Anomalous Diffusion and Basic Theorems on Statistical Mechanics

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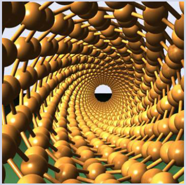
UnB

Sumário

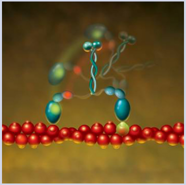
Anomalous Diffusion

Diffusion in cellular media

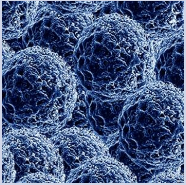
Balístic Transport



Pattern Formation

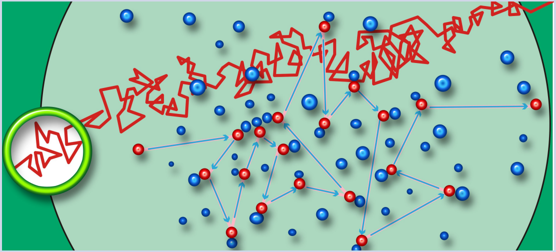


Nanoscale conduction



General Concepts

Brownian Motion



- $\lim_{t\to\infty}\langle x^2(t)\rangle \sim 2Dt$, with $D = \frac{k_B T}{m\gamma}$

Einstein Relation

$$\lim_{t\to\infty}\langle x^2(t)\rangle \sim t^\alpha$$

Diffusion Exponent

- $\alpha < 1$, Subdiffusion;
- $\alpha = 1$, Normal Diffusion;
- $\alpha > 1$, Superdiffusion.

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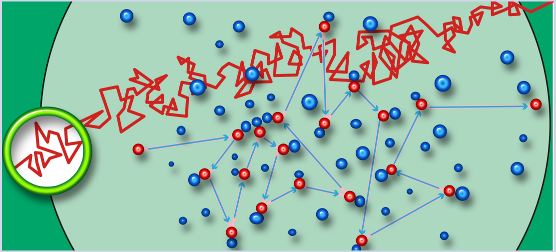

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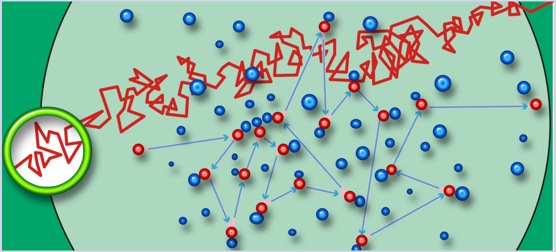

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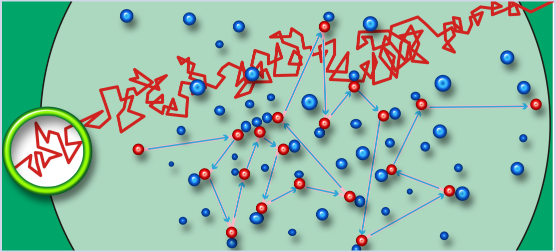

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Langevin´s Equation

Langevin (1908)

$$\frac{d}{dt}p(t) = -\gamma p(t) + \xi(t)$$

Properties

- The noise $\xi(t)$ fulfils $\langle \xi(t) \rangle = 0$ e $\langle p(0)\xi(t) \rangle = 0$.
- Fluctuation-Dissipation Theorem:

$$\langle \xi(t)\xi(t') \rangle = 2m\gamma k_B T \delta(t-t')$$

Diffusion Constant

$$D = \int_0^\infty C_v(t)dt = \int_0^\infty < v(t)v(0) > dt = \frac{k_B T}{m\gamma}$$

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Generalized Langevin´s Equation

Mori equation´s (1964)

$$m\frac{dv(t)}{dt} = -m\int_0^t \Gamma(t-t')v(t')dt' + \xi(t)$$

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$$v(t) = v(0)R(t) + \int_0^t \xi(t')R(t-t')dt'$$

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Anomalous diffusion

Correlation function $C_V(t)$

$$\frac{dC_v(t)}{dt} = -\int_0^t \Gamma(t-t')C_v(t')dt'$$

- If $<x^2(t)>= Dt$ and $<x^2(t)>\sim t^\alpha$ for $\alpha \neq 1$.
- D must be a function of t

$$\lim_{t\to\infty} D(t) = \lim_{t\to\infty}\int_0^t C_v(t')dt' = \lim_{z\to 0}\int_0^\infty C_v(t)\exp(-zt) = \lim_{z\to 0}\widetilde{C}_v(z)$$

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Classification of diffusion

- Consider $\lim_{z\to 0}\widetilde{\Gamma}(z) \sim z^{\nu}$
- $-1 < \nu < 1$

$$\lim_{t\to\infty} D(t) = \lim_{z\to 0}\widetilde{C}_v(z) = \lim_{z\to 0}\frac{C_v(0)}{z+\widetilde{\Gamma}(z)} \sim \lim_{z\to 0}\widetilde{\Gamma}(z)^{-1} \sim t^{\nu}$$

$$< x^2(t) >= 2D(t)t \sim t^{\nu+1} \sim t^{\alpha}$$

$$\alpha = \nu + 1$$

F. A. Oliveira et al , *Phy. Rev. Lett.* 86, 5839 (2001).

R. Morgado et al , *Phy. Rev. Lett.* 89, 100601 (2002).

From the noise

$$\xi(t) = \int_0^\infty \sqrt{\frac{\rho_r(\omega)}{2mk_BT}} \cos[\omega t + \phi(\omega)] d\omega$$

- $\rho_r(\omega)$ is the spectral density
- ϕ are random numbers $0 < \phi < 2\pi$.

Fluctuation Dissipation

$$\langle \xi(t)\xi(t') \rangle = \langle (mv)^2 \rangle_{eq} \Gamma(t-t')$$

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Irreversibility

$$\lim_{t\to\infty} R(t) = 0$$

$$D = \lim_{t\to\infty} \frac{\langle x^2(t)\rangle}{2t} \sim t^{\alpha} \Rightarrow \lim_{z\to 0}\widetilde{\Gamma}(z) = bz^{\nu} \quad \text{with} \quad \alpha = \nu + 1$$

$$\lim_{t\to\infty} R(t) = \lim_{z\to 0} z\widetilde{R}(z) = \lim_{z\to 0} \frac{z}{z+\widetilde{\Gamma}(z)} = \lim_{z\to 0}\left(1+\frac{\widetilde{\Gamma}(z)}{z}\right)^{-1} \quad \text{now} \quad \frac{\widetilde{\Gamma}(z)}{z} = bz^{\nu-1}$$

Anomalous Diffusion

- $-1 < \nu < 1 \ (0 < \alpha < 2)$
- $\lim_{z\to 0} \frac{\widetilde{\Gamma}(z)}{z} \to \infty$
- $R(t\to\infty) = 0$

Balístic Diffusion

- $\nu = 1 \ (\alpha = 2)$
- $R(t\to\infty) = \frac{1}{1+b} = \kappa \neq 0$

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Lee conjecture´s (prl 2007)

$p(t)$ is ergodic if and only if,

$$0 < W = \int_0^\infty R(t)dt < \infty$$

Our calculations

$$\langle p^2(t)\rangle = \langle p^2\rangle_{eq} + R^2(t)\left[\langle p^2(0)\rangle - \langle p^2\rangle_{eq}\right]$$

- The Khinchin Theorem holds for all kind of diffusion

L. C. Lapas, R. Morgado, M. H. Vainstein, J. M. Rubí, and F. A. Oliveira, *Phy. Rev. Lett.* 101, 230602 (2008).

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Fluctuation-Dissipation Theorem

- Ergodicity does work for anomalous diffusion
- Ergodicity does not holds for ballistic diffusion,
- The same for the fluctuation-dissipation theorem.

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Friction and memory

$$\gamma = \lim_{z\to 0}\widetilde{\Gamma}(z) \sim z^{\nu} \to \begin{cases} 0 & \text{, Superdiffusion } (\nu > 0) \\ \text{constant} & \text{, Normal dif. } (\nu = 0) \\ \infty & \text{, Subdiffusion } (\nu < 0) \end{cases}$$

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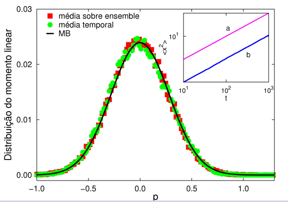
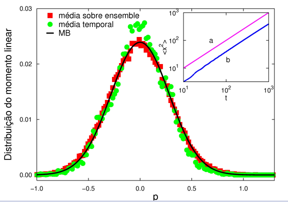
Ergodicity in Anomalous Diffusion

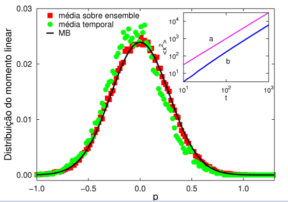
Subdiffusion $\alpha = 0.5$



Normal Diffusion



Superdiffusion $\alpha = 1.5$



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Effective temperature

$$T_{eff} = T_0 + \left[1 - R^2(t)\right](T_{res} - T_0)$$

Condition

$$0 \le \lim_{t\to\infty} R^2(t) \le 1 \text{ or } 0 \le (1+b)^{-1} \le 1 \text{ or } b \ge 0$$

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$$\Gamma(t) = \int_0^\infty \rho_r(\omega)\cos(\omega t)d\omega \implies b = \lim_{z\to 0}\frac{\widetilde{\Gamma}(z)}{z} = \int_0^\infty \frac{\rho_r(\omega)}{\omega^2}d\omega \ge 0$$

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$$0 \leq \lim_{t\to\infty} R^2(t) \leq 1 \text{ or } 0 \leq (1+b)^{-1} \leq 1 \text{ or } b \geq 0$$

:

$$\Gamma(t) = \int_0^\infty \rho_r(\omega)\cos(\omega t)d\omega \implies b = \lim_{z\to 0}\frac{\widetilde{\Gamma}(z)}{z} = \int_0^\infty \frac{\rho_r(\omega)}{\omega^2}d\omega \geq 0$$

- The spectral density $\rho_r(\omega)$ must be positive

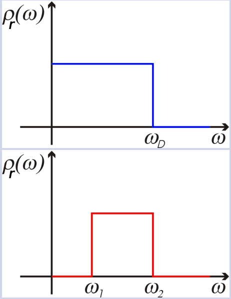
Noise espectral density:

$$\rho_r(\omega) = \begin{cases} \frac{2\gamma_0}{\pi} & , 0 < \omega < \omega_D \\ 0 & , \text{otherwise} \end{cases}$$

Process Ornstein-Zernike:

$$\rho_{DB}(\omega) = \rho_{\omega_2}(\omega) - \rho_{\omega_1}(\omega)$$

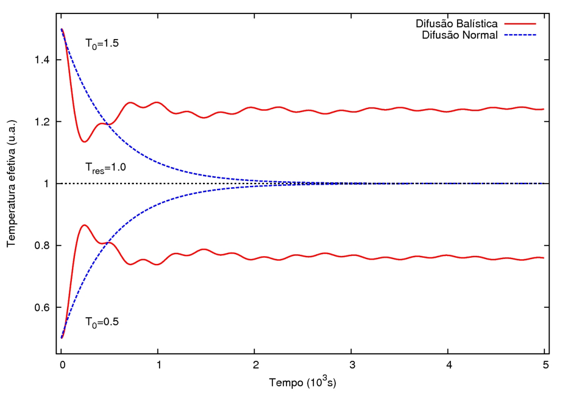
Normal and ballistic diffusion



Memory Function

$$\Gamma(t) = \frac{2\gamma_0}{\pi}\left[\frac{\sin(\omega_2 t)}{t} - \frac{\sin(\omega_1 t)}{t}\right]$$

Effective Temperature



Entropy

- Variation of entropy:

$$\Delta S = \int_{T_0}^{T_{ef}} c_v(T') \left(\frac{1}{T'} - \frac{1}{T_{res}} \right) dT' \geq 0.$$

- Residual entropy:

$$\Delta S' = \int_{T_{ef}}^{T_{res}} c_v(T') \left(\frac{1}{T'} - \frac{1}{T_{res}} \right) dT' \geq 0.$$

- final entropy:

$$S = S_{max} - \Delta S'$$

- Gibbs entropy:
  Maximum of entropy $\Longleftrightarrow$ Gaussian distribution

$$S(t) = -k_B \int \rho(p,t) \ln \frac{\rho(p,t)}{\rho_{eq}(p)} dp + S_{eq}$$

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Non Gaussian Behavior

Third momentum

$$\left\langle p^3(t)\right\rangle = \left\langle p^3(0)\right\rangle R^3(t) + 3\left\langle p(0)\right\rangle \left\langle p^2\right\rangle_{eq}\left[1-R^2(t)\right]R(t)$$

Forth momentum

$$\begin{aligned}\left\langle p^4(t)\right\rangle &= \left\langle p^4(0)\right\rangle R^4(t) + 3\left\langle p^2\right\rangle_{eq}^2\left[1-R^2(t)\right]^2 + \\ &\quad 6\left\langle p^2(0)\right\rangle\left\langle p^2\right\rangle_{eq}\left[1-R^2(t)\right]R^2(t)\end{aligned}$$

Skewness

$$\varsigma(t) = \left[\frac{\sigma_p(0)}{\sigma_p(t)}\right]^3 \varsigma(0)R^3(t)$$

Non Gaussian factor

$$\eta(t) = \left[\frac{\left\langle p^2(0)\right\rangle}{\left\langle p^2(t)\right\rangle}\right]^2 \eta(0)R^4(t)$$

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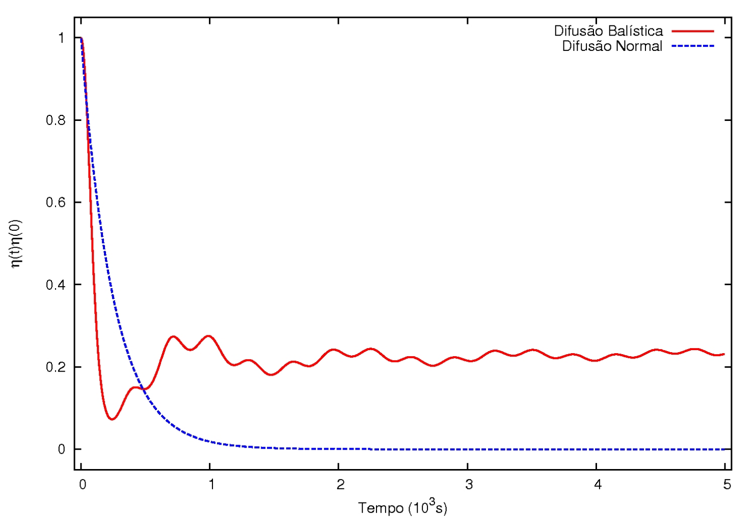

Conclusions

- Anomalous diffusion $\lim_{t\to\infty}\langle x^2(t)\rangle \sim t^{\alpha}$ holds for $0 \leq \alpha \leq 2$.
- From the memory $\lim_{z\to 0}\widetilde{\Gamma}(z) \sim z^{\nu}$ we get $\alpha = \nu + 1$.
- Second law is valid for all diffusive regimes.
- All process ends up in a Gaussiana, except the ballistic one;
- The ballistic evolves towards a Gaussian without reach it.
- The temperature evolves towards the reservoir temperature.
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