中心极限定理 Central Limit Theorem

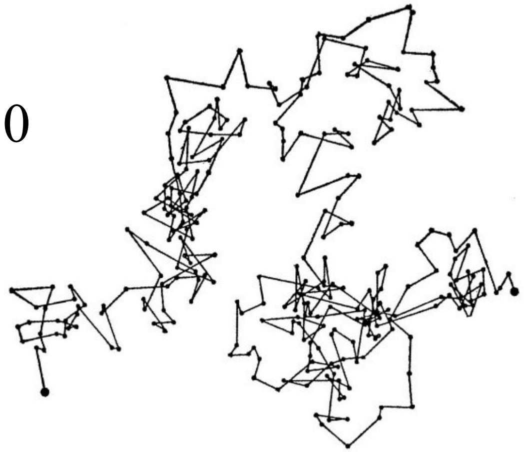
给定一组随机变量序列 $X_1, X_2, \cdots X_N$ ，它们是相互独立的，服从相同的随机分布

$$\boxed{\langle X \rangle = \frac{1}{N}\sum_{i=1}^{N} X_i} \qquad \boxed{\mathrm{var}\left\{\sum_{i=1}^{N} X_i\right\} = \sum_{i=1}^{N}\mathrm{var}\{X_i\}}$$

3. 由方差的推导：有 N 步，共有 n 条轨迹总距离

$$\mu = \langle X_i \rangle = \lim_{n\to\infty}\frac{1}{n}\sum_{j=1}^{n} X_{i,j} \to 0 \qquad \langle X \rangle = \frac{1}{N}\sum_{i=1}^{N} X_i = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{n} X_{i,j} = 0$$

第 i 步　　　第 i 步，第 j 条轨迹



单独一步对所有轨迹的平均

$$\sigma^2 = \mathrm{var}\{X_i\} = \langle X_i^2 \rangle - \langle X_i \rangle^2 = \langle X_i^2 \rangle = \frac{1}{2}(+\ell)^2 + \frac{1}{2}(-\ell)^2 = \ell^2$$

走 N 步后对所有轨迹的平均

$$\mathrm{var}\left\{\sum_{i=1}^{N} X_i\right\} = \sum_{i=1}^{N}\mathrm{var}\{X_i\} = N\ell^2 \qquad \boxed{\langle x^2(t) \rangle = \langle m^2 \rangle \ell^2 = n\ell^2 = \ell^2\frac{t}{\tau} \equiv 2Dt \quad \left(D = \frac{\ell^2}{2\tau}\right)}$$

6. 涨落与自相关函数

方差 variance $\mathrm{var}\{x\}=\left\langle\left(x-\langle x\rangle\right)^2\right\rangle=\langle x^2\rangle-\langle x\rangle^2$

协方差 variance $\mathrm{cov}\{x,y\}=\left\langle\left(x-\langle x\rangle\right)\left(y-\langle y\rangle\right)\right\rangle=\langle xy\rangle-\langle x\rangle\langle y\rangle$

相关系数 $$\mathrm{cor}\{x,y\}=\frac{\langle xy\rangle-\langle x\rangle\langle y\rangle}{\sqrt{\langle x^2\rangle-\langle x\rangle^2}\sqrt{\langle y^2\rangle-\langle y\rangle^2}}=\frac{\mathrm{cov}\{x,y\}}{\sqrt{\mathrm{var}\{x\}\,\mathrm{var}\{y\}}}$$

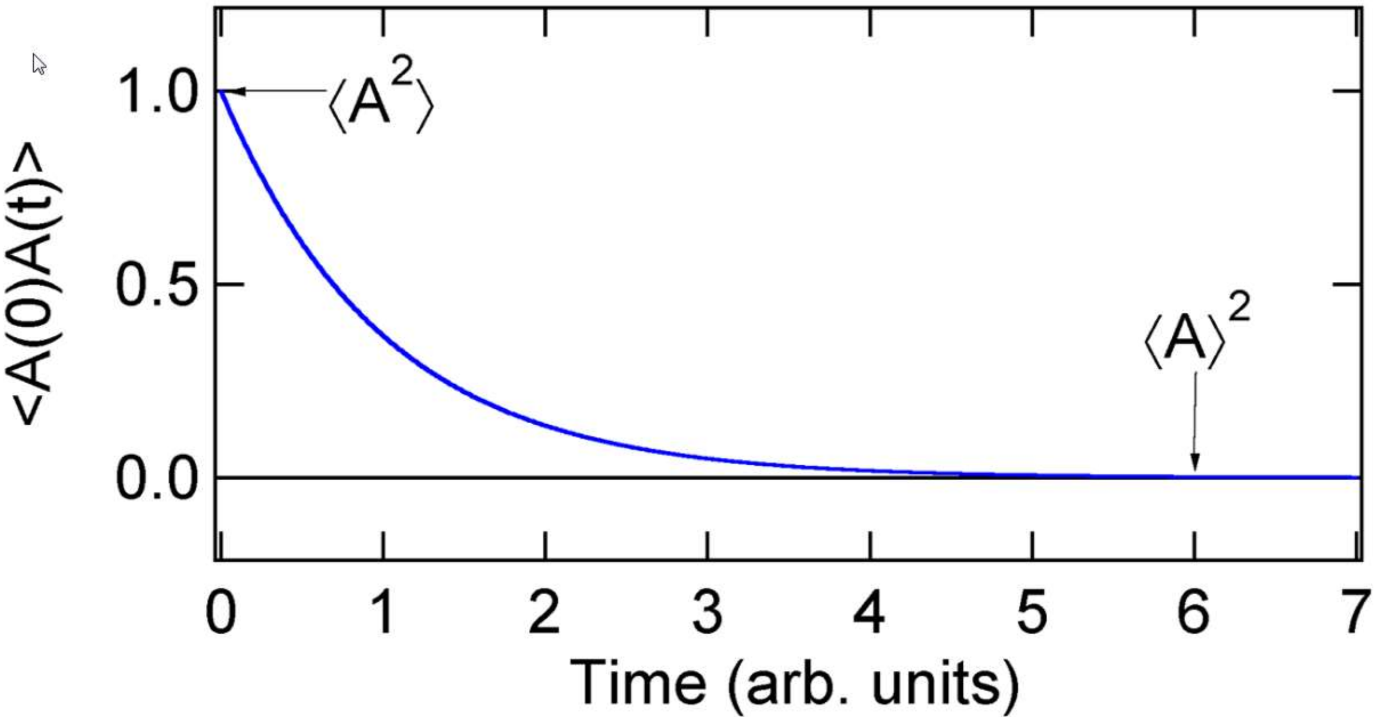
涨落 $\delta A(t)\equiv A(t)-\langle A\rangle$ $\qquad \langle A(t)\rangle=\langle A(0)\rangle=\langle A\rangle$

自相关函数 $$C(t)\equiv\mathrm{cov}\{A(t),A(0)\}=\langle\delta A(t)\,\delta A(0)\rangle$$
$$=\left\langle\left(A(t)-\langle A\rangle\right)\left(A(0)-\langle A\rangle\right)\right\rangle=\langle A(t)A(0)\rangle-\langle A\rangle^2$$
$$=\left\langle\left(A(0)-\langle A\rangle\right)\left(A(-t)-\langle A\rangle\right)\right\rangle=C(-t)$$

$$C(0)=\left\langle\left(\delta A(0)\right)^2\right\rangle=\left\langle(\delta A)^2\right\rangle=\langle A^2\rangle-\langle A\rangle^2$$

同时间下的相关函数为有限大小

$$\lim_{t\to\infty} C(t) = \lim_{t\to\infty} \langle \delta A(t)\delta A(0)\rangle = \langle \delta A(t)\rangle\langle \delta A(0)\rangle = 0$$



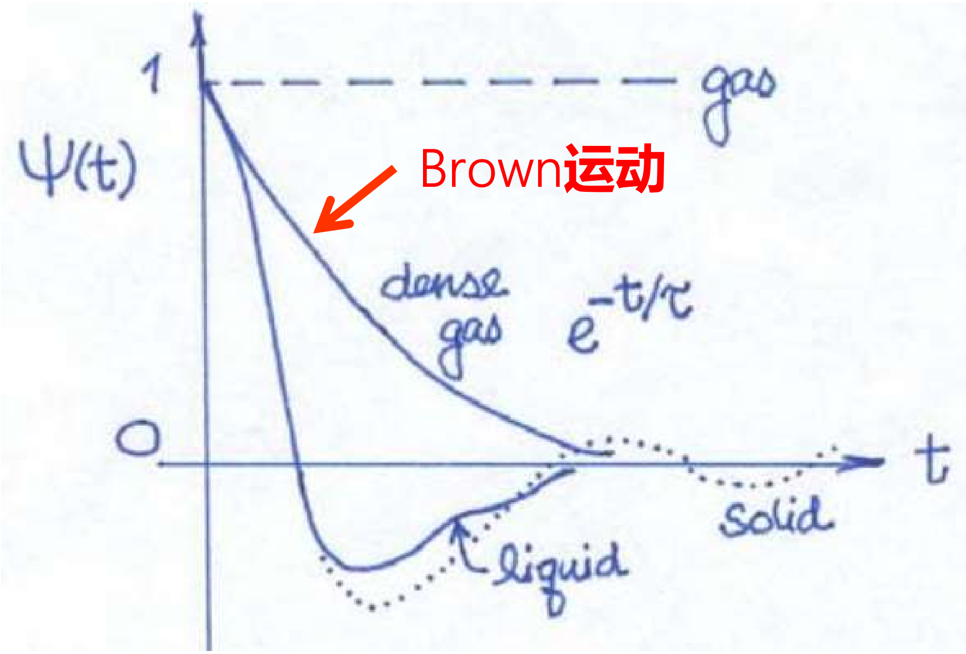
$$C(t) = \langle A(t)A(0)\rangle - \langle A\rangle^2$$

自发涨落回归: $$\langle A(t)A(0)\rangle = \begin{cases} \langle A^2\rangle & t=0 \\ \langle A\rangle^2 & t\to\infty \end{cases}$$

例：液体分子速度的自相关函数

$$C(t)=\langle v_x(t)v_x(0)\rangle=\begin{cases}\langle v_x^2\rangle=\dfrac{kT}{m} & t=0\\ \langle v_x\rangle^2=v_x(0)^2e^{-t/\tau}\to 0 & t\to\infty\end{cases}$$

$$=\frac{1}{3}\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle=\begin{cases}\dfrac{1}{3}\langle v^2\rangle=\dfrac{kT}{m} & t=0\\ \dfrac{1}{3}\langle v^2\rangle e^{-t/\tau}=C(0)e^{-t/\tau}\to 0 & t\to\infty\end{cases}$$



平衡系统中自发微观涨落的回归

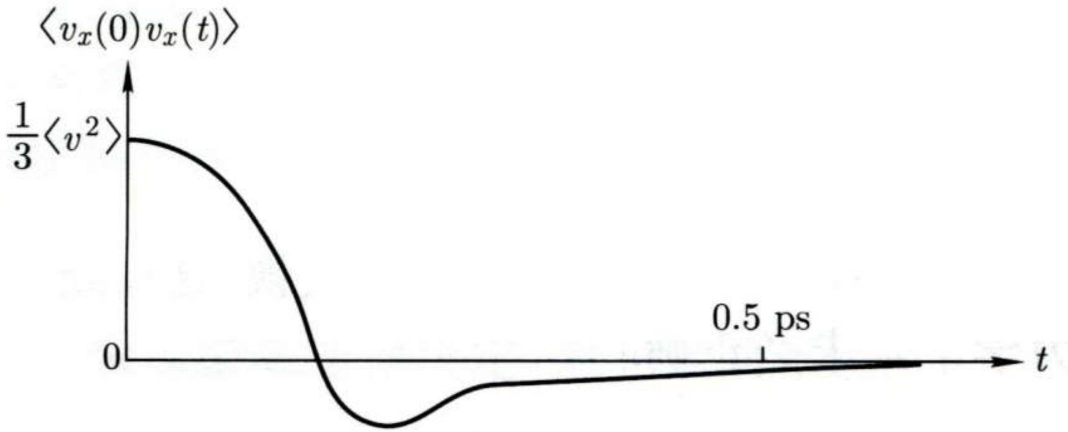


图 8.4　液体的速度关联函数

$$dX = V dt \qquad \frac{d\langle X\rangle}{dt} = \langle V\rangle \qquad \frac{d\langle X^2\rangle}{dt} = 2\langle XV\rangle$$

$$\frac{d}{dt}\operatorname{var}\{X\} = \frac{d}{dt}\left(\langle X^2\rangle - \langle X\rangle^2\right) = 2\langle XV\rangle - 2\langle X\rangle\langle V\rangle = 2\operatorname{cov}\{X,V\}$$

$$\mathbf{r}(t) - \mathbf{r}(0) = \int_0^t \mathbf{v}(t')\,dt'$$

$$\frac{d}{dt}\operatorname{var}\{\mathbf{r}(t)-\mathbf{r}(0)\} = 2\operatorname{cov}\{\mathbf{r}(t)-\mathbf{r}(0),\mathbf{v}(t)\}$$

$$= 2\langle(\mathbf{r}(t)-\mathbf{r}(0))\cdot\mathbf{v}(t)\rangle - 2\langle\mathbf{r}(t)-\mathbf{r}(0)\rangle\cdot\langle\mathbf{v}(t)\rangle$$

$$= 2\int_0^t \langle\mathbf{v}(t')\cdot\mathbf{v}(t)\rangle\,dt' \quad = \quad 2\int_0^t \langle\mathbf{v}(0)\cdot\mathbf{v}(t-t')\rangle\,dt'$$

速度关联函数不依赖于时间原点，将原点平移 t'

$t - t' \to t''$

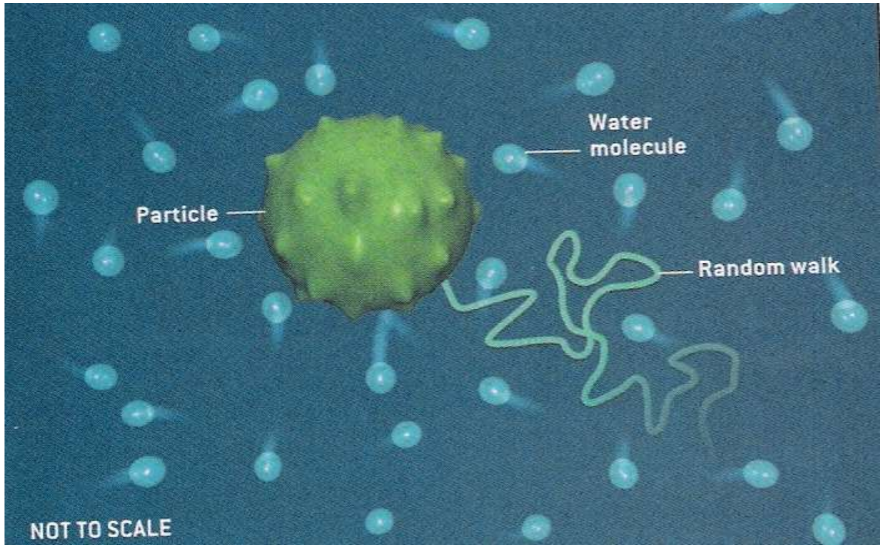
$$= \ 2\int_0^t \langle\mathbf{v}(t'')\cdot\mathbf{v}(0)\rangle\,dt'' \ \xrightarrow{t\to\infty}\ 6D$$

$$D = \frac{1}{3}\int_0^\infty \langle\mathbf{v}(t)\cdot\mathbf{v}(0)\rangle\,dt = \int_0^\infty C(t)\,dt$$

第一涨落耗散定理（**Green-Kubo公式**）

宏观扩散系数是微观速度自相关函数的积分

7. Langevin 理论（1906）Brownian动力学



Brown粒子处于流体环境中，受到两个作用力：

1、粘滞阻力，$-v/B$ （B是迁移率）
2、快速涨落力 $F(t)$ （系统特征时间 τ >>碰撞时间）

$$m\frac{d\mathbf{v}}{dt}=-\frac{1}{B}\mathbf{v}+\mathbf{F}(t)$$

Langevin方程，随机微分方程

长时间平均： $\overline{\mathbf{F}(t)}=0$

B是宏观唯象系数 $\frac{1}{B}=6\pi\eta a$

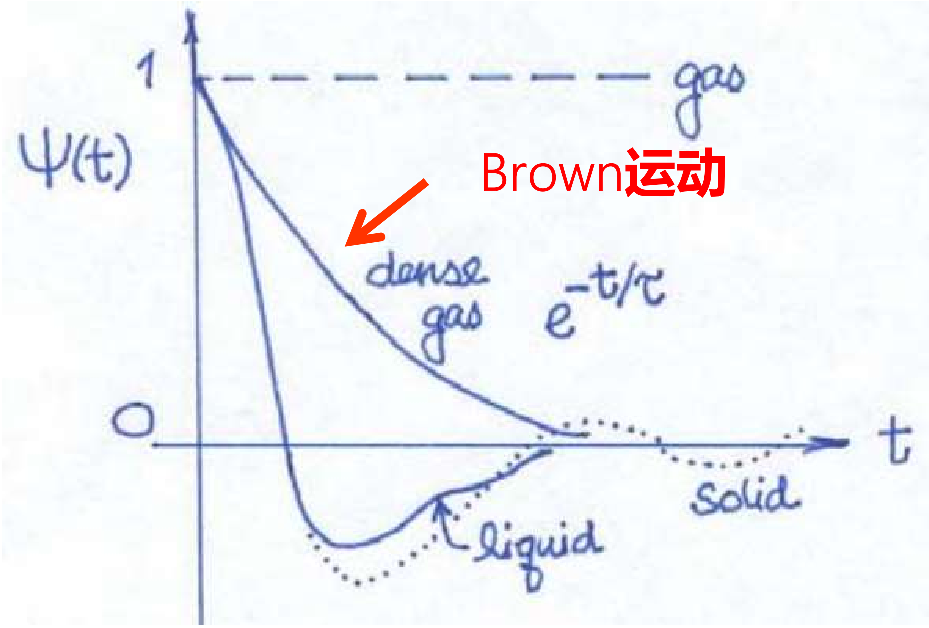
系综平均：

$$\langle\mathbf{F}(t)\rangle=0$$

$$\langle\mathbf{F}(t)\cdot\mathbf{F}(0)\rangle=D'\delta(t)$$

$$\frac{d\mathbf{v}}{dt} = -\frac{1}{\tau}\mathbf{v} + \mathbf{A}(t) \qquad (\tau = mB)$$

$$\mathbf{v}(t) = \mathbf{v}(0)\, e^{-t/\tau} + e^{-t/\tau}\int_0^t e^{t'/\tau}\ \mathbf{A}(t')\,dt'$$



$$\mathbf{v}(t)\cdot\mathbf{v}(0) = v^2(0)e^{-t/\tau} + e^{-t/\tau}\int_0^t e^{t'/\tau}\ \mathbf{v}(0)\cdot\mathbf{A}(t')\,dt'$$

$$C(t) = \frac{1}{3}\left\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\right\rangle$$

$$= \frac{1}{3}\left\langle v^2(0)\right\rangle e^{-t/\tau} + \frac{1}{3}e^{-t/\tau}\int_0^t e^{t'/\tau}\left\langle \mathbf{v}(0)\cdot\mathbf{A}(t')\right\rangle dt' = C(0)e^{-t/\tau}$$

$$D = \int_0^\infty C(t)\,dt = \frac{1}{3}\int_0^\infty \left\langle v^2(0)\right\rangle e^{-t/\tau}dt = \frac{1}{3}\left\langle v^2\right\rangle \tau = \frac{kT}{m}\tau = kTB$$

$$\boxed{D = kTB = \frac{kT}{6\pi\eta a} \qquad \text{Einstein 关系}}$$

$$\left\langle \mathbf{v}(t) \right\rangle = \left\langle \mathbf{v}(0) \right\rangle e^{-t/\tau} + e^{-t/\tau} \int_0^t e^{t'/\tau} \left\langle \mathbf{A}(t') \right\rangle dt' = \left\langle \mathbf{v}(0) \right\rangle e^{-t/\tau}$$

$$= \int \mathbf{v} p d\mathbf{v}$$

平均漂移速度将随时间递减，而单个粒子的速度由于涨落力的存在而一直持续

$$\left\langle v^2(t) \right\rangle = e^{-2t/\tau} \left\{ \left\langle v^2(0) \right\rangle + \int_0^t \int_0^t e^{t'/\tau} e^{t''/\tau} \left\langle \mathbf{A}(t') \cdot \mathbf{A}(t'') \right\rangle dt' dt'' \right\}$$

$$= \left\langle v^2(0) \right\rangle e^{-2t/\tau} + D'\tau \left(1 - e^{-2t/\tau}\right) / 2$$

$$= \int v^2 p d\mathbf{v}$$

$$p\left(\mathbf{v}, t \middle| \mathbf{v}_0\right) = \frac{1}{\sqrt{2\pi\sigma^2\xi}} \exp\left\{ -\frac{\left(\mathbf{v} - \mathbf{v}_0 \eta\right)^2}{2\sigma^2 \xi} \right\}$$

$\sigma^2 = D'\tau$，$\eta = e^{-t/\tau}$，$\xi = 1 - \eta^2$

$$\lim_{t\to\infty} p\left(\mathbf{v},t\middle|\mathbf{v}_0\right)=p\left(v\right)=\frac{1}{\sqrt{2\pi\sigma^2}}\exp\left\{-\frac{mv^2}{2}\frac{B}{D'}\right\} \qquad D'=D=kTB=\frac{kT}{6\pi\eta a}$$

与初始速度无关，趋于Maxwell速度分布： $p\left(v\right)=\sqrt{\frac{m}{2\pi kT}}\exp\left\{-\frac{mv^2}{2kT}\right\}$

$$\left\langle \mathbf{F}\left(t\right)\cdot\mathbf{F}\left(0\right)\right\rangle = kTB\delta\left(t\right)$$

第二涨落耗散定理：阻力摩擦力等与涨落有关。摩擦越小，涨落力越大。

取点积于Langevin方程 $$m\frac{d\mathbf{v}}{dt}=-\frac{1}{B}\mathbf{v}+\mathbf{F}\left(t\right)$$

$$\mathbf{r}\cdot\frac{d\mathbf{v}}{dt}=\frac{1}{2}\frac{d^2}{dt^2}r^2-v^2=\frac{d}{dt}\left(\mathbf{r}\cdot\mathbf{v}\right)-v^2$$

取平均

$$\left\langle \mathbf{r}\cdot\mathbf{A}\right\rangle =0$$

$$\frac{d^2}{dt^2}\left\langle r^2\right\rangle+\frac{1}{\tau}\frac{d}{dt}\left\langle r^2\right\rangle=2\left\langle v^2\right\rangle$$

由能量均分定理 $\frac{1}{2}m\left\langle v_x^2\right\rangle = \frac{1}{2}m\left\langle v_x^2\right\rangle = \frac{1}{2}m\left\langle v_x^2\right\rangle = \frac{1}{2}kT$ $\left\langle v^2\right\rangle = \frac{3kT}{m}$

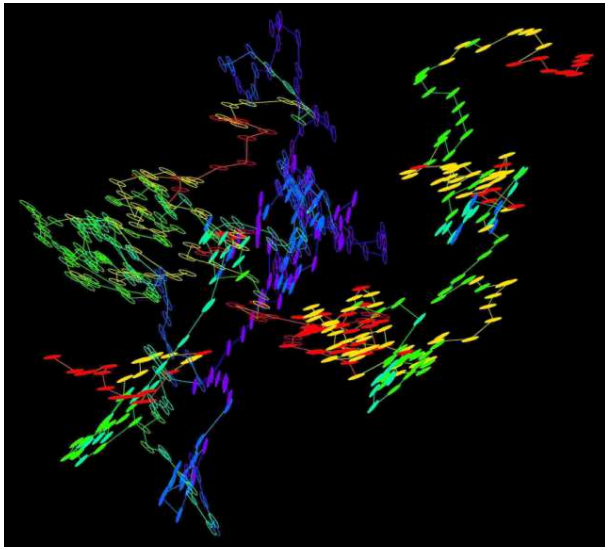
$$\left\langle r^2\right\rangle = \frac{6kT}{m}\tau^2\left\{\frac{t}{\tau} - \left[1 - \exp\left(-t/\tau\right)\right]\right\}$$

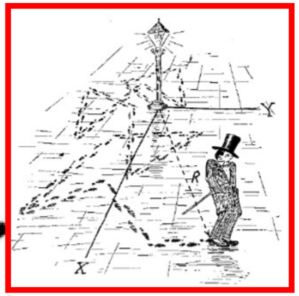
$$\exp\left(-t/\tau\right) \approx 1 - \frac{t}{\tau} + \frac{1}{2}\left(\frac{t}{\tau}\right)^2$$

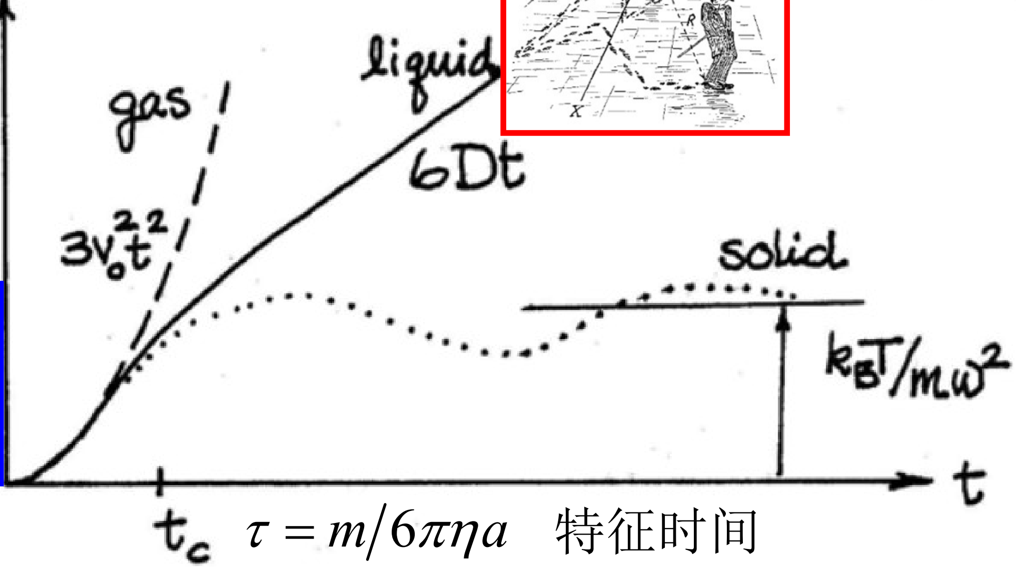
$$\approx \begin{cases} \frac{3kT}{m}t^2 = \left\langle v^2\right\rangle t^2 & \left(t << \tau\right) \\ \frac{6kT}{m}\tau t = 6Dt & \left(t >> \tau\right) \end{cases}$$

$\mathbf{r} = \mathbf{v}t$ 特征时间段内是直线行走

长时间是随机行走 （录像）







$\tau = m/6\pi\eta a$ 特征时间