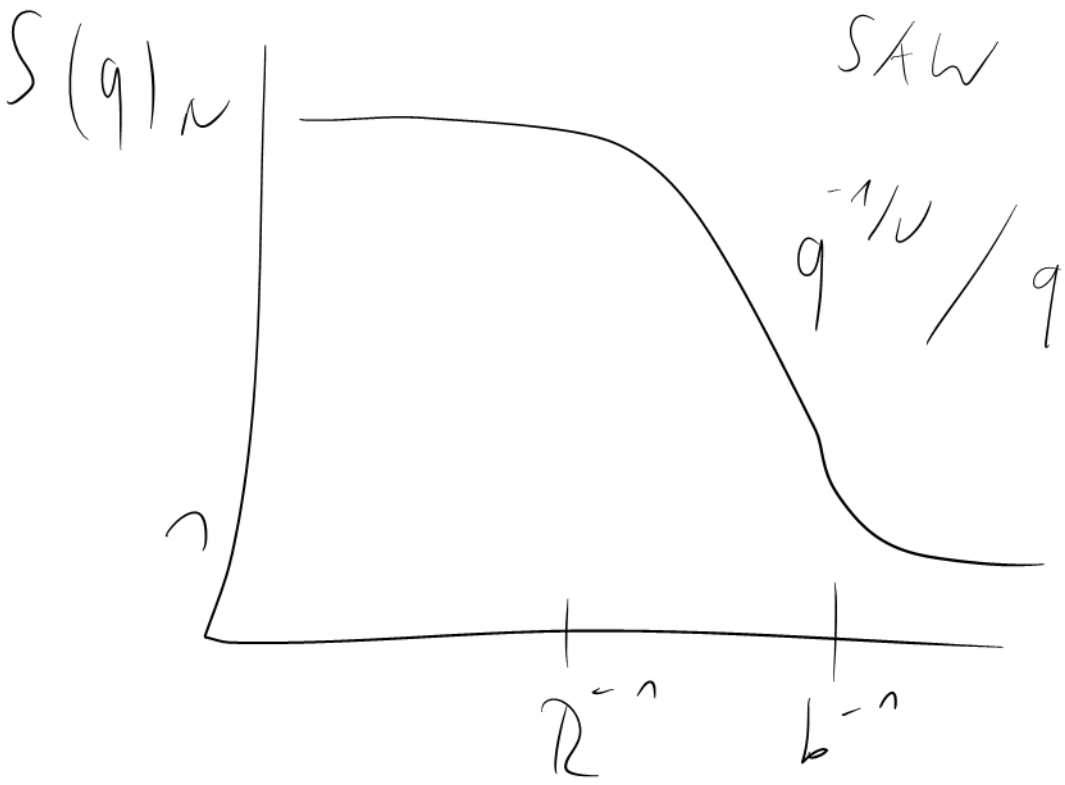
"Blobology"

"blob size" ξ: length scale BETWEEN b and R, and physically important

So far: only b and R were important



semidil. solutions

ξ^{-1}

reason for ξ:

→ interactions

↳ steric int.

↳ short-range attr.

↳ θ collapse

4.1. Semidilute Solutions

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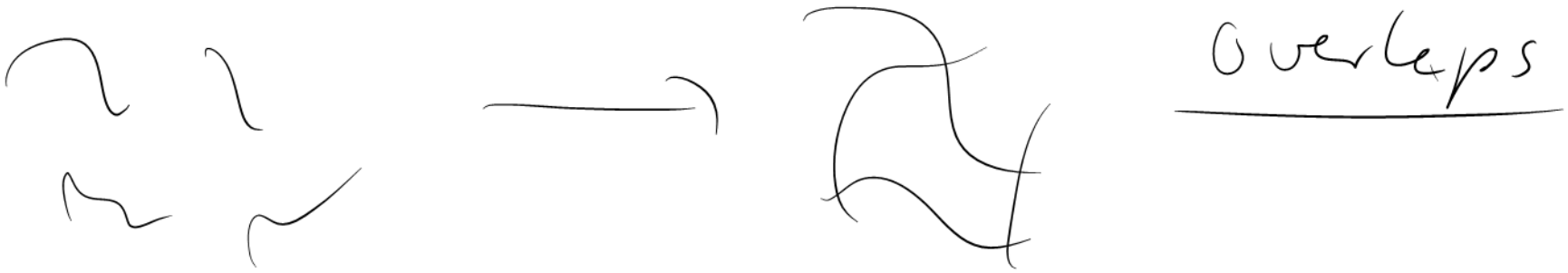
good solvent. Low concentrations:

isolated coils, structure: SAW: $R \sim b N^{\nu}$

$\nu \simeq 0.59$

increase concentration

($c \equiv$ # of monomers per unit volume)



Overlaps

Semidilute solution:

- c is very small
- chains are long → strong overlap

overlap concentration c^*: governs the crossover dilute ⟷ semidilute

At c^*, the arrangement of non-overlapping SAWs is just space-filling!

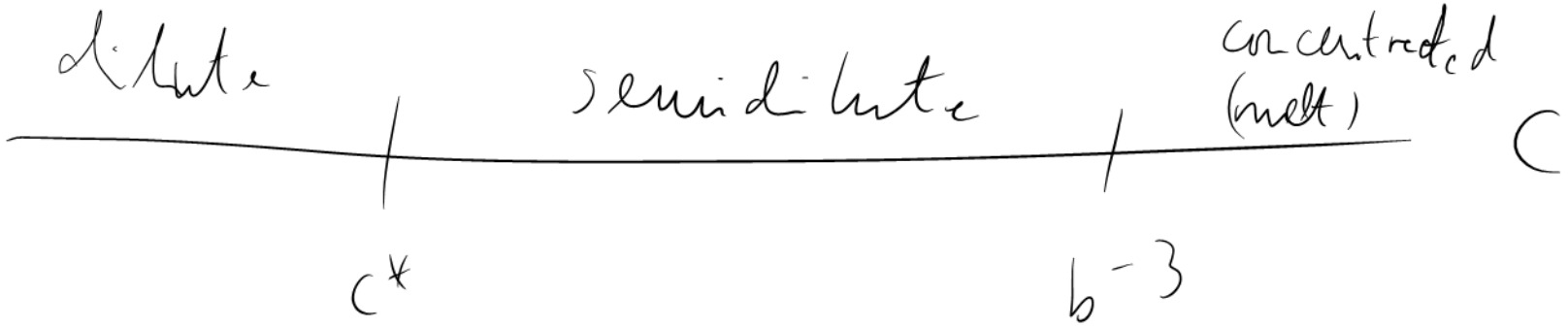
$$\Rightarrow \quad c^* \approx \frac{N}{(bN^\nu)^3}$$

ignore prefactors of order unity!

$$\sim b^{-3} N^{-(3\nu-1)} \sim b^{-3} N^{-0.77}$$

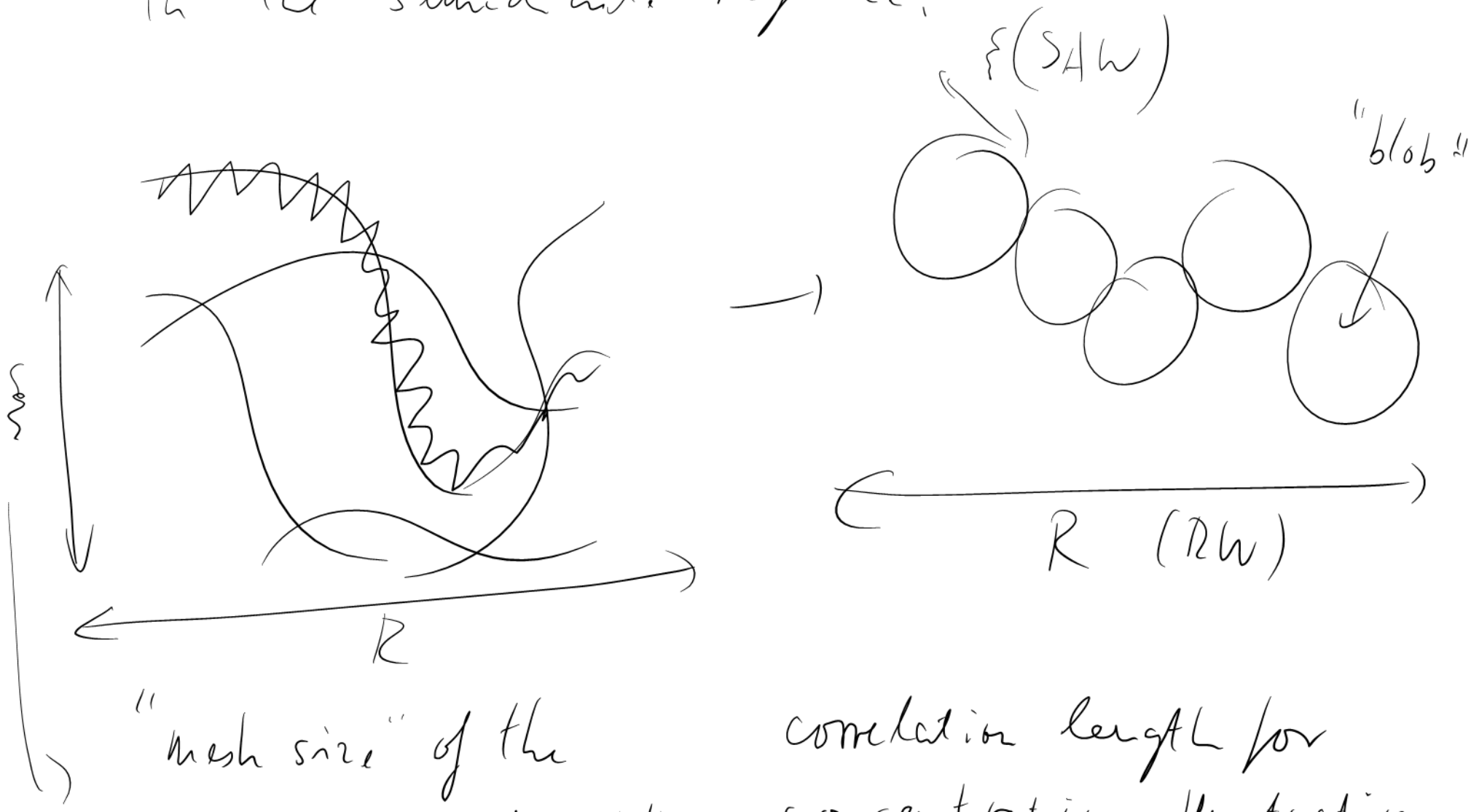
$$\ll b^{-3}$$

concentration of the dense melt



$b \ll \xi \ll R$

in the semidilut. regime:



"mesh size" of the "temporary network"

correlation length for concentration fluctuations

length scale $\ll \xi$: strong density fluctuations, SAW conformations

length scale $\gg \xi$: solution homogeneous, small density fluctuations

RW conformations

n : # of monomers within a blob

$$\xi \sim b\, n^{\nu} \qquad (SAW)$$

$\frac{N}{n}$: # of blobs

$$R \sim \xi \left(\frac{N}{n}\right)^{1/2} \qquad (RW)$$

$$c \sim \frac{n}{\xi^3} \sim \frac{n}{b^3 n^{3\nu}} = b^{-3}\, n^{-(3\nu-1)}$$

blobs are space-filling

$$\left(b^3 c\right)^{-\frac{1}{3\nu-1}} \sim n$$

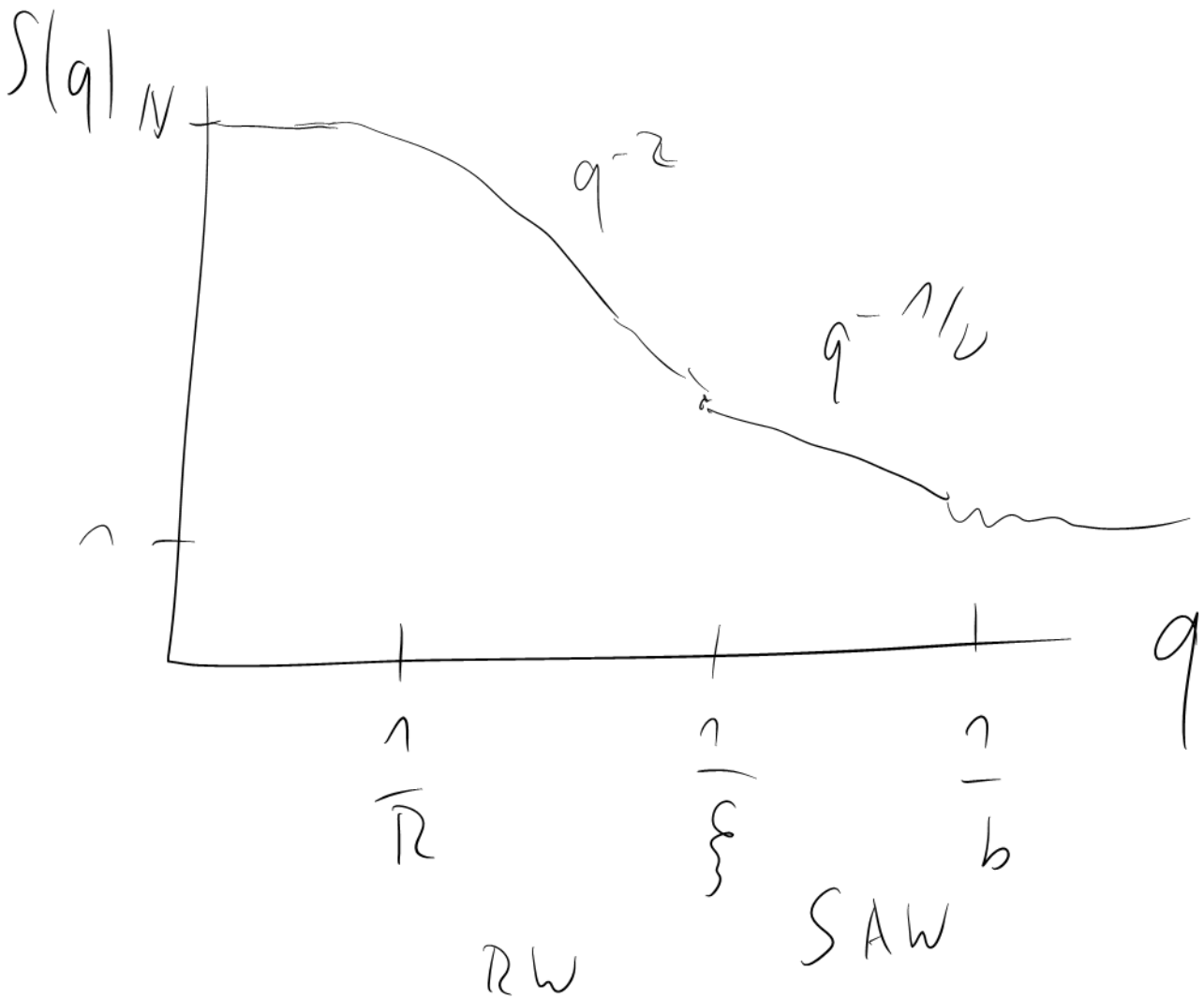
$$\xi \sim b h^{\nu} \sim b \left(b^3 c\right)^{-\frac{\nu}{3\nu-1}}$$

$$\propto c^{-\frac{\nu}{3\nu-1}} = c^{-0.77}$$

$$\eta \sim \xi \left(\frac{N}{h}\right)^{1/2} \sim b \left(b^3 c\right)^{-\frac{\nu}{3\nu-1}} N^{1/2} \left(b^3 c\right)^{+\frac{1}{2}\frac{1}{3\nu-1}}$$

$$\sim b N^{1/2} \left(b^3 c\right)^{-\frac{\nu-1/2}{3\nu-1}} \propto c^{-0.12}$$

structure factor:



Scaling: $S(q) = N f(qR, q\xi)$

in the regime $\frac{1}{R} \ll q \ll \frac{1}{b}$

$S(q)$ is <u>independent</u> of N

$N \longrightarrow \lambda N$

$\xi \longrightarrow \xi$ $\quad (c = \text{const.})$

$R \longrightarrow \lambda^{1/2} R$

$$N\, f(q\underbrace{R}_{x}, q\underbrace{\xi}_{y}) = \lambda N\, f(q\lambda^{1/2}R, q\xi)$$

$$f(x,y) = \lambda f(\lambda^{1/2}x, y) \qquad \lambda = x^{-2}$$

$$\lambda^{1/2} = x^{-1}$$

$$f(x,y) = x^{-2} f(1,y) \qquad \lambda^{1/2}x = 1$$

$$S(q) = N(qR)^{-2} g(q\xi)$$

crossover scaling function

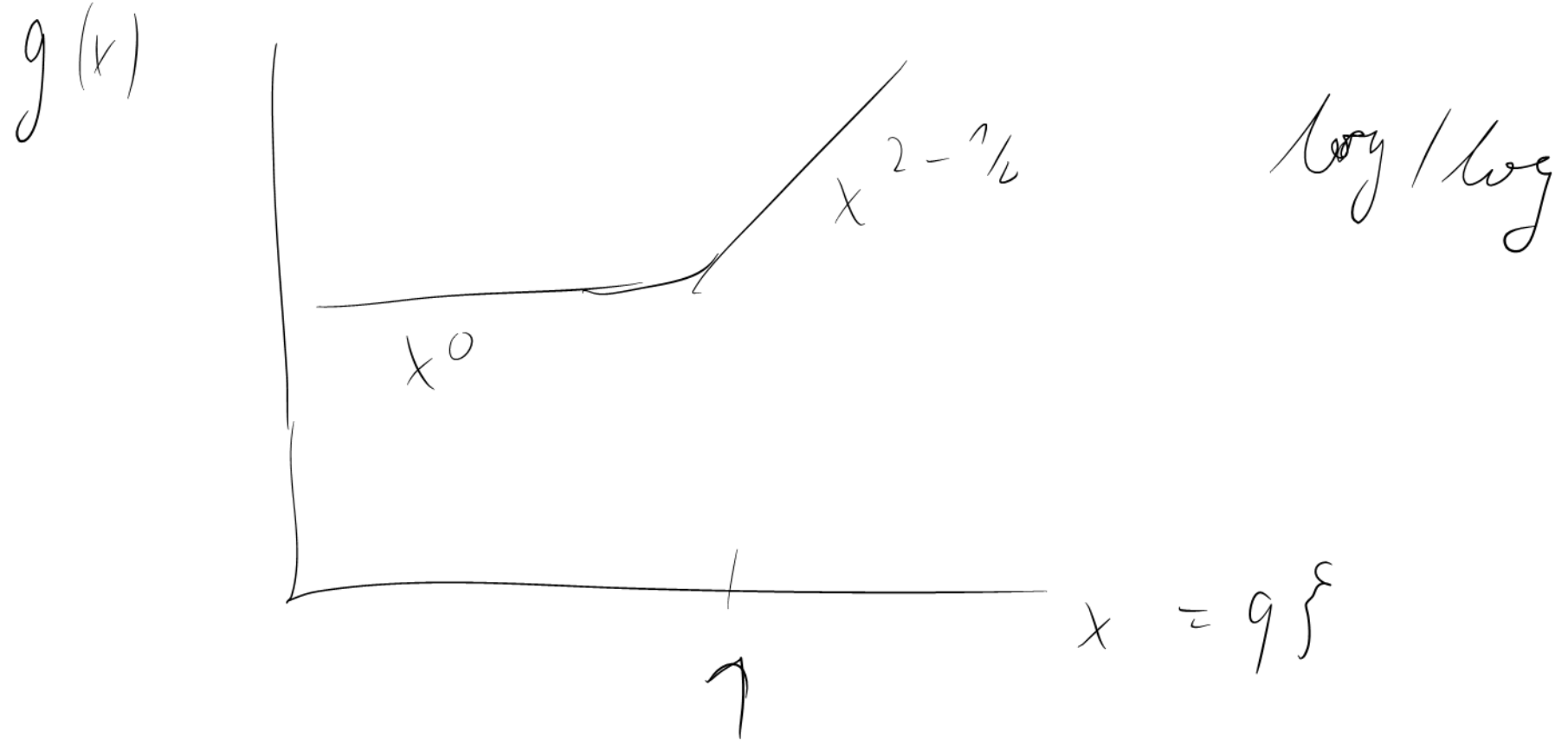
$$g(x) \sim \begin{cases} x^0 & x \ll 1 \quad (RW) \\ x^{2-1/\nu} & x \gg 1 \quad (fAW) \end{cases}$$

$$N (qR)^{-2} (q\xi)^{2-1/\nu}$$

$$\sim N q^{-2} R^{-2} q^2 q^{-1/\nu} \xi^{2-1/\nu}$$

$$\sim q^{-1/\nu} N \left(\frac{R}{\xi}\right)^{-2} \xi^{-1/\nu} \sim q^{-1/\nu} N \left(\frac{N}{n}\right)^{-1} \left(b n^{\nu}\right)^{-1/\nu}$$

$$\sim \underline{(bq)^{-1/\nu}}$$



W. Paul, K. Binder 90s

(bond fluctuation model)

Osmotic pressure

$c \ll c^*$ ideal gas of SAWs

van't Hoff law $\quad p = k_B T \frac{c}{N}$

for $c \gg c^*$: p <u>independent</u> of N !

Crossover scaling

$$p = k_B T \frac{c}{N} f\left(\frac{c}{c^*}\right)$$

crossover scaling fct.

$$c^* = b^{-3} N^{-(3\nu-1)}, \quad c/c^* = c b^3 N^{+(3\nu-1)}$$

$$f(x) \sim \begin{cases} x^0 & x \ll 1 \\ x^{\frac{1}{3\nu-1}} & x \gg 1 \end{cases}$$

$\hookrightarrow$ N dependence cancels!

for $c \gg c^*$:

$$p \sim k_B T \, c \left(c b^3\right)^{\frac{1}{3\nu-1}} \sim \frac{k_B T}{b^3} \left(c b^3\right)^{\frac{3\nu}{3\nu-1}} \sim$$

$$\sim \frac{k_B T}{\left[b \left(c b^3\right)^{-\nu/(3\nu-1)}\right]^3} \sim \frac{k_B T}{\xi^3}$$

"$k_B T$ per blob"

4.2. Theta Collapse

Single chain, start at good-solvent conditions:

$T \downarrow$, decrease solvent quality $\longrightarrow$

build up an effective attractive interaction between monomers

$\longrightarrow$ tends to compensate excluded volume !

→ there is a temperature $T = \Theta$

effective net interaction is

$$\begin{cases} \text{repulsive} & T > \Theta \\ 0 & T = \Theta \\ \text{attractive} & T < \Theta \end{cases}$$

$$R \propto \begin{cases} N^{\nu} & T \gg \Theta \quad \text{SAW} \\ N^{1/2} & T \simeq \Theta \quad \text{RW} \\ N^{1/3} & T \ll \Theta \end{cases}$$

compact globules

estimate the range of the Θ region

(N - dependent)

contacts in a RW chain $\sim N^{1/2}$

($d = 3$)

interaction per contact: $v(T) \sim k_B(T - \Theta)$

chain will remain Gaussian if

$$|v(T)\, N^{1/2}| \ll k_B T \sim k_B \Theta$$

$$\left| \frac{T}{\theta} - 1 \right| N^{1/2} \ll 1$$

$$\tau := \frac{T}{\theta} - 1$$ normalized distance from the transition point

$$|\tau| N^{1/2} \ll 1 \qquad N \ll |\tau|^{-2}$$

Suppose, $|\tau| \ll 1$ (close to θ)

but $N \gg |\tau|^{-2}$

assume $\tau > 0$ (moderately good solvent)

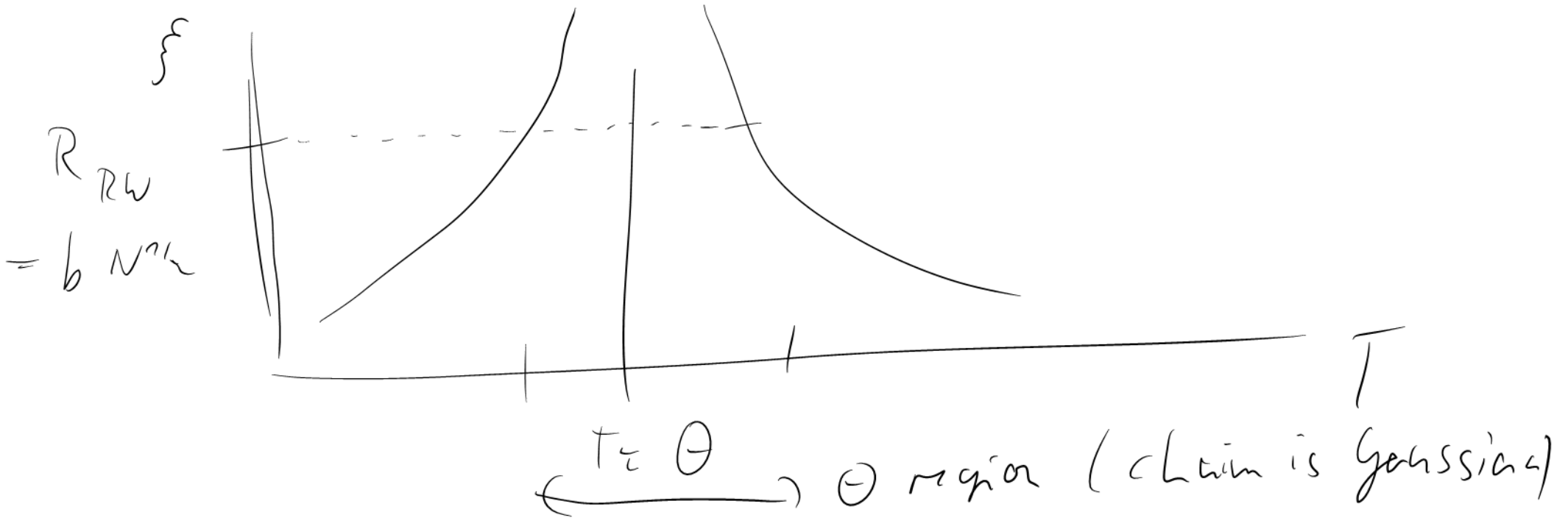
→ asymptotically $R \propto N^{\nu}$

within the "thermal blob", the net repulsion is buried under thermal fluctuations!

$\xi \sim b\, n^{\nu/2}$ $\quad$ n # of monomers in the blob

$n \sim \tau^{-2} \Rightarrow \xi \sim b\, \tau^{-\nu}$

$\underline{\tau < 0}$: $n \sim |\tau|^{-2}$, $\xi \sim b\, |\tau|^{-\nu}$



Crossover scaling:

$$\eta = b N^{1/2} \tilde{f}\left(\frac{N^{1/2}}{n^{1/2}}\right)$$

$$= b N^{1/2} f\left(N^{1/2} \tau\right)$$

Crossover scaling function

$$f(x) \propto \begin{cases} x^{2\nu-1} & x \gg 1 \\ x^{0} & x = 0 \\ |x|^{-1/3} & |x| \gg 1 \end{cases} \qquad \begin{matrix} |x| \\ \ll 1 \end{matrix}$$

$x < 0$

$x = N^{1/2} \tau$

$\xi = b \tau^{-1}$

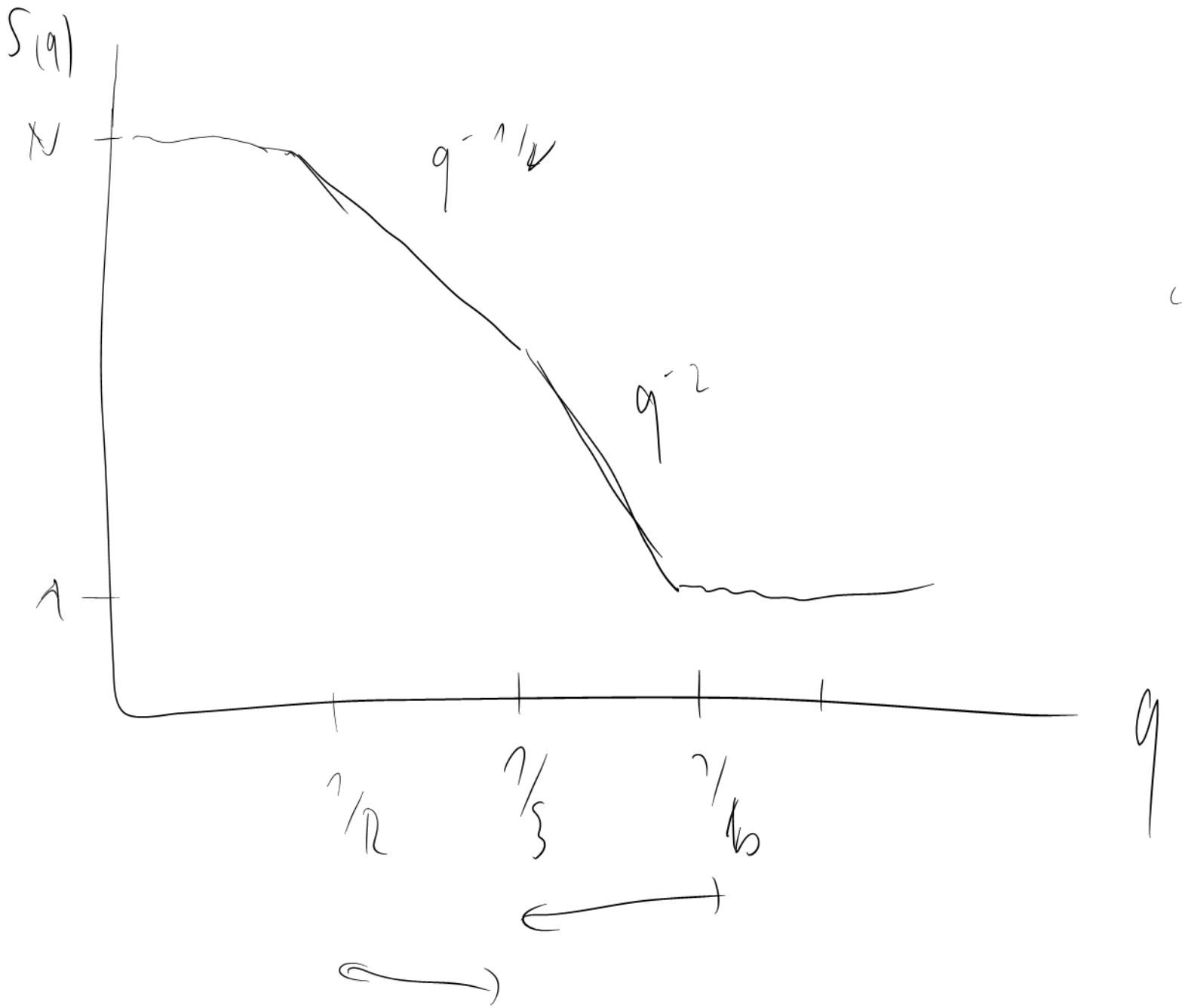
$R_{RW} = b N^{1/2}$

$\tau = b/\xi$

$bx = b N^{1/2} \tau = R_{RW} \tau$

$= R_{RW} \frac{b}{\xi}$

$x = \frac{R_{RW}}{\xi}$


S(q)
N
1
$q^{-1/\nu}$
q^{-2}
q
π/R
π/ξ
π/b