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 $\to$ 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. $\dfrac{\partial n}{\partial x} \to$ 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 fluactuation of density ρ: grow/decay.
$G = -\alpha|\overset{\uparrow}{\Delta\mu}|R^3 + \beta\sigma \overset{\downarrow}{\cdot} R^2$. 需要足够大的凝结核.

0.1.1.1 Static Thermodynamic Analysis

研究发生 $\overset{\text{equilibrium}}{f_0} \to \overset{\text{fluactuated}}{f_0 + \delta f}$ 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

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

于是迁移概率为 $P_1 \propto \exp\left(-\dfrac{\Delta E - T\Delta S + p\Delta V}{k_B T}\right)$. 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:

$$\Delta E(S,V) = \overset{T}{\left(\frac{\partial E}{\partial S}\right)_0} \Delta S + \overset{-p}{\left(\frac{\partial E}{\partial V}\right)_0} \Delta V + \frac{1}{2}\left[\left(\frac{\partial^2 E}{\partial S^2}\right)_0 (\Delta S)^2 + 2\left(\frac{\partial^2 E}{\partial S \partial V}\right)_0 \Delta S \Delta V + \left(\frac{\partial^2 E}{\partial V^2}\right)_0 (\Delta V)^2\right] + \cdots$$

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

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

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

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

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

计算涨落: $\langle(\Delta T)^2\rangle = \dfrac{\displaystyle\int (\Delta T)^2 P(\Delta T, \Delta V)\mathrm{d}(\Delta T)}{\displaystyle\int P(\Delta T, \Delta V)\mathrm{d}(\Delta T)} = \dfrac{k_B T^2}{C_v} \propto \dfrac{1}{V}, \quad \langle(\Delta V)^2\rangle = k_B T k_T V \propto V$

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

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

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

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

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

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

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

0.1.1.2 Time Analysis of Fluctuations

$x_0 \to x_f(t)$. 视涨落为含时信号 $A(t)$. 时间平均 $\langle A\rangle = \dfrac{1}{T}\displaystyle\int_0^T A(t)\mathrm{d}t$; 定义时间关联函数 $\phi(t) = \dfrac{1}{T}\displaystyle\int_0^T \delta A(u)\delta A(u+t)\mathrm{d}u$.
假定 ergodic(各态历经), 时间平均化为系综平均: $\phi(t_1,t_2) \overset{\text{ensemble}}{=} \langle\delta A(t_1)\delta A(t_2)\rangle$. 时间平移不变性: $\phi(t_1,t_2)\to\phi(t_2-t_1)$.
时间平移不变性 in Joint probability $P_n(x_1,t_1;x_2,t_2;\cdots;x_n,t_n) = P_n(x_1,t_1+\Delta t;x_2,t_2+\Delta t;\cdots;x_n,t_n+\Delta t)$

[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 $\dfrac{1}{2}L\langle\theta^2\rangle = \dfrac{1}{2}k_BT \Rightarrow \langle\theta^2\rangle = \dfrac{k_BT}{L}$. (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.

$\widetilde{x}(\omega) = \displaystyle\int_{-\infty}^{+\infty} x(t)e^{i\omega t}\mathrm{d}t, \quad x(t) = \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{+\infty}\widetilde{x}(\omega)e^{-i\omega t}\mathrm{d}\omega$

对 statistically stationary signal(稳态信号), 关联函数 $\phi(t'-t) = \langle x(t')x(t)\rangle = \displaystyle\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\langle\widetilde{x}(\omega)\widetilde{x}(\omega')\rangle e^{-i\left(\omega t+\omega' t'\right)}\mathrm{d}\omega\mathrm{d}\omega'$,
可推断频域内关联函数为 $\langle\widetilde{x}(\omega)\widetilde{x}(\omega')\rangle = 2\pi\left[\widetilde{x^2}(\omega)\right]\delta(\omega-\omega')$, 那么变换回时域形式: $\phi(t) = \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{+\infty}\widetilde{x^2}(\omega)e^{-i\omega t}\mathrm{d}\omega$,
其中 $\widetilde{x^2}(\omega)$ 是 $x^2(t)$ 的傅里叶变换. 令 $\widetilde{x^2}(\omega)$ 对频域积分并归一化, 得到
$\phi(0) = \left\langle\widetilde{x^2}(\omega)\right\rangle = \displaystyle\int_{-\infty}^{+\infty}\widetilde{x^2}(\omega)\dfrac{\mathrm{d}\omega}{2\pi} = 2\int_0^{+\infty}\widetilde{x^2}(\omega)\dfrac{\mathrm{d}\omega}{2\pi}$, 即得出 **Wiener-Khinchin theorem**(for random process & statistically stationary signal).

[Example] $\phi(t) = \langle x(0)x(t)\rangle = \langle x(0)^2\rangle e^{-\lambda|t|}$. $\widetilde{x^2}(\omega) = \langle x(0)^2\rangle\dfrac{2\lambda}{\omega^2+\lambda^2}$, $\langle x^2(t)\rangle = \left\langle 2\displaystyle\int_0^{+\infty}\widetilde{x^2}(\omega)\dfrac{\mathrm{d}\omega}{2\pi}\right\rangle$,
$\displaystyle\int_0^{+\infty}\dfrac{\lambda}{\omega^2+\lambda^2}\mathrm{d}\omega = \int_0^{+\infty}\dfrac{1}{\omega'^2+1}\mathrm{d}\omega' = \dfrac{\pi}{2} \Rightarrow \langle x^2(t)\rangle = \langle x^2(0)\rangle$.

0.1.2 Relaxation of Weakly Non-equilibrium State

形如 $\dfrac{\mathrm{d}x(t)}{\mathrm{d}t} = -\lambda x(t) \Rightarrow x(t) = x(0)e^{-\lambda t}$ 的(描述性) Relaxation equation. 物质输运和热量输运是耦合的, 则
$\langle x_i(t)\rangle \Rightarrow \dfrac{\mathrm{d}x_i(t)}{\mathrm{d}t} = -\displaystyle\sum_k\lambda_{ik}x_k(t)$. 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 $X_i = \dfrac{\partial S}{\partial x_i}$ 以引入熵 $S(x_1,x_2,\cdots,x_n)$. $\dot{x}_i(t), X_i(t)$ 分别为 flux 和 force.
Taylor 展开: $S(x_i) = \overset{\text{equilibrium}}{S(0)} + \cancel{\left(\dfrac{\partial S}{\partial x_i}\right)_{x_i=0}x_i} + \dfrac{1}{2}\left(\dfrac{\partial^2 S}{\partial x_i\partial x_j}\right)_{x_i=x_j=0}x_ix_j + \cdots = S(0) - \dfrac{1}{2}\beta_{ij}x_ix_j$, 其中 $\beta_{ij} = \beta_{ji}$.
代入展开式: $X_i = \dfrac{\partial S}{\partial x_i} = \dfrac{\partial}{\partial x_i}\left[S(0) - \dfrac{1}{2}\beta_{jk}x_jx_k\right] = -\dfrac{\beta_{jk}}{2}\dfrac{\partial}{\partial x_i}(x_jx_k) = -\dfrac{\beta_{jk}}{2}(\delta_{ij}x_k + x_j\delta_{ik}) = -\beta_{ik}x_k$.
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: $S = \dfrac{1}{2}X_ix_i$,
变化率为 $\dfrac{\mathrm{d}S}{\mathrm{d}t} = \dfrac{1}{2}\left(\dot{X}_ix_i + X_i\dot{x}_i\right)$. 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 $\dot{S} = X_i\dot{x}_i = \dfrac{\partial S}{\partial x_i}\dot{x}_i$, 显然就是链式求导规则.

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

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

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

平衡态时, $\langle\dot{x}_i\rangle=0,\langle x_i\rangle=\widetilde{x}_i$. $\langle x_iX_j\rangle=\underset{x_i}{\mathrm{Tr}}\left[x_iX_jAe^{\Delta S(x_1,x_2,\cdots,x_n)/k_B}\right]=\underset{x_i}{\mathrm{Tr}}\left[x_iX_jAe^{\frac{1}{2k_B}\beta_{ij}(x_i-\widetilde{x}_i)(x_j-\widetilde{x}_j)}\right]$

$$\frac{\partial\langle x_i\rangle}{\partial\widetilde{x}_j}=\delta_{ij}=\frac{\partial}{\partial\widetilde{x}_j}\underset{x_i}{\mathrm{Tr}}\left[x_iAe^{-\frac{1}{2k_B}\beta_{ij}(x_i-\widetilde{x}_i)(x_j-\widetilde{x}_j)}\right]=\underset{x_i}{\mathrm{Tr}}\left[x_i\frac{\overset{-X_j}{\beta_{ij}x_i}}{k_B}Ae^{-\frac{1}{2k_B}\beta_{ij}(x_i-\widetilde{x}_i)(x_j-\widetilde{x}_j)}\right]=-\frac{1}{k_B}\langle x_ix_j\rangle.$$

于是得到关系 $\boxed{\langle x_iX_j\rangle=-k_B\delta_{ij}}$.

Time reversal symmetry of x_i : $\overset{\phi_{ij}(-t)}{\langle x_i(0)x_j(t)\rangle}=\overset{\phi_{ij}(t)}{\langle x_i(t)x_j(0)\rangle}\overset{t=0}{\Longrightarrow}\langle x_i(0)\dot{x}_j(0)\rangle=\langle\dot{x}_i(0)x_j(0)\rangle$.

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

若将 $\dot{x}_i=\gamma_{ij}X_j$ 定义为 $\dfrac{\partial f}{\partial X_i}$, 则有 $f=\dfrac{1}{2}\gamma_{ij}X_iX_j$. 熵变化率可表述为 $\dfrac{\mathrm{d}S}{\mathrm{d}t}=X_i\dot{x}_i=X_i\dfrac{\partial f}{\partial X_i}=2f$

[Discussion] Dynamics of fluactuation $x_i=0\to x_i\neq 0$. 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 $\dot{x}_i'=-\lambda_ix_i'$;
2. 且 Γ_{ik} antisymmetric(特征值纯虚数), 即 $\dot{x}_i=-\lambda_{ik}^Ax_k$, 则动力学为 oscillatory(振荡).

0.1.2.3 Fluactuation Phenomena

0.1.2.3.1 XY Model Hamiltonian $H=-\frac{1}{2}J\sum_{\langle i,j\rangle}\left\langle\vec{S}_i\cdot\vec{S}_j\right\rangle$, 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

$\lim\limits_{\theta\to 0}H=\dfrac{J}{4}\sum\limits_{\vec{R}}\sum\limits_{\vec{a}}\left[\theta\left(\vec{R}\right)-\theta\left(\vec{R}+\vec{a}\right)\right]^2$; 使用 Fourier 变换 $\theta_{\vec{k}}=\dfrac{1}{\sqrt{N}}\sum\limits_{\vec{R}}\theta\left(\vec{R}\right)e^{-i\vec{k}\cdot\vec{R}}$,

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

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

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 $\oint\mathrm{d}\theta=2\pi k,k\in\mathbb{Z}$.

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 $\dfrac{\partial\theta}{\partial r}=0\Rightarrow\nabla\theta=\dfrac{1}{r}\dfrac{\partial\theta}{\partial\phi}\hat{e}_\phi+\cancel{\dfrac{\partial\theta}{\partial r}}\hat{e}_r$,,

$\oint\mathrm{d}\theta=\oint\nabla\theta\cdot\mathrm{d}\vec{l}=\dfrac{1}{r}\dfrac{\partial\theta}{\partial\phi}2\pi r=2\pi k\Rightarrow\dfrac{\partial\theta}{\partial\phi}=k\Rightarrow\theta=k\phi+c_0$, c_0 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. One defect: $E=\overset{\text{core energy}}{\varepsilon_0(a)}+\dfrac{K}{2}\int(\nabla\theta)^2\mathrm{d}^2\vec{x}\overset{\theta=k\phi}{=}\varepsilon_0(a)+\pi Kk^2\ln\left(\dfrac{R}{a}\right)$

2. Two defects. r 为两缺陷间距, $E_{\text{int}}=2\pi k_1k_2K\ln\left(\dfrac{R}{r}\right)$, 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(fluactuation/growth of interfaces). $h\left(\vec{x},t\right)$ 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 $\sqrt{\left\langle \vec{R}^2\right\rangle}\sim L^{\frac{1}{2}+\delta}$, 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

$P_n(m)\overset{x=ml}{=}C_n^{\frac{n+m}{2}}\left(\frac{1}{2}\right)^{\frac{n+m}{2}}\left(\frac{1}{2}\right)^{\frac{n-m}{2}}$, 设 $k=\dfrac{n+m}{2}$ 检验归一化: $\sum\limits_{m=-n}^{n}P_n(m)=\sum\limits_{k=0}^{n}C_n^kP_L^kP_R^{n-k}=1$.

$\langle m\rangle=\sum\limits_{m=-n}^{n}mP_n(m)=0,\quad \langle m^2\rangle=\sum\limits_{m=-n}^{n}m^2P_n(m)=n\to\langle x^2\rangle\propto t.$

极限下取高斯分布 $\lim\limits_{n\to\infty}P_n(m)=\dfrac{1}{\sqrt{2\pi n}}\exp\left(-\dfrac{m^2}{2n}\right)$. 使用 $\begin{cases}x=ml\\ t=n\tau\end{cases}$ 连续化为 $P(x,t)\mathrm{d}x=\dfrac{\mathrm{d}x}{\sqrt{4\pi Dt}}\exp\left(-\dfrac{x^2}{4Dt}\right)$, 其中扩散系数 $D=\dfrac{l^2}{2t}$, 在气体中约 $\left(10^{-6},10^{-5}\right)$ m^2/s, 在液体中约 $\left(10^{-10},10^{-9}\right)$ m^2/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 $P(x,t_1)\mathrm{d}x\to n(\vec{x},t)\,\mathrm{d}x$. 这就是扩散现象.

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

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

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

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

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

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

Galton Board. 每层都是 $X_i=\pm1$ 的离散随机变量. 最后位置 $S_n=\sum\limits_{i=1}^{n}X_i$, 处于 k 的概率 $P(S=k)=C_n^kp^k(1-p)^k$.

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 $\langle S_n\rangle=\sum\limits_{i=1}^{n}\langle X_i\rangle=nl(2p-1)$.

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

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

根据独立性有 $\langle r^2\rangle=\sum\limits_{\alpha=1}^{d}\langle x_\alpha^2\rangle$, 各轴 $\langle x_\alpha^2\rangle=a^2\sum\limits_{i=1}\langle\cos\theta_i\rangle+\cancel{a^2\sum\limits_{i\neq j}^{\langle\cos\theta_i\rangle=0}\langle\cos\theta_i\cos\theta_j\rangle}=Na^2\langle\cos^2\theta\rangle$.

对2维球面 $\mathrm{d}\Omega=\sin\theta\overset{[0,\pi]}{\mathrm{d}\theta}\overset{[0,2\pi]}{\mathrm{d}\phi}$, 推广至 $(d-1)$ 维球面: $\mathrm{d}\Omega=\sin^{d-2}\theta_1\sin^{d-3}\theta_2\cdots\sin^1\theta_{d-2}\mathrm{d}\theta_1\mathrm{d}\theta_2\cdots\mathrm{d}\theta_{d-1}\mathrm{d}\phi$.

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

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

计算 $\left\langle\cos^2\theta_1\right\rangle=\int\cos^2\theta_1P_0\mathrm{d}\Omega=\Omega'\int_0^\pi P_0\cos^2\theta_1\sin^{d-2}\theta_1\mathrm{d}\theta_1=\frac{1}{d}$, 于是 $\left\langle r^2\right\rangle=\sum_{\alpha=1}^{d}Na^2\left\langle\cos^2\theta\right\rangle=Na^2\sum_{\alpha=1}^{d}\frac{1}{d}=Na^2$.
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 $\left\langle r^2\right\rangle$ 与维数无关.

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

0.1.3.2 Stochastic process

Static continuous random variable $X_i:\quad \overset{t_0}{\{x_0\}}\to\overset{t_1}{[x_1,x_1+\mathrm{d}x]}\to\overset{t_2}{[x_2,x_2+\mathrm{d}x]}\to\cdots$
令 $P_1(x,t)=\text{Prob}\left[x<x(t)<x+\mathrm{d}x\right]$ 为 t 时刻 $x\in(x,x+\mathrm{d}x)$ 的概率,
$P_n(x_0,t_0;x_1,t_1;\cdots;x_{n-1},t_{n-1})\mathrm{d}x_0\cdots\mathrm{d}x_{n-1}=\text{Prob}\left[x_0<x(t_0)<x_0+\mathrm{d}x_0,\cdots,x_{n-1}<x(t_{n-1})<x_{n-1}+\mathrm{d}x_{n-1}\right]$
定义 **Transition Probability**: $\text{Prob}\left[(x_0,t_0)\to(x_1,t_1)\right]\mathrm{d}x_1=\dfrac{P_2(x_0,t_0;x_1,t_1)\mathrm{d}x_1}{P_1(x_0,t_0)}$.

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

0.1.3.3 Smoluchowski's Approach

从 x_0 出发, 经过 n 步后到达 x 的概率为 $\text{Prob}\left(x_0\xrightarrow{n\text{ steps}}x\right)=P_n(x_0|x)$, 可写作递推形式($n\geq1$) $\sum_{z=-\infty}^{+\infty}P_{n-1}(x_0|z)P_1(z|x)$,
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
$P_1(z|x)=\frac{1}{2}\left(\delta_{z,x+1}+\delta_{z,x-1}\right),P_0(z|x)=\delta_{z,x}$, 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:

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

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 $P_n(x_0|x)=\left(\frac{1}{2}\right)^nC_n^{[n+(x-x_0)]/2}$, 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: $P(n,s)\to P(n,s+1)\to P(n,s+2)\to\cdots$, 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

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

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

$$\begin{aligned}P(n,s)&=\sum_{m,m_1,m_2,\cdots,m_{s-1}}\overset{m\to m_1\to m_2\to\cdots\to m_{s-1}}{P(m,0)P(m,0|m_1,1)P(m_1,1|m_2,2)\cdots P(m_{s-1},s-1|n,s)}\\&=\sum_{m,m_1,m_2,\cdots,m_{s-1}}P(m,0)Q_{mm_1}(1)Q_{m_1m_2}(2)\cdots Q_{m_{s-1}n}(s-1)=\sum_{m}P(m,0)\left(Q^S\right)_{mn},P(m,s_0|n,s)=\left(Q^{s-s_0}\right)_{mn}\end{aligned}$$

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. $Q_{n,n+1} = Q_{n+1,n} = \frac{1}{2}, n \in \mathbb{N}$.

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

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: $\tau\frac{\mathrm{d}P_n(t)}{\mathrm{d}t} = \frac{1}{2}\left[P_{n-1}(t) + P_{n+1}(t) - 2P_n(t)\right]$; Then let n be continuous:

$\tau\frac{\mathrm{d}P_n(t)}{\mathrm{d}t} = \frac{a^2}{2}\frac{P_{n-1}(t) + P_{n+1}(t) - 2P_n(t)}{a^2} \Rightarrow \frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2}, \quad D \sim \frac{a^2}{2\tau}$. 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.

介观(mesoscopic) level: $M\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = -\overset{\text{viscosity}}{\frac{\vec{v}}{B}} + \overset{\text{random}}{\vec{F}(t)}$. $f_{\text{stokes}} = f(\overset{\text{半径}}{a}, \overset{\text{粘度}}{\eta}, \overset{\text{速度}}{v}, \cancel{\overset{\text{质量}}{m}}) = 6\pi\eta a v \Rightarrow B = \frac{1}{6\pi\eta a}$

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

[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.

[Example] Irregular part(noise) of collective electron motion in circuit. $L\frac{\mathrm{d}I}{\mathrm{d}t} = \overset{\text{dissipation}}{-RI} + \overset{\text{fluactuation}}{V(t)}$

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

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

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

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

平衡态: $\frac{C_1}{2M} = \frac{2}{\tau}\cdot\frac{1}{2}k_BT \Rightarrow \boxed{C_1 = \frac{2k_BT}{B}}$, **Fluactuation-Dissipation Theorem(涨落耗散定理)**.

0.1.3.5.1 Analysis of Particle Postion

检查 Langevin 语言下的 $\left\langle r^2(t)\right\rangle = 2dDt$ 是否仍然满足.

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

$\frac{\mathrm{d}^2}{\mathrm{d}t^2}r^2 + \frac{1}{\tau}\frac{\mathrm{d}}{\mathrm{d}t}r^2 = 2v^2 + \vec{r}\cdot\vec{A} \Rightarrow \frac{\mathrm{d}^2}{\mathrm{d}t^2}\left\langle r^2\right\rangle + \frac{1}{\tau}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle r^2\right\rangle + 2\left\langle v^2\right\rangle + \overset{\vec{A}\not\leftrightarrow\vec{r}}{\cancel{\left\langle \vec{r}\cdot\vec{A}\right\rangle}}$, 因为 $\vec{A}$ 和 $\vec{r}$ 无关, 所以该期望项为 0.

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

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

2. $t \gg \tau$, $\left\langle r^2(t)\right\rangle = \frac{6k_BT\tau}{M}t = 6Bk_BTt \overset{d=3}{=} 6Dt \Rightarrow \boxed{D = Bk_BT}$, $\forall d$, another form of **Fluactuation-Dissipation Theorem**, or **Einstein's Relation**.

0.1.3.5.2 Analysis of Particle Velocity

$\vec{v}(t)$

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

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

[Discussion] 速度发散 $\lim_{\delta t\to 0}\frac{\langle|x(t+\delta t)-x(t)|\rangle}{\delta t} \sim \lim_{\delta t\to 0}\frac{(\delta t)^{\frac{1}{2}}}{\delta t} \to \infty$. 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 → field-based approach). 场 $f(x,t)$, 则位置为 $\rho(x) = q\delta(x-x_0)$, $\int \rho(x)\mathrm{d}x = q$. 如果是匀速直线运动, 则 $f(x,t) = \delta(x-vt)$. 若粒子 $x \to x+\delta x$, 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 $\frac{n_i(t+\delta t)-n_i(t)}{\delta t} = -\sum_{j\neq i} n_i(t)P_{i\to j} + \sum_{j\neq i} n_j(t)P_{j\to i}$, 这类方程被称为 **Master equation**.

1. 假定为 Markov Process;

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

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

$\frac{\mathrm{d}n_+}{\mathrm{d}t} = -n_+\omega_- + n_-\omega_+, \quad \frac{\mathrm{d}n_-}{\mathrm{d}t} = -n_-\omega_+ + n_+\omega_-$

Relaxation dynamics: 设 $n(t) = n_- - n_+$. 则微分方程化为 $\frac{\mathrm{d}n(t)}{\mathrm{d}t} = \frac{1}{\tau}\left[n(t)-n^0\right]$, 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**: $\int_{-\infty}^{+\infty} f(x,t)\mathrm{d}x = 1$;

2. **概率函数定义**: $f(x,t)\mathrm{d}x$ 是粒子在 t 时刻处于 $[x, x+\mathrm{d}x]$ 的概率.

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

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

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

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

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

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

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

$\langle x\rangle = 0, \quad \langle x^2\rangle = \int_{-\infty}^{+\infty} x^2 f(x,\infty)\mathrm{d}x = \frac{k_BT}{\lambda}$

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

该模型对应的 Langevin 方程为 $\eta\frac{\mathrm{d}x}{\mathrm{d}t} = \overset{\text{potential}}{-U'(x)} + \overset{\text{random}}{F(t)}$, 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 $\left\langle x^2(t)\right\rangle = \left\langle\left(\int_0^t \mathrm{d}u_1 v(u_1)\right)\left(\int_0^t \mathrm{d}u_1 v(u_1)\right)\right\rangle = \int_0^t \mathrm{d}u_1\int_0^t \mathrm{d}u_2\left\langle v(u_1)v(u_2)\right\rangle$. 利用微积分性质 $\frac{\mathrm{d}}{\mathrm{d}t}\int_0^t f(u)\mathrm{d}u = f$

得到 $\frac{\mathrm{d}\left\langle x^2(t)\right\rangle}{\mathrm{d}t} = 2\int_0^t \mathrm{d}u\langle v(u)v(t)\rangle \overset{\text{time reversal symmetry}}{=} 2\int_{-t}^0 \mathrm{d}u\left\langle v(u)v(0)\right\rangle = 2\int_0^t \mathrm{d}u\left\langle v(u)v(0)\right\rangle = 2Dd$

观察对比得到 $\int_0^t \langle v(u)v(0)\rangle\mathrm{d}u = Dd$.

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

0.1.3.5.4 Fourier Transformation of Langevin Equation .

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

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

频域内速度关联为 $\langle\widetilde{v}^*(\omega)\widetilde{v}(\omega')\rangle=S(\omega)\delta(\omega+\omega')$, 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 $\langle\widetilde{v}^*(\omega)\widetilde{v}(t=0)\rangle=S(\omega)$; 再令其在 ω 域积分, 得到 $\langle v(t)v(0)\rangle=\int_{-\infty}^{+\infty}S(\omega)e^{-i\omega t}\frac{\mathrm{d}\omega}{2\pi}$.

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