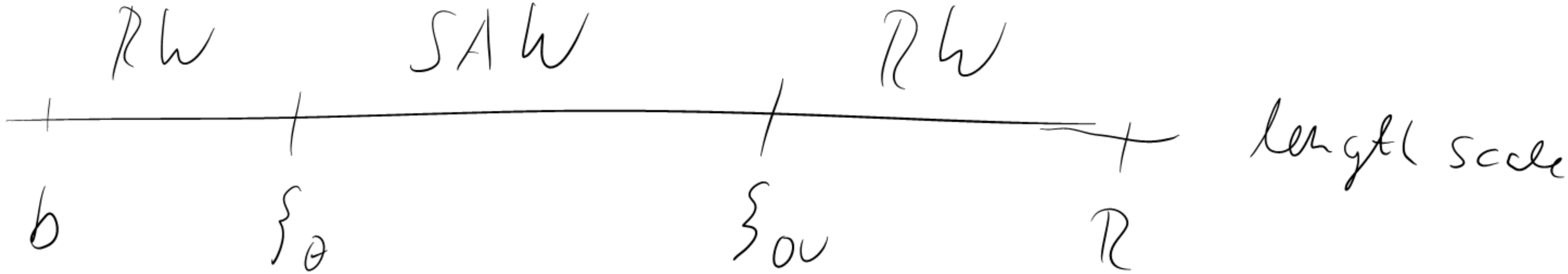
c^* / c^{**}

Semidilute solution in fairly good, but not perfectly good solvent

→ ξ_θ due to solvent quality (small)

→ ξ_{ov} due to overlap



$$\xi_{ov} \sim \xi_\theta \, n^\nu \qquad \nu = 0.59$$

n ↳ # of θ-blobs in an overlap blob

$$\xi_\theta \sim b \, m^{1/2}$$

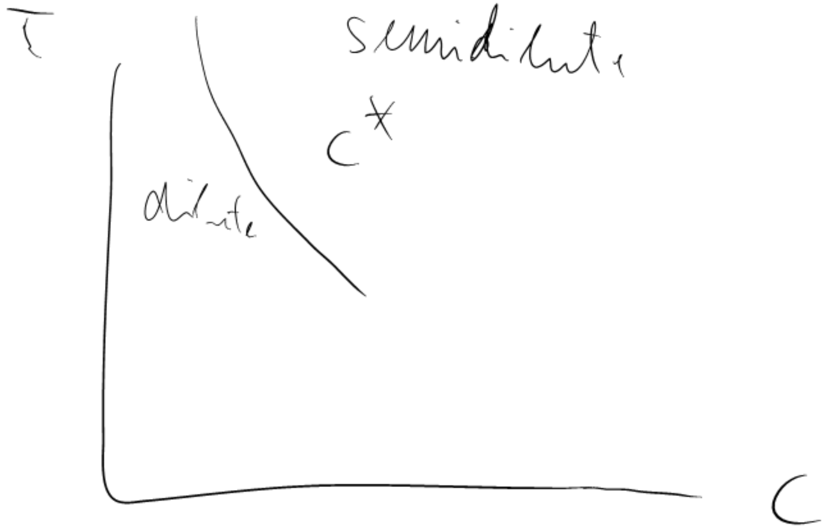
m ↳ # of monomers in a θ blob

$$\xi_\theta \sim b \, \tau^{-1} \qquad \tau = \frac{T-\theta}{\theta} \qquad m \sim \tau^{-2}$$

$$c \sim \frac{mn}{\xi_{ov}^3}$$

Before overlap: $R \sim b N^{\nu} \tau^{2\nu-1}$

$$c^* \sim \frac{N}{[b N^{\nu} \tau^{2\nu-1}]^3} \sim b^{-3} N^{-(3\nu-1)} \tau^{-(6\nu-3)}$$



$$c^* \sim \tau^{-(6\nu-3)} \sim \tau^{-0.6}$$

$$R \sim b N^{1/2} \underbrace{f(N^{1/2}\tau)}_{(N^{1/2}\tau)^{2\nu-1}}$$

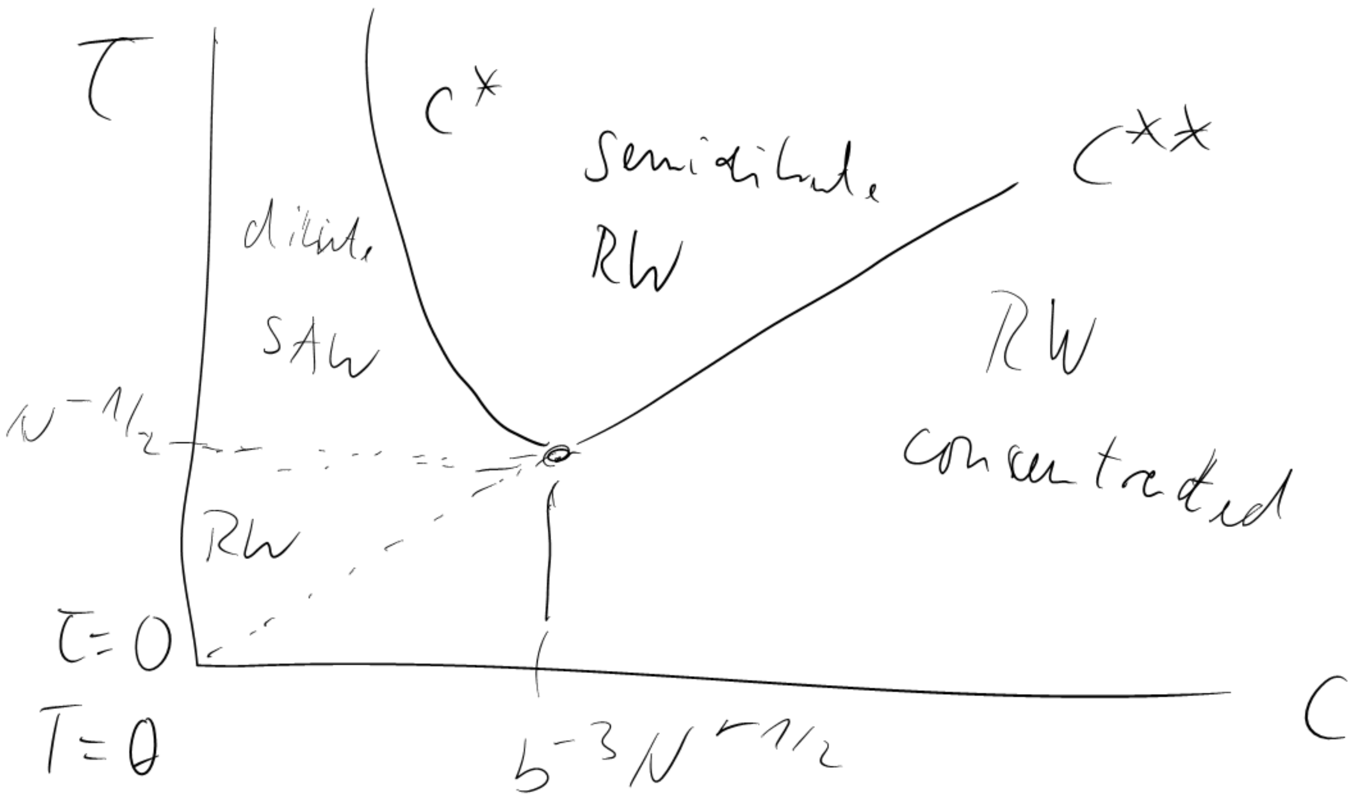
τ fixed, increase c

ξ_θ = const., ξ_{ov} decreases

at some point $\xi_{ov} = \xi_\theta$ is reached, no SAW window left. What is the concentration c^{**} where this happens?

$n = 1$, $m \sim \tau^{-2}$ $\xi_{ov} = \xi_\theta = b\tau^{-1}$

$$c^{**} = \frac{mn}{\xi_\theta^3} = \frac{\tau^{-2}}{(b\tau^{-1})^3} = b^{-3}\tau$$



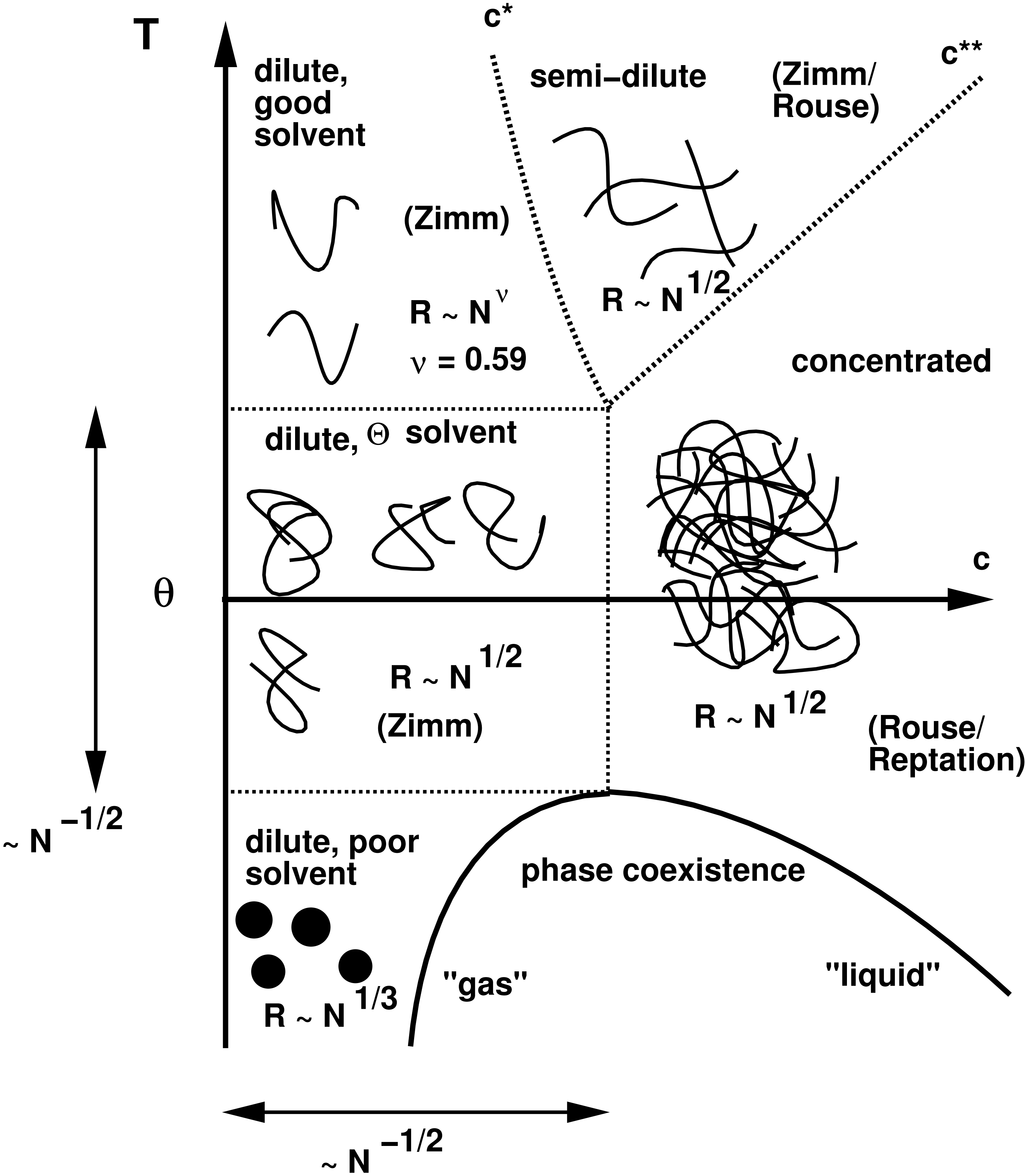
$$c^* = c^{**}$$

$$\frac{1}{b^3} N^{-(3\nu-1)} \tau^{-(6\nu-3)} = \frac{1}{b^3} \tau$$

$$N^{-(3\nu-1)} = \tau^{1+6\nu-3} = \tau^{6\nu-2} = \tau^{2(3\nu-1)}$$

$$N^{-1} = \tau^2 \qquad \boxed{\tau = N^{-1/2}}$$

$$C = \frac{1}{b^3}\tau = \boxed{\frac{1}{b^3} N^{-1/2}}$$



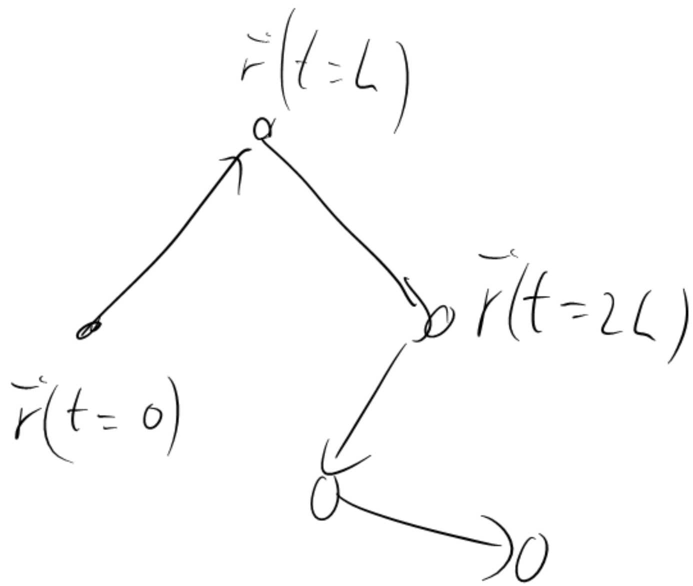
T
c*
c**
dilute,
good
solvent
semi-dilute
(Zimm/
Rouse)
(Zimm)
R ~ N^ν
ν = 0.59
R ~ N^1/2
concentrated
dilute, Θ solvent
c
θ
R ~ N^1/2
(Zimm)
R ~ N^1/2
(Rouse/
Reptation)
~ N^−1/2
dilute, poor
solvent
phase coexistence
"gas"
"liquid"
R ~ N^1/3
~ N^−1/2

5. DYNAMICS

5.1. Brownian Motion:

The Smoluchowski Equation

Look at one particle performing FREE Brownian motion, "time step" h



$t=0,\ t=h,\ t=2h,\ \ldots$

etc.

This is a RW !

mean square displacement $\propto$ time

$$\langle \Delta \vec{r}^{\,2} \rangle = \langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle = 6 D t$$

6 = 2 · spatial dimension (3D)

D → diffusion constant

requirement: $\langle \Delta \vec{r}^2 \rangle^{1/2} \gg$ atomic length scales

Just as for the Gaussian polymer chain

$$P(\Delta \vec{r}) = \left(\frac{1}{\sqrt{2\pi \cdot 2Dt}} \right)^3 \exp\left(-\frac{\Delta \vec{r}^2}{2 \cdot 2Dt} \right)$$

$$\langle \Delta \vec{r}^2 \rangle = \underbrace{\langle \Delta x^2 \rangle}_{2Dt} + \underbrace{\langle \Delta y^2 \rangle}_{2Dt} + \underbrace{\langle \Delta z^2 \rangle}_{2Dt}$$

$$\parallel$$

$$6Dt = 3 \cdot 2Dt$$

$$P(\Delta\vec{r}) = (4\pi D t)^{-3/2} \exp\left(-\frac{\Delta\vec{r}^2}{4Dt}\right)$$

we know already:

This is the solution of the diffusion equation

$$\frac{\partial}{\partial t} P(\Delta\vec{r}, t) = D \nabla^2 P(\Delta\vec{r}, t)$$

with initial condition

$$P(\Delta\vec{r}, t=0) = \delta(\Delta\vec{r})$$

Now, study Brownian motion on a <u>lattice</u>.

Simple cubic lattice in 3D, lattice spacing a, nearest-neighbor hops, time step h

$$\vec{c}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{c}_2 = \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{c}_3 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \vec{c}_4 = \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix}$$

$$\vec{c}_5 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad \vec{c}_6 = \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix}$$

Unit vectors to the nearest neighbors

$p(\vec{r}, t)$: probability to find the particle at site $\vec{r}$, at time t, start at $\vec{r} = 0$

$$p(\vec{r}, t = 0) = \delta_{\vec{r}, 0}$$

$$\langle \Delta \vec{r}^2 \rangle_h = \frac{1}{6} a^2 \vec{c}_1^{\,2} + \frac{1}{6} a^2 \vec{c}_2^{\,2} + \ldots + \frac{1}{6} a^2 \vec{c}_6^{\,2} = a^2 \overset{!}{=} 6Dh$$

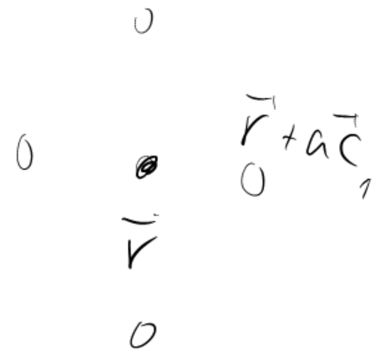
$\frac{1}{6}$ → probability to hop in $\vec{c}_1$ direction; $\vec{c}_1^{\,2} = 1$

$$D = \frac{a^2}{6h}, \quad h = \frac{a^2}{6D}$$

question: continuum limit $a \to 0$, $h \to 0$

but keep D constant

(diffusive scaling)



overdamped motion, no mass

pure random hops

p satisfies a Master equation

$$p(\vec r, t+h) = \frac{1}{6} \sum_{i=1}^{6} p(\vec r + a\vec c_i, t)$$

target — transition probability — source

$$p\left(\vec{r}, t + \frac{a^2}{6D}\right) = \frac{1}{6} \sum_i p(\vec{r} + a\vec{c}_i, t)$$

$a \to 0$, Taylor expansion up to order a^2

some algebra: - $\alpha, \beta, \gamma \ldots$ Cartesian indexes

- Einstein summation convention:

If a Greek index occurs twice, then it is being summed over.

E.g. $\vec{r}^2 = r_\alpha r_\alpha$, $\delta_{\alpha\alpha} = 3$

$$\frac{1}{6}\sum_i 1 = 1$$

$$\frac{1}{6}\sum_i \vec{c}_i = 0 \quad \text{symmetry}$$

$$\frac{1}{6}\sum_i c_{i\alpha} c_{i\beta} = A\,\delta_{\alpha\beta} \qquad A = ?$$

$$1 = \frac{1}{6}\sum_i 1 = \frac{1}{6}\sum_i c_{i\alpha} c_{i\alpha} = A\,\delta_{\alpha\alpha} = 3A \Rightarrow A = 1/3$$

$$(1/6)\sum_i c_{i\alpha} c_{i\beta} = (1/3)\,\delta_{\alpha\beta}$$

$$p\left(\vec{r}, t + \frac{a^2}{6D}\right) = \frac{1}{6}\sum_i p(\vec{r} + a\vec{c}_i, t)$$

<u>lhs:</u> $$p\left(\vec{r}, t + \frac{a^2}{6D}\right) \simeq p(\vec{r}, t) + \frac{a^2}{6D}\,\partial_t\, p(\vec{r}, t)$$

<u>rhs</u> $$p(\vec{r} + a\vec{c}_i, t) \simeq p(\vec{r}, t) + a\, c_{i\alpha}\, \partial_\alpha\, p(\vec{r}, t) + \frac{a^2}{2} c_{i\alpha} c_{i\beta}\, \partial_\alpha \partial_\beta\, p(\vec{r}, t) \quad \Big| \frac{1}{6}\sum_i$$

$$\frac{1}{6}\sum_i p(\vec{r} + a\vec{c}_i, t) \simeq p(\vec{r}, t) + \frac{a^2}{2}\,\frac{1}{3}\,\delta_{\alpha\beta}\,\partial_\alpha \partial_\beta\, p(\vec{r}, t)$$

$$= p(\vec{r}, t) + \frac{a^2}{6}\, \nabla^2\, p(\vec{r}, t)$$

$$\frac{a^2}{6D} \partial_t p(\vec{r},t) = \frac{a^2}{6} \nabla^2 p(\vec{r},t)$$

$$\partial_t p(\vec{r},t) = D \nabla^2 p(\vec{r},t) \qquad \Big| \frac{1}{a^3} \quad p \to P$$

$$\boxed{\partial_t P(\vec{r},t) = D \nabla^2 P(\vec{r},t)}$$

diffusion equation