作 } \frac{d\vec{v}}{dt} = -\frac{\vec{v}}{\tau} + \vec{A}(t), \text{ 其中 } \vec{A}(t) = \frac{\vec{F}}{M}. \text{ 因为 } \frac{d^2 r^2}{dt^2} = 2v^2 + 2\vec{r} \cdot \frac{d\vec{r}}{dt}, \text{ 等号两边同乘 } \vec{r} \text{ 后求系综平均 } \langle \cdot \rangle, \text{ 有}$$

$$\frac{d^2}{dt^2} r^2 + \frac{1}{\tau} \frac{d}{dt} r^2 = 2v^2 + \vec{r} \cdot \vec{A} \Rightarrow \frac{d^2}{dt^2} \langle r^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle r^2 \rangle + 2 \langle v^2 \rangle + \langle \vec{r} \cdot \vec{A} \rangle, \text{ 因为 } \vec{A} \text{ 和 } \vec{r} \text{ 无关, 所以该期望项为 } 0.$$

$$\text{三维动能均值为 } \frac{1}{2} M \langle v^2 \rangle = \frac{1}{2} k_B T \times 3, \text{ 解得位移方均 } \langle r^2(t) \rangle = \frac{6k_B T \tau^2}{M} \left[\frac{t}{\tau} - (1 - e^{-t/\tau}) \right]$$

$$1. t \ll \tau, \langle r^2(t) \rangle = \frac{3k_B T}{M} t^2 = \langle v^2 \rangle t^2, \text{ 即 Ballistic motion(弹道运动). 然而 Langevin 方程在 } t \rightarrow 0 \text{ 时有效性存疑.}$$

$$2. t \gg \tau, \langle r^2(t) \rangle = \frac{6k_B T \tau}{M} t = 6Bk_B T t \stackrel{d=3}{=} 6Dt \Rightarrow D = Bk_B T, \forall d, \text{ another form of Fluctuation-Dissipation Theorem, or Einstein's Relation.}$$

0.1.3.5.2 Analysis of Particle Velocity $\vec{v}(t)$

$$\langle v^2(t) \rangle = \left\langle \left[v(0) + \frac{1}{M} \int_0^t dt' e^{-(t-t')/\tau} F(t') \right]^2 \right\rangle = v^2(0) e^{-2t/\tau} + \frac{C}{M^2} \frac{\tau}{2} (1 - e^{-2t/\tau}), \text{ 其中带入了 } v(t) \text{ 表达式.}$$

Requires $\frac{1}{2}M \langle v^2(t) \rangle = \frac{3}{2}k_B T \Rightarrow C = \frac{6k_B T}{B}$. Let $x \equiv \langle v^2(t) \rangle - \langle v^2(\infty) \rangle$, 则 $\frac{d}{dt}x = -\frac{2}{\tau}x$

[Discussion] 速度发散 $\lim_{\delta t \rightarrow 0} \frac{\langle |x(t+\delta t) - x(t)| \rangle}{\delta t} \sim \lim_{\delta t \rightarrow 0} \frac{(\delta t)^{\frac{1}{2}}}{\delta t} \rightarrow \infty$. Solution:

1. Stochastic Differential Equation 严格化;

2. 从场的观点出发. 将随机性转移至概率分布函数 (particle-based approach \rightarrow field-based approach). 场 $f(x, t)$, 则位置为 $\rho(x) = q\delta(x - x_0)$, $\int \rho(x)dx = q$. 如果是匀速直线运动, 则 $f(x, t) = \delta(x - vt)$. 若粒子 $x \rightarrow x + \delta x$, 则 $f(x, t) = \langle \delta[x - x(t)] \rangle$, 即场与粒子观点的转换.

约束 $\sum_i n_i = N$. 态迁移率 (transition rate) 为 $\frac{n_i(t+\delta t) - n_i(t)}{\delta t} = -\sum_{j \neq i} n_i(t)P_{i \rightarrow j} + \sum_{j \neq i} n_j(t)P_{j \rightarrow i}$, 这类方程被称为

Master equation.

1. 假定为 Markov Process;

2. 粒子数守恒: $\frac{1}{\delta t} \left[\sum_i n_i(t+\delta t) - \sum_i n_i \right] = \sum_i \left(\sum_{j \neq i} n_j P_{j \rightarrow i} - \sum_{i \neq j} n_i P_{i \rightarrow j} \right) = 0$.

[Application] 2-state system. $n_+ : |+\rangle$, $n_- : |-\rangle$. 迁移速率 ω_{\pm} . 平衡态: $\frac{n_+^0}{n_-^0} = \frac{\omega_+}{\omega_-}$

$$\frac{dn_+}{dt} = -n_+\omega_- + n_-\omega_+, \quad \frac{dn_-}{dt} = -n_-\omega_+ + n_+\omega_-$$

Relaxation dynamics: 设 $n(t) = n_- - n_+$. 则微分方程化为 $\frac{dn(t)}{dt} = \frac{1}{\tau} [n(t) - n^0]$, 其中 $\tau = \frac{1}{\omega_+ + \omega_-}$, $n^0 = n_-^0 - n_+^0$.

[Discussion] 连续变量 Master Equation. 前提: 1. 归一化条件: $\int_{-\infty}^{+\infty} f(x, t)dx = 1$;

2. 概率函数定义: $f(x, t)dx$ 是粒子在 t 时刻处于 $[x, x+dx]$ 的概率.

3. 动力学: $\frac{\partial f(x, t)}{\partial t} = \int_{-\infty}^{+\infty} [-f(x, t)W(x, x') + f(x', t)W(x', x)]dx'$, $W(x, x')dx'$ 是 $x \rightarrow x'$ 的迁移概率.

以上动力学方程可改写为 $\frac{\partial}{\partial t} f(x, t) = -\frac{\partial}{\partial x} (\mu_1(x)f(x, t)) + \frac{1}{2} \frac{\partial^2}{\partial x^2} [\mu_2(x)f(x, t)]$, 即 **Fokker-Planck** 方程.

其中矩系数 $\mu_1(x) = \int_{-\infty}^{+\infty} d\xi \xi W(x, \xi) = \frac{\langle \delta x \rangle_{\delta t}}{\delta t} = \langle v_x \rangle$, $\mu_2(x) = \int_{-\infty}^{+\infty} d\xi \xi^2 W(x, \xi) = \frac{\langle (\delta x)^2 \rangle_{\delta t}}{\delta t}$.

写作概率流形式: $\frac{\partial}{\partial t} f(x, t) = -\frac{\partial}{\partial x} j(x, t)$, $j(x, t) = \mu_1(x)f(x, t) - \frac{1}{2} \frac{\partial}{\partial x} [\mu_2(x)f(x, t)]$.

[Example] 粘液中振子. 矩系数信息为 $\mu_1(x) = -\lambda Bx$, $\mu_2(x) = \frac{\langle \delta x^2 \rangle}{\delta t} = 2Bk_B T$

Fokker-Planck 方程为 $\frac{\partial f(x, t)}{\partial t} = \lambda B \frac{\partial}{\partial x} (x f(x, t)) + Bk_B T \frac{\partial^2 f(x, t)}{\partial x^2}$

平衡态解: $\lambda B \frac{\partial}{\partial x} (x f(x, \infty)) + Bk_B T \frac{\partial^2 f(x, \infty)}{\partial x^2} = 0 \Rightarrow f(x, \infty) = \left(\frac{\lambda}{2\pi k_B T} \right)^{\frac{1}{2}} e^{-\frac{\lambda x^2}{2k_B T}}$.

$$\langle x \rangle = 0, \quad \langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 f(x, \infty) dx = \frac{k_B T}{\lambda}$$

设初始为 δx 分布, 则一般含时解为 $f(x, t) = \left[\frac{\lambda}{2\pi k_B T (1 - e^{-2\lambda B t})} \right]^{\frac{1}{2}} \exp \left[-\frac{\lambda x^2}{2k_B T (1 - e^{-2\lambda B t})} \right]$.

该模型对应的 Langevin 方程为 $\eta \frac{dx}{dt} = -U'(x) + F(t)$, 其中 $U(x) = \frac{1}{2} \lambda x^2$, $U'(x) = \lambda x$ 为势能的导数.

0.1.3.5.3 Time Correlation of Velocity $v(t)$. 令时间变量 u_1, u_2 .

则位移方均 $\langle x^2(t) \rangle = \left\langle \left(\int_0^t du_1 v(u_1) \right) \left(\int_0^t du_2 v(u_2) \right) \right\rangle = \int_0^t du_1 \int_0^t du_2 \langle v(u_1) v(u_2) \rangle$. 利用微积分性质 $\frac{d}{dt} \int_0^t f(u) du = f(t)$

得到 $\frac{d \langle x^2(t) \rangle}{dt} = 2 \int_0^t du \langle v(u) v(t) \rangle \stackrel{\text{time reversal symmetry}}{=} 2 \int_{-t}^0 du \langle v(u) v(0) \rangle = 2 \int_0^t du \langle v(u) v(0) \rangle = 2D$

观察对比得到 $\int_0^t \langle v(u) v(0) \rangle du = D t$.

$$\frac{\partial f(x,t)}{\partial t} = \frac{1}{\eta} \frac{\partial}{\partial x} (U'(x)f(x,t)) + \frac{k_B T}{\eta} \frac{\partial^2}{\partial x^2} f(x,t)$$

0.1.3.5.4 Fourier Transformation of Langevin Equation .

约化 Langevin 方程形为 $\frac{dv(t)}{dt} = -\frac{v(t)}{\tau} + A(t)$, 其中 $\langle A(t)A(t') \rangle = C_1' \delta(t-t')$.

速度变换为 $\tilde{v}(\omega) = \frac{\tilde{A}(\omega)}{-i\omega + \tau^{-1}}$, 约化随机力变换后满足 $\langle \tilde{A}(\omega)\tilde{A}(\omega') \rangle = 2\pi C_1' \delta(\omega + \omega')$

频域内速度关联为 $\langle \tilde{v}^*(\omega)\tilde{v}(\omega') \rangle = S(\omega)\delta(\omega + \omega')$, 其中 $S(\omega) = \frac{2\pi C_1}{\tau^{-2} + \omega^2}$. 令速度关联在 ω' 域积分,

得到 $\langle \tilde{v}^*(\omega)\tilde{v}(t=0) \rangle = S(\omega)$; 再令其在 ω 域积分, 得到 $\langle v(t)v(0) \rangle = \int_{-\infty}^{+\infty} S(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}$.

令自由参数 $t=0$, 则 $\langle v(0)^2 \rangle = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} S(\omega)$; 根据对称性, $S(0) = 2 \int_0^{+\infty} dt \langle v(t)v(0) \rangle = \frac{2\pi C_1}{\tau^{-2}} = 2D$.