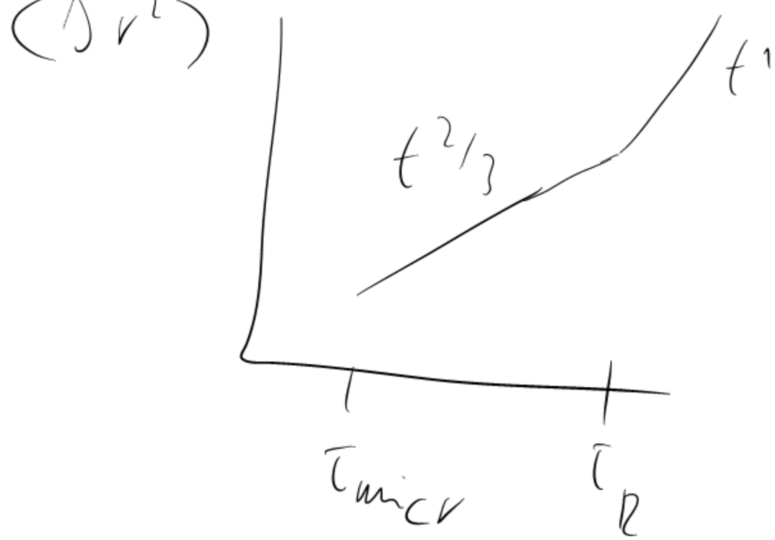
Zimm model: $D \sim \frac{1}{R} \sim R^{2-z} \qquad z = 3$

$t_R \sim R^z \qquad D\,t_R \sim R^2$



works well for dilut. solutions

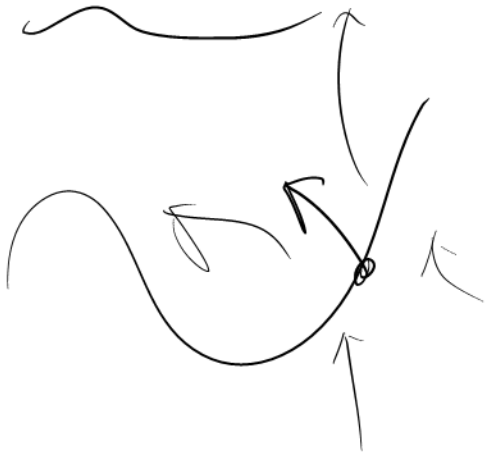
short-chain melts $\longrightarrow$ Rouse

long-chain " $\longrightarrow$ Reptation in melts, both

- excluded-volume AND
- hydrodynamic interactions are screened

HOW COME??

solution:



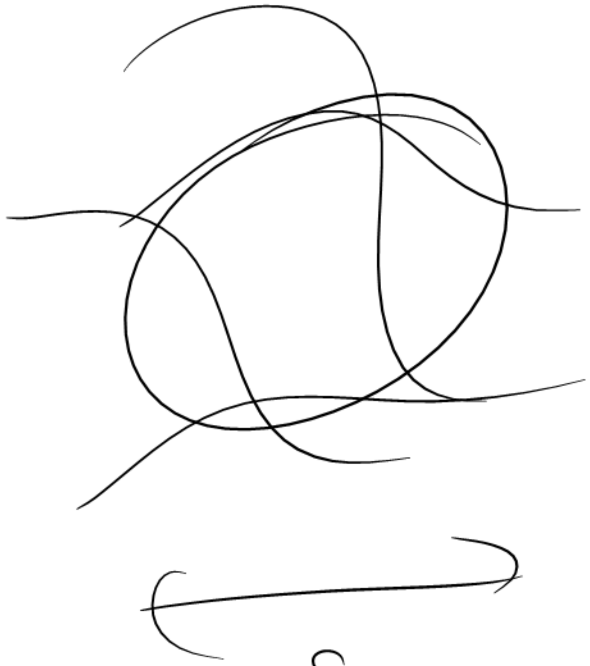
melt:

← chain gets "elastically distorted"

- "signal" spreads along the backbone
- "cascade" of collision events, however random
- correlations are destroyed, due to the random arrangement of chains
- Rouse

alternative view for semidilute solutions

motion of blobs:



ξ

- quasi-free motion up to displacement of order ξ

$D_\xi \sim \frac{k_B T}{\eta \xi} \longrightarrow$ blob relaxation time

$\tau_\xi : D_\xi \tau_\xi \sim \xi^2$

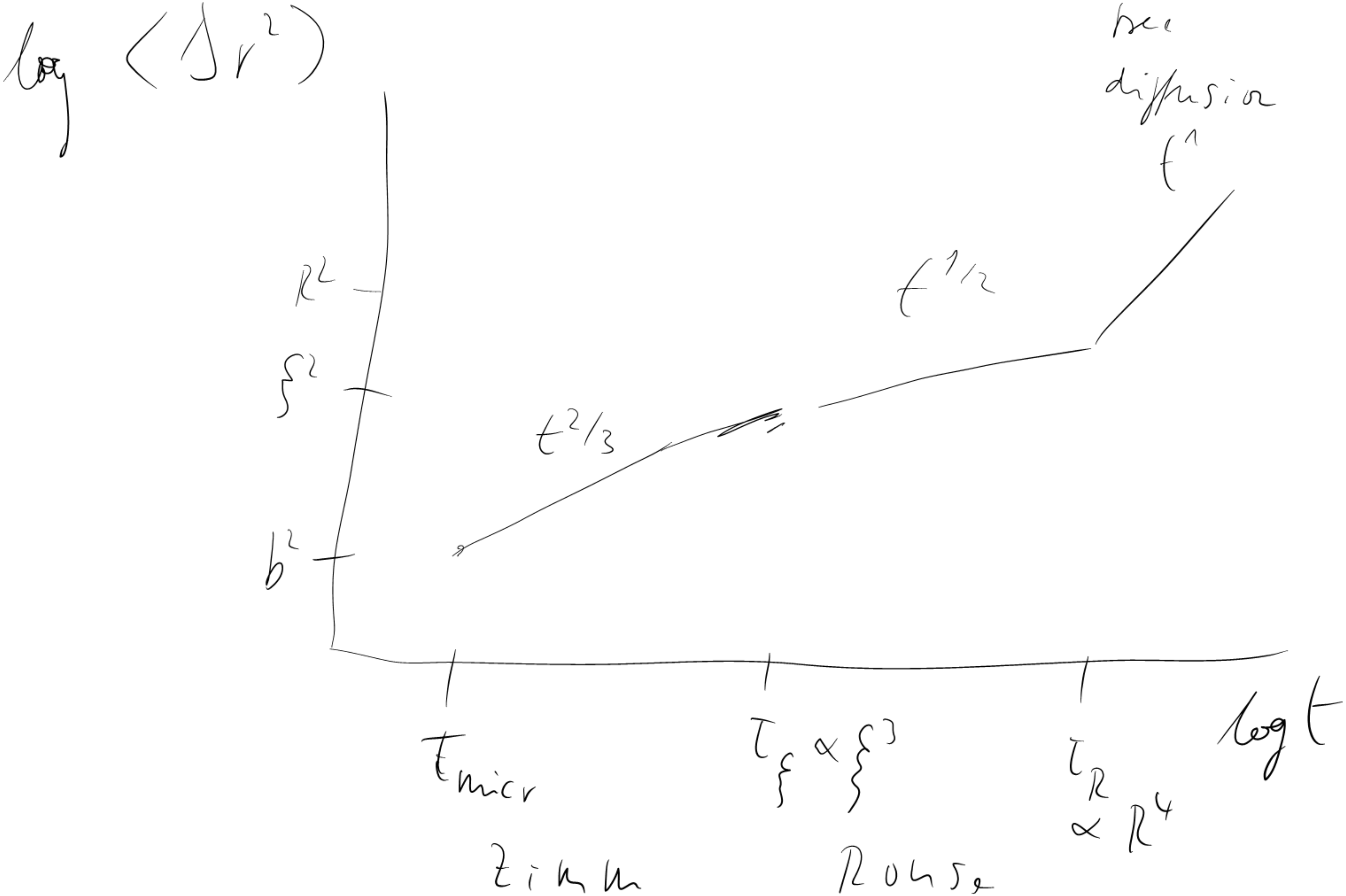
$\tau_\xi \sim \frac{\eta \xi^3}{k_B T}$

$\eta \equiv$ solvent viscosity

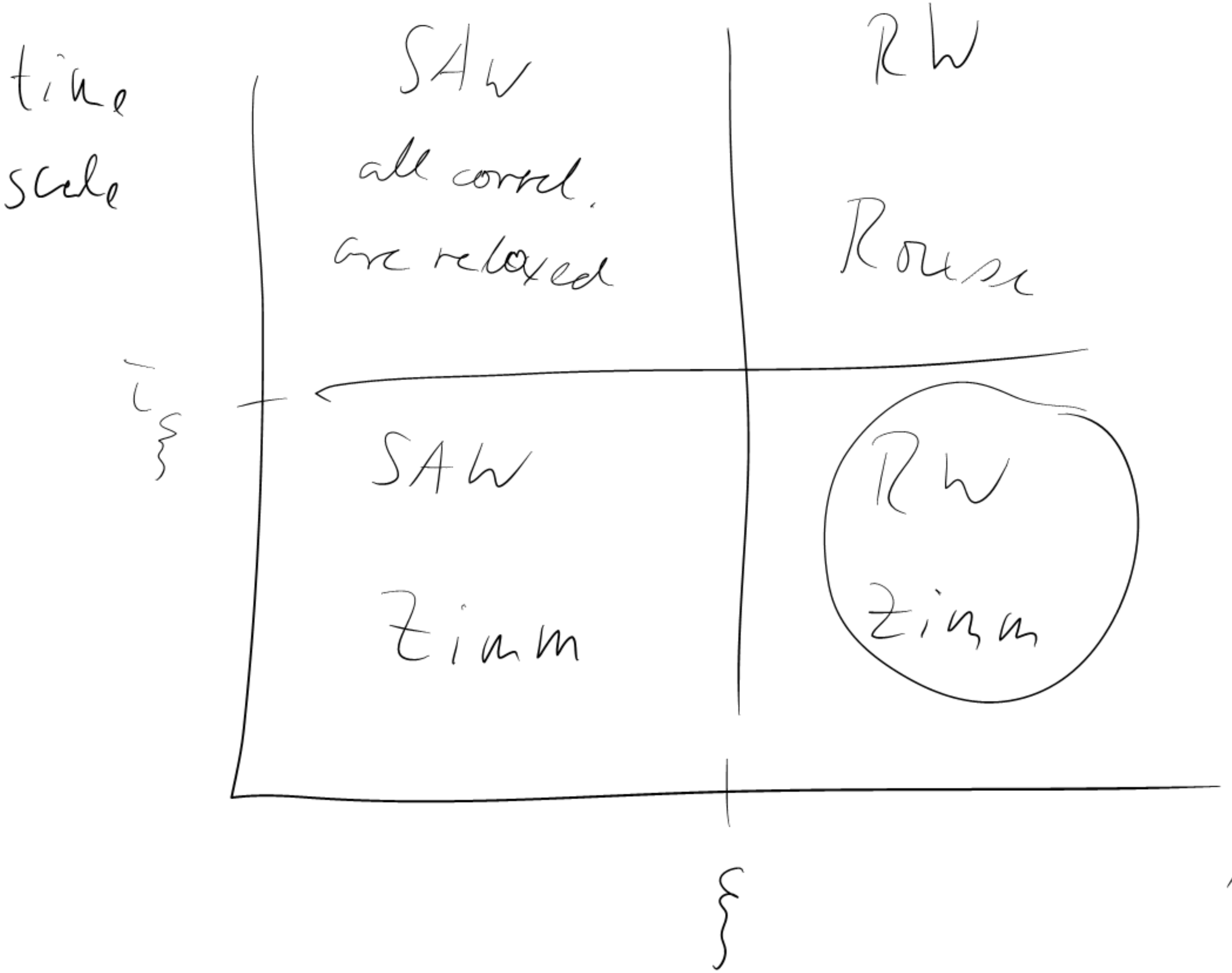
after τ_ξ: blob feels the presence of other chains, gets slowed down or "stuck"

"locked up in an elastic network"

randomization / screening becomes important $\longrightarrow$ Rouse-like motion



log ⟨Δr²⟩
free diffusion
t¹
t^{1/2}
t^{2/3}
R²
ξ²
b²
log t
t_micr
τ_ξ ∝ ξ³
τ_R ∝ R⁴
Zimm
Rouse



"incomplete screening" is a short-time effect!

P. Ahlrichs, R. Everaers, B.D.

PRE 2001

now look at

length $\gg \xi$ time $\gg t_\xi$ (Rouse)

try to find a simple phenomenological description of hydrodynamic correlations.

<u>expectation</u> : typical decay length of order ξ

$\rightarrow$ DARCY FLOW

idea: blob acts as an obstacle to flow

Stokes friction coeff.: $\eta \xi$

flow velocity $\vec{u} \rightarrow$ friction force $\vec{F} \propto \eta \xi \vec{u}$

force per unit volume $\sim \frac{\eta \xi \vec{u}}{\xi^3} \sim \frac{\eta}{\xi^2} \vec{u}$

$$\vec{\nabla} \cdot \vec{u} = 0$$

external force generates $\vec{u}$

$$\eta \vec{\nabla}^2 \vec{u} - \vec{\nabla} p - \frac{A\eta}{\xi^2} \vec{u} + \vec{F} \delta(\vec{r}) = 0$$

A: some numerical factor

Fourier: $-\eta k^2 \longrightarrow -\eta k^2 - \frac{A\eta}{\xi^2}$

$$\frac{1}{\eta k^2} \longrightarrow \frac{1}{\eta k^2 + \frac{A\eta}{\xi^2}} \qquad \varkappa^2 = \frac{A}{\xi^2}$$

$$\frac{1}{k^2} \longrightarrow \frac{1}{k^2 + \varkappa^2}$$

$$\mathrm{Tr}\, \breve{\mu} = \frac{1}{\eta \pi^2} \int_0^\infty dk \, \frac{k^2}{k^2 + \varkappa^2} \frac{\sin(kr)}{kr} =$$

$$= \frac{1}{4\pi^2 r} \int_0^\infty dx \, \frac{x^2}{x^2 + (\kappa r)^2} \, \frac{\sin x}{x} =$$

$$= \frac{1}{4\pi^2 r} \, \frac{\pi}{2} \, \exp(-\kappa r) =$$ Yukawa-like decay

$$= \frac{1}{2 \cdot 4\pi r} \exp(-\kappa r)$$

$$\kappa^2 = \frac{A}{\xi^2}$$

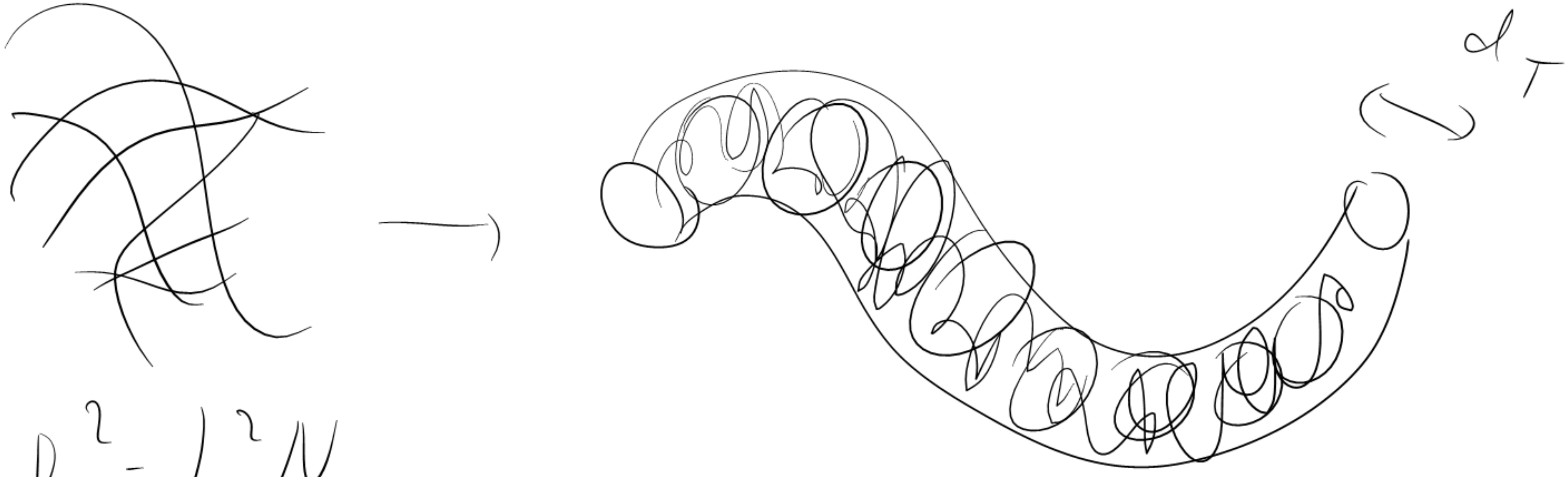
$$\kappa r = \frac{\sqrt{A}\, r}{\xi}$$

decay length of order ξ

5.8. Reptation ("reptile"-like motion)

(curvilinear motion)

- dense polymer melts
- long chains
- topological constraints
- isotropic motion (Rouse-like) in transversal direction is possible, but only up to certain length scale d_T ("tube diameter")



$R^2 = b^2 N$

tube is a RW

chain in the tube is a RW

$d_T^2 = b^2 N_e$ definition of N_e entanglement length

$N \ll N_e \to$ Rouse $\quad N \gg N_e$ reptation length of tube:

$$R_E \propto d_T \cdot \left(\frac{N}{N_e}\right)^{1/2} \propto N_e^{1/2} \cdot \left(\frac{N}{N_e}\right)^{1/2} \propto N^{1/2}$$

contour length:

$$d_T \cdot \frac{N}{N_e} \propto N_e^{1/2} \cdot \frac{N}{N_e} \propto \left(\frac{N^2}{N_e}\right)^{1/2}$$

reptation $\equiv$ 1D diffusion along the tube curvilinear diffusion coeff.

$$D_{curv} \propto \frac{1}{N}$$

longest relaxation time τ_d

"disengagement time"

(leave old tube, generate a new tube)

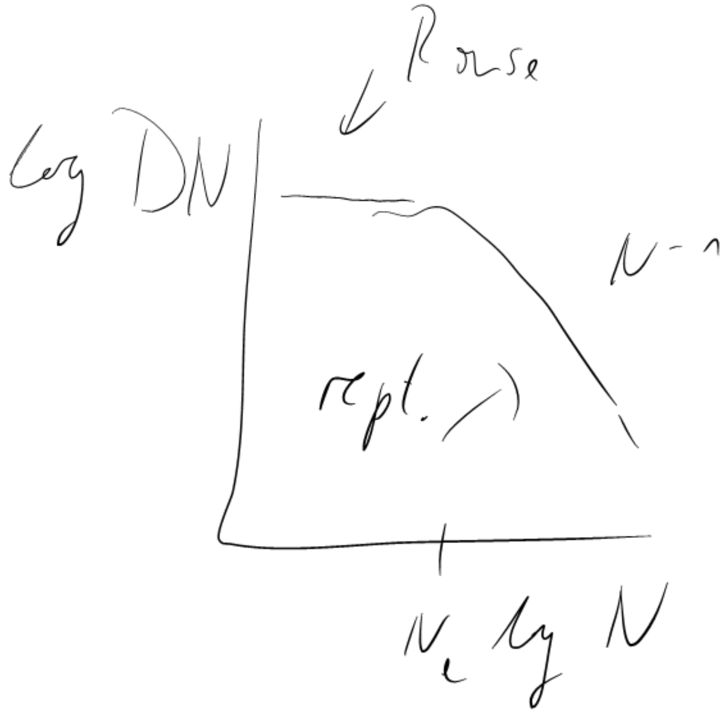
$$D_{curv}\, \tau_d \sim (\text{tube length})^2 \propto \frac{N^2}{N_e}$$

$$\tau_d \propto \frac{N^3}{N_e} \propto R^6 \qquad \underline{\underline{z = 6}}$$

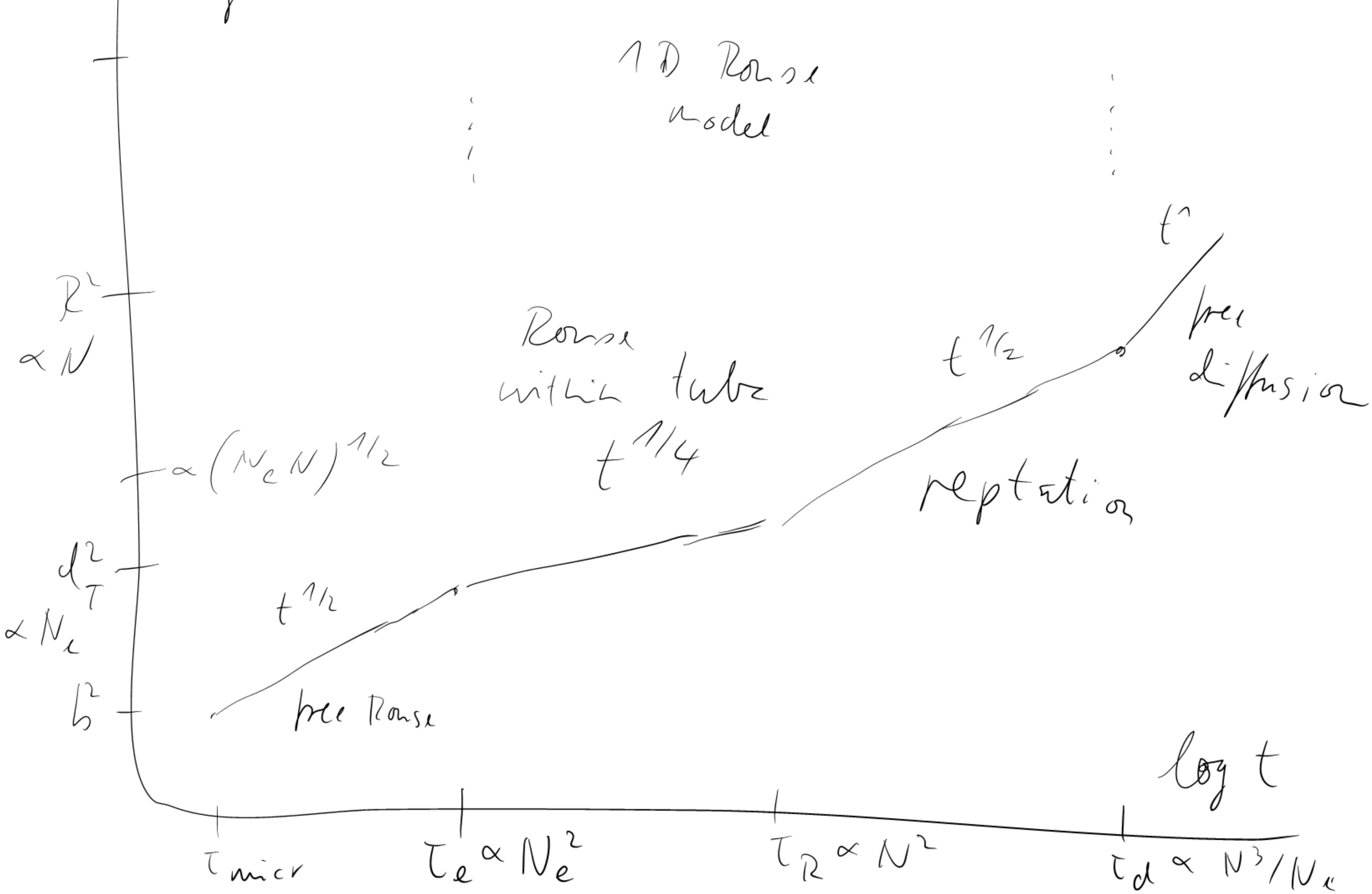
real space:

$$D \, \tau_d \sim R^2 \propto N$$

$$D \propto N \frac{N_e}{N^3} = \frac{N_e}{N^2}$$



τ_e: entanglement time



1d Rouse: $\langle \Delta r^2 \rangle_{curv} \propto \begin{cases} t^{1/2} & t \ll \tau_R \\ t^1 & t \gg \tau_R \end{cases}$

$$\langle \Delta r^2 \rangle_{real} \propto \sqrt{\langle \Delta r^2 \rangle_{curv}} \propto \begin{cases} t^{1/4} & t \ll \tau_R \\ t^{1/2} & t \gg \tau_R \end{cases}$$

tube is a RW

$$\frac{\langle \Delta r^2 \rangle \big|_{\tau_d}}{\langle \Delta r^2 \rangle \big|_{\tau_R}} \propto \left(\frac{\tau_d}{\tau_R} \right)^{1/2} \propto \left(\frac{N^3/N_e}{N^2} \right)^{1/2} \propto \left(\frac{N}{N_e} \right)^{1/2}$$

$$\langle \Delta r^2 \rangle \big|_{\tau_R} \propto \left(\frac{N_e}{N} \right)^{1/2} \underbrace{\langle \Delta r^2 \rangle \big|_{\tau_d}}_{\propto N} \propto \left(\frac{N_e}{N} \right)^{1/2} N = \left(N_e N \right)^{1/2}$$

THANK YOU
VERY MUCH FOR
YOUR ATTENTION
& CONTRIBUTIONS!