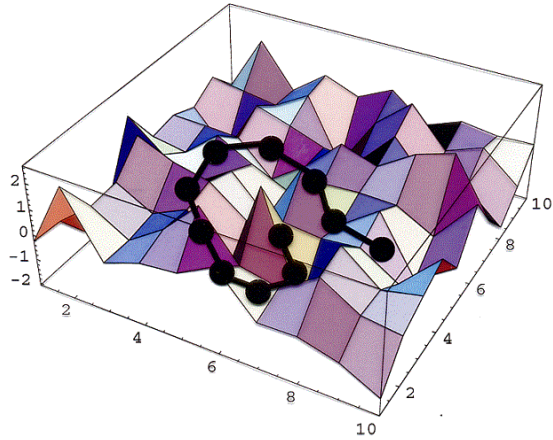


Polymers in Random Media

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Part of this work has been done in collaboration
with **Yohannes Shiferaw** and **Sandeep Tyagi**

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Published work

Y. Y. Goldschmidt, Phys. Rev. E61, 1729 (2000);

Y. Shiferaw and Y. Y. Goldschmidt, Phys. Rev. E63, 051803 (2001)

Y. Y. Goldschmidt and Y. Shiferaw, Eur.Phys.J. B 25,351 (2002), ibid 32, 87 (2003)

Y. Y. Golschmidt, Phys. Rev. B 56, 2800 (1997)

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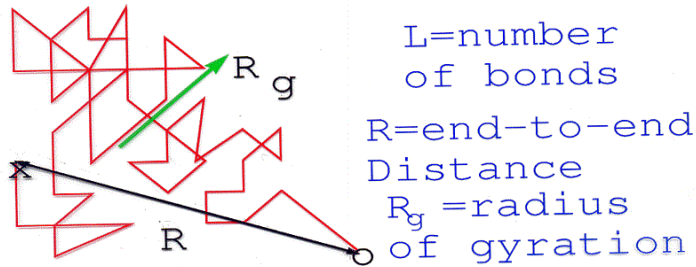
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Some properties of polymers

A polymer chain: A very long molecule consisting of a large number L of monomers:



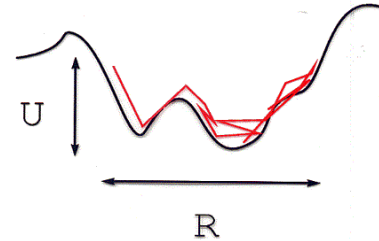
Neglecting excluded volume effects, the chain behaves as if it is the trajectory of a random walker (e.g. a drunken sailor) starting at a given point in space and propagating L steps of length b each.



A chain as a random walk.

$$\langle R^2 \rangle = L b^2$$

When a gaussian random potential is present, a very long chain will typically curl up in some small region of low potential energy.



Main results:

For a system of volume \mathcal{V} in d dimensions and a gaussian random potential of strength g , the end-to-end distance of a chain that is free to move is given, for large L , by:

$$R \sim (g \ln \mathcal{V})^{-1/(4-d)}, \quad 1 \leq d < 4$$

Independent of L !

The depth of the well entrapping the chain is

approximately

$$U_{min} \sim -(g \ln \mathcal{V})^{2/(4-d)}.$$

Note that the annealed and quenched results are different. In the annealed case the polymer collapses to a point. The annealed result is argued to apply in the quenched case for a system of infinite volume.

- Previously advocated by Cates and Ball, Nattermann and Renz, using Flory arguments. J. Phys. (France) **89**, 2435 (1988); Phys. Rev. A **40**, 4675 (1989)
- Y. Y. Goldschmidt: Derived from first principles using the Replica technique with one-step breaking. Phys. Rev. E61, 1729 (2000)
- Y. Shiferaw and Y. Y. Goldschmidt: Have derived the results from the localization of a quantum particle in a random medium and have given physical interpretation to the replica calculation. Brought together two apparently disparate fields of polymers

and quantum particles in random media.
Phys. Rev. E63, 051803 (2001)

The gaussian chain in a random potential

To define the model of a polymer chain in a random potential plus a fixed harmonic potential we use the Gaussian chain approximation to write:

$$H = \int_0^L du \left[\frac{dk_B T}{2b^2} \left(\frac{\partial \mathbf{R}(u)}{\partial u} \right)^2 + \frac{\mu}{2} \mathbf{R}^2(u) + V(\mathbf{R}(u)) \right],$$

where $\mathbf{R}(u)$ is the d -dimensional position vector of the chain at arc-length u ($0 \leq u \leq L$),

$L \rightarrow$ proportional to the number of monomers.

μ governs the strength of the harmonic potential. It is introduced to induce a finite volume for the system instead of hard walls of a box.

$V(\mathbf{R})$ is the random potential satisfying:

$$\langle V(\mathbf{R}) \rangle = 0, \quad \langle V(\mathbf{R})V(\mathbf{R}') \rangle = g \delta^{(d)}(\mathbf{R} - \mathbf{R}').$$

The partition sum (Green's function) is given by the

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functional integral

$$Z(\mathbf{R}, \mathbf{R}', L, \beta) = \int_{\mathbf{R}(0)=\mathbf{R}}^{\mathbf{R}(L)=\mathbf{R}'} \mathcal{D}\mathbf{R}(u) \exp(-\beta H).$$

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A quantum particle at finite temperature

The polymer problem can be mapped into that of a quantum particle in a random potential + a harmonic potential. The **density matrix** for a quantum particle in such a potential at a finite temperature $T = 1/k\beta$ reads:

$$\rho(\mathbf{R}, \mathbf{R}', \beta) = \int_{\mathbf{R}(0)=\mathbf{R}}^{\mathbf{R}(\hbar\beta)=\mathbf{R}'} \mathcal{D}\mathbf{R}(u) \exp\left(-\frac{1}{\hbar}S\right).$$

with

$$S = \int_0^{\hbar\beta} du \left[\frac{m}{2} \left(\frac{\partial \mathbf{R}(u)}{\partial u} \right)^2 + \frac{\mu}{2} \mathbf{R}^2(u) + V(\mathbf{R}(u)) \right],$$

with the variable u representing the imaginary time. The mapping from a quantum particle of mass m at a finite temperature $1/\beta$ to a polymer chain is given by

$$\hbar \rightarrow kT, \quad \hbar\beta \rightarrow L, \quad m \rightarrow dkT/b^2$$

From this mapping we learn that for the polymer problem too we can consider solutions of the

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Schrödinger equation in imaginary time. Thus:

$$Z(\mathbf{R}, \mathbf{R}'; L) = \langle \mathbf{R} | \exp(-\beta L \hat{H}) | \mathbf{R}' \rangle,$$

where

$$\hat{H} = -\frac{1}{2M\beta^2} \frac{\partial^2}{\partial \hat{\mathbf{R}}^2} + \frac{\mu}{2} \hat{\mathbf{R}}^2 + V(\hat{\mathbf{R}}).$$

We compute the matrix element by expanding it in terms of the energy eigenstates of \hat{H}

$$Z(\mathbf{R}, \mathbf{R}'; L) = \sum_m \exp(-\beta L E_m) \Phi_m(\mathbf{R})^* \Phi_m(\mathbf{R}').$$

Thus knowing the structure of eigenfunctions and eigenvalues of the Schrödinger equation in a random potential enables us to solve the polymer problem. There are many known results from the study of electron localization, but they have to be somewhat modified for a system of finite size.

In a finite volume there is always a lowest energy even for a gaussian random potential. The lowest

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energy states dominate the partition sum for large L .
Localized states are given by

$$\phi(\mathbf{R}) \sim \exp(-|\mathbf{R} - \mathbf{R}_m|/\ell_m)$$

where the localization length ℓ_m is related to the energy of the state E_m by

$$\ell_m \sim 1/\sqrt{|E_m|}$$

We can study eigenfunction properties in $d=1$ by solving the Schrödinger equation on a lattice. Random potential with short range correlations is generated numerically.

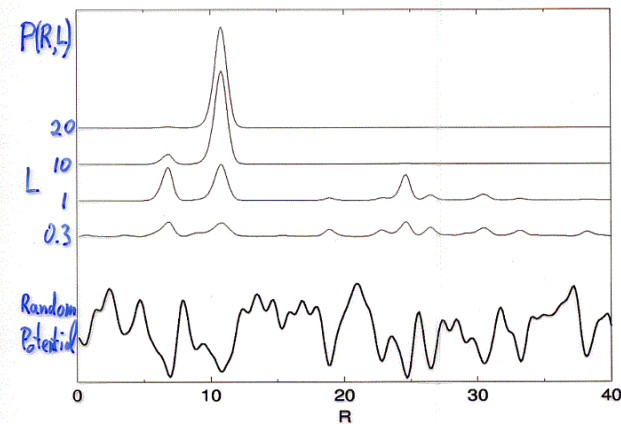
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How eigenfunctions affect chain properties

Probability of finding a polymer loop passing through a point \mathbf{R} :

$$P(\mathbf{R}, L) = \frac{Z(\mathbf{R}, \mathbf{R}, L)}{\int d\mathbf{R}' Z(\mathbf{R}, \mathbf{R}', L)}$$

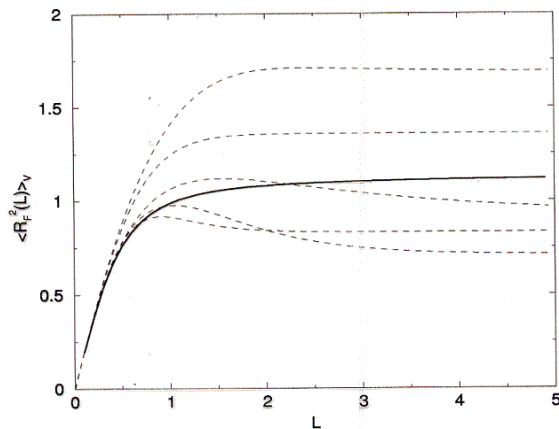
As L is increased the chain is more likely to be located near the minima of the potential which coincide with the position of the low lying localized states.



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The average end-to-end distance

- Short L : $\overline{\langle \mathbf{R}_F^2(L) \rangle} \sim L$: Simple diffusion, extended states dominance
- Long L : $\overline{\langle \mathbf{R}_F^2(L) \rangle} \sim \text{constant}$: Localization, ground state dominance



Localized state dominance is associated with glassy behavior and large sample to sample fluctuations.

Derivation of the end-to-end distance from the density of states

Density of states for a gaussian random potential $\rho(E)$ of strength g :

$$\rho(E) \propto \exp(-(B/g)|E|^\delta),$$

with $\delta = (4 - d)/2$ (Lifshits, Halperin...) This is for an infinite volume.

For a finite volume \mathcal{V} we can estimate the lowest energy E_0 from the tail of the distribution:

$$\int_{-\infty}^{E_0} dE \exp(-(1/g)|E|^\delta) \approx 1/\mathcal{V},$$

which gives

$$E_0 = -(g \log \mathcal{V})^{1/\delta}$$

Thus the localization length l_0 associated with the ground state (and also the end-to-end distance of a chain) is given by

$$l_0 \sim 1/\sqrt{|E_0|} \sim (g \log \mathcal{V})^{-1/(2\delta)}$$

The replica method and variational approximation

In order to average over the quenched random potential we use the replica method.

The replica trick:

$$-\beta \bar{F} = \overline{\ln(Z)} = \lim_{n \rightarrow 0} \frac{\overline{Z^n - 1}}{n}.$$

$\overline{Z^n}$ can be evaluated by introducing n identical copies (replicas) of the system and then averaging over the random potential.

After introducing n -copies of the chain and averaging over the random potential one obtains

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$$\langle Z^n \rangle = \int \mathcal{D}\mathbf{R}_1 \cdots \mathcal{D}\mathbf{R}_n \exp(-\beta H_n),$$

with

$$H_n = \int_0^L du \sum_{a=1}^n \left[\frac{M}{2} \left(\frac{\partial \mathbf{R}_a(u)}{\partial u} \right)^2 + \frac{\mu}{2} \mathbf{R}_a^2(u) \right] - \frac{\beta g}{2} \int_0^L du \int_0^L du' \sum_{ab} \delta^{(d)}(\mathbf{R}_a(u) - \mathbf{R}_b(u')).$$

which is a peculiar form of n -body interactions. We have to obtain an approximate analytical solution valid for general n and then take the limit of $n \rightarrow 0$.

In order to proceed we use a quadratic variational Hamiltonian to be the best approximation to H_n . This is given by [Y.Y.G., Phys. Rev. E 61, 1729 (2000)]

$$h_n = \int_0^L du \sum_{a=1}^n \left[\frac{M}{2} \left(\frac{\partial \mathbf{R}_a(u)}{\partial u} \right)^2 + \frac{\mu}{2} \mathbf{R}_a^2(u) \right] - \frac{1}{4L} \int_0^L du \int_0^L du' \sum_{ab} p_{ab} (\mathbf{R}_a(u) - \mathbf{R}_b(u'))^2,$$

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where the $n \times n$ matrix p_{ab} is to be determined variationally with $n \rightarrow 0$ at the end. It is determined from the stationarity of the variational free energy which is given by:

$$n \langle F \rangle_R = \langle H_n - h_n \rangle_{h_n} - \frac{1}{\beta} \ln \int \mathcal{D}\mathbf{R}_1 \cdots \mathcal{D}\mathbf{R}_n \exp(-\beta h_n).$$

Our parametrization of h_n preserves an important translational symmetry of H_n in the limit $\mu \rightarrow 0$ (the large volume limit), which is given by

$$\mathbf{R}_a(u) \rightarrow \mathbf{R}_a(u) + \mathbf{C}, \quad a = 1, \dots, n$$

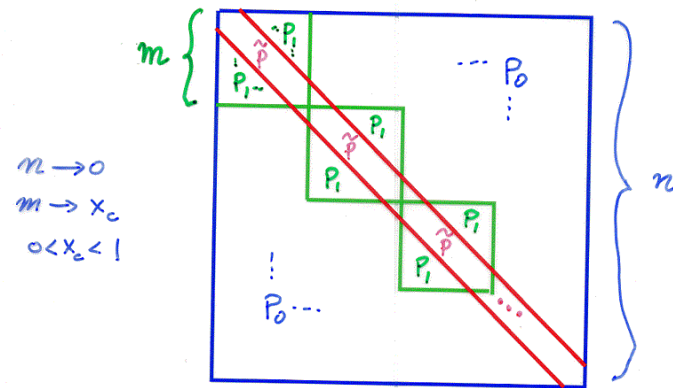
This symmetry has been explicitly broken by the one parameter choice of Edwards and Muthukumar who used for the infinite volume case

$$h_n = \int_0^L du \sum_{a=1}^n \left[\frac{M}{2} \left(\frac{\partial \mathbf{R}_a(u)}{\partial u} \right)^2 + q^2 \mathbf{R}_a^2(u) \right]$$

Preserving this symmetry is crucial for the correct solution of the problem and obtaining the $\log V$ dependence of the radius of gyration.

The 1-step replica symmetry breaking ansatz

With replica symmetry breaking we have two more parameters:



The $n \rightarrow 0$ can be taken to yield a variational free energy $F(\tilde{p}, p_0, p_1, x_c)$, where the size of the diagonal blocks m becomes an additional variational parameter x_c ($0 < x_c < 1$). The stationarity of the free energy yields four coupled non-linear equations for the four

variational parameters. In the limit of small μ (large volume) and long chains (L large) these equations were solved analytically.

Denoting

$$\lambda = \mu - \tilde{p} + (1 - x_c)p_1 + x_cp_0,$$

we find

$$\lambda \sim (g |\ln \mu|)^{4/(4-d)}.$$

From this final result we obtain the radius of gyration

$$\begin{aligned} R_g &\sim \lambda^{-1/4} \sim (g |\ln \mu|)^{-1/(4-d)} \\ &\sim (g \ln V)^{-1/(4-d)}. \end{aligned}$$

For any value of μ and L the equations could be solved numerically.

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Physical interpretation of the 1-step RSB solution

Interpretation of the 1-step RSB in terms of exponentially localized tail states. The following analysis is valid for a very long polymer (large L) when the system becomes glassy. What is the interpretation of the 1-step replica solution? Recall from the Schrödinger equation

$$P(\mathbf{R}) = \frac{Z(\mathbf{R}, \mathbf{R}, L)}{\int d\mathbf{R} Z(\mathbf{R}, \mathbf{R}, L)} = \sum_{\alpha} A_{\alpha} |\Phi_{\alpha}(\mathbf{R})|^2,$$

where

$$A_{\alpha} = \frac{\exp(-\beta L E_{\alpha})}{\sum_{\gamma} \exp(-\beta L E_{\gamma})}.$$

This agrees with the interpretation of the replica solution as a sum over "states" provided we identify

$$\Phi_{\alpha}^2(\mathbf{R}) \propto \exp\left(-\frac{(\mathbf{R} - \mathbf{R}_{\alpha})^2}{2(\tilde{q} - q_1)}\right).$$

and \mathbf{R}_{α} are an infinite set of uncorrelated random

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variables distributed according to

$$\mathcal{P}(\mathbf{R}_1, \mathbf{R}_2, \dots) = \prod_{\alpha} \frac{1}{(2\pi(q_1 - q_0))^{d/2}} \exp\left(-\frac{(\mathbf{R}_{\alpha} - \mathbf{R}_0)^2}{2(q_1 - q_0)}\right)$$

with \mathbf{R}_0 being picked from the distribution

$$\mathcal{P}(\mathbf{R}_0) = \frac{1}{(2\pi q_0)^{d/2}} \exp\left(-\frac{\mathbf{R}_0^2}{2q_0}\right).$$

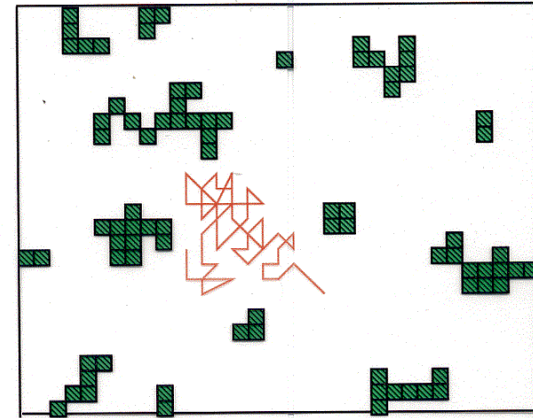
\tilde{q} , q_0 and q_1 are related to \tilde{p} , p_0 and p_1 of the 1-step RSB solution. Hence, the "states" labeled by α are in our case the actual eigenstates of the Schrödinger equation. These are localized tail states centered at position \mathbf{R}_{α} with an associated "weight" A_{α} . Thus the 1-step RSB solution approximates the tail states by a fixed Gaussian form of constant width w_0 .

The exponential distribution of energies as governed by x_c is consistent with the density of states in the tail in the vicinity of E_0

$$\rho(E) \sim \exp((1/g)|E_0|^{\delta-1}E) \sim \exp(x_c L E).$$

$$\text{RSB: } x_c \sim \frac{1}{L} (g^2 |\ln \mu|^{d-2})^{\frac{1}{4-d}}$$

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Random Obstacles

Let

x = Probability that a site is occupied by an obstacle

An obstacle prevents the chain to visit the site (volume a^d). We will measure all lengths in units of a which is also taken to be the chain's mean monomer size. Assume that the chain is occupying a spherical region (lacuna) of volume R^d . In this region the actual volume fraction of obstacles will be denoted by \hat{x} . This is a fluctuating quantity which occurs with probability $b(R^d \hat{x}; R^d, x)$, where

$$b(k; n, p) = \binom{n}{k} p^k (1-p)^{n-k},$$

denotes the binomial probability distribution.

In the limit where the system has infinite volume \mathcal{V} the free energy for the chain is given by

$$F(R, \hat{x}) = -L \ln(z) + \frac{L}{R^2} + L\hat{x} - \ln[b(R^d \hat{x}; R^d, x)],$$

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All these terms originate from entropy $F = -TS$ where for simplicity we take $T = 1$ since the temperature does not play a significant role here with respect to the results. This free energy for $\mathcal{V} \rightarrow \infty$ is called the annealed free energy since when the polymer can sample the entire space it is the same as the random potential adjusting itself to the polymer configuration. The free energy has to be minimized (the entropy maximized) with respect to R and \hat{x} . The most favorable value of \hat{x} is 0. Since $b(0; R^d, x) = (1-x)^{R^d}$, we find

$$F(R) = -L \ln(z) + \frac{L}{R^2} - R^d \ln(1-x).$$

This free energy has now to be minimized with respect to R to yield

$$R_{m,annealed} \sim \left(\frac{L}{|\ln(1-x)|} \right)^{1/(d+2)}.$$

Thus the size of the chain grows with L , but with an exponent smaller than $1/2$, the free chain exponent.

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Summary of results for the obstacle case

Region I $\mathcal{V} < \mathcal{V}_1 \simeq \exp(x^{-(d-2)/2})$

$$R_{mI} \sim (x \ln \mathcal{V})^{-1/(4-d)}$$

Region II $\mathcal{V}_1 < \mathcal{V} < \mathcal{V}_2 \sim \exp(x^{2/(d+2)} L^{d/(d+2)})$

$$R_{mII} \sim \left(\frac{\ln \mathcal{V}}{|\ln(1-x)|} \right)^{1/d}$$

region III $\mathcal{V}_2 < \mathcal{V}$

$$R_m \sim \left(\frac{L}{|\ln(1-x)|} \right)^{1/(d+2)}$$

In Region I one can approximate the binomial distribution by a gaussian distribution, and hence the results agree with the gaussian random potential case.

The behavior in region II can be deduced from known results of the density of states for a

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quantum particle in the presence of obstacles (repulsive impurities). In that case (Lifshits) the density of states is given by (when the obstacles are placed on a lattice)

$$\rho(E) \sim \exp(-c|\ln(1-x)|E^{-d/2}), \quad E > 0$$

with c being some dimension dependent constant and x is the density of impurities. Note that $\rho(E)$ vanishes for $E < 0$. We can estimate the lowest energy in a finite volume \mathcal{V} from the integral

$$\int_0^{E_c} dE \rho(E) \simeq 1/\mathcal{V},$$

and find

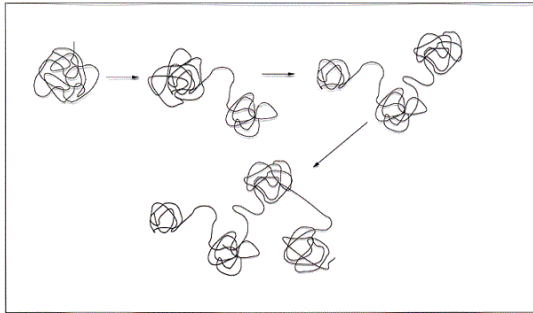
$$E_c \sim \left(\frac{\ln \mathcal{V}}{|\ln(1-x)|} \right)^{-2/d},$$

and thus the localization length is given by

$$\ell_c \sim |E_c|^{-1/2} \sim \left(\frac{\ln \mathcal{V}}{|\ln(1-x)|} \right)^{1/d}$$

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Excluded Volume



Two parameters: g - variance of random potential;
 v - strength of self-avoidance

Conformation of chains consists of many "blobs" with connecting segments. As L increases the first blob "overflows" and there is "hopping" to another deep minimum. Competition between length of connecting segment and probability to find a deep minimum nearby. We evaluated average number of monomers in a blob and length and number of monomers in connecting segments. For $g \gg v$, chain still attached to a given region of space.

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The free energy per monomer:

$$\frac{F(w, m, Y; L)}{L} \approx \frac{1}{w + m} \left(\frac{Y^2}{m} + \frac{m}{Y^2} + \frac{vm^2}{Y^3} - wG(Y^3)^2 + vw^2G(Y^3)^3 \right).$$

w - the number of monomers in each blob,

m - the number of monomers in each connecting segment.

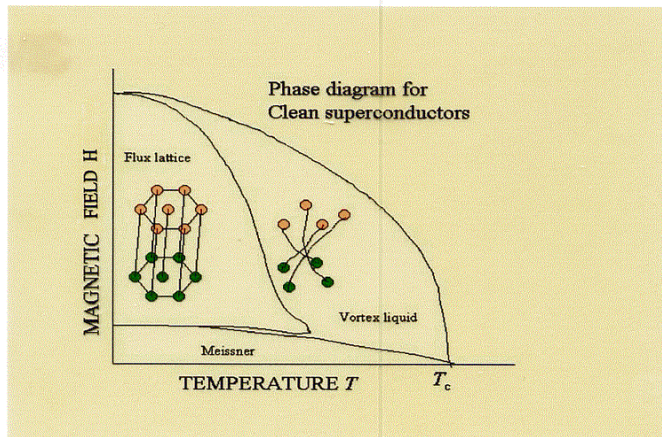
Y - the length of the jump (distance)

$$G(Y^3) = 3g \ln(Y)$$

The free-energy has to be minimized with respect to w , m and Y to find the parameters giving rise to its lowest value.

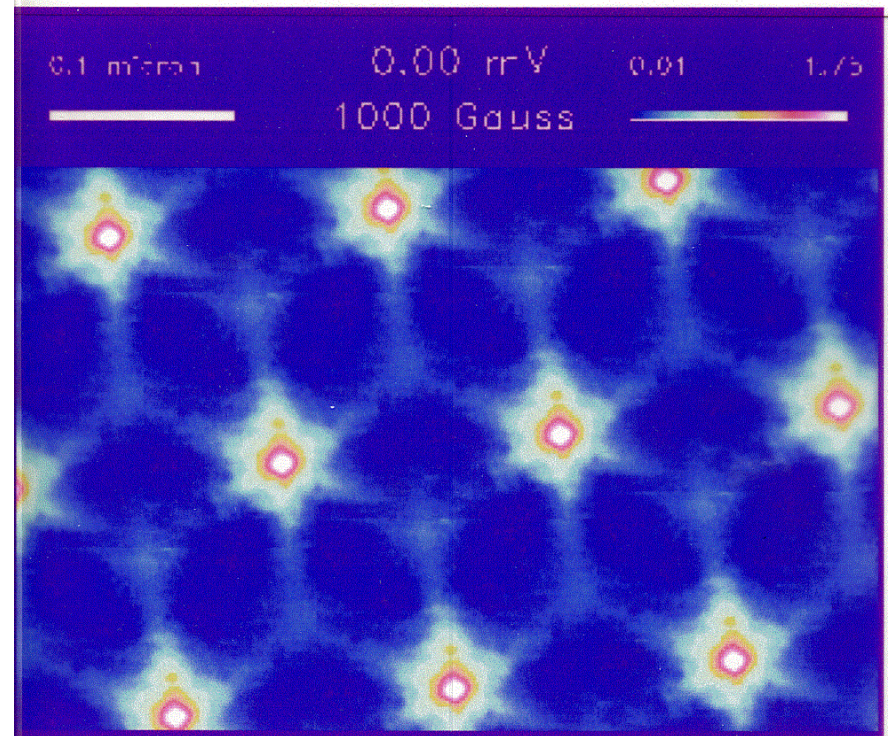
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Introduction

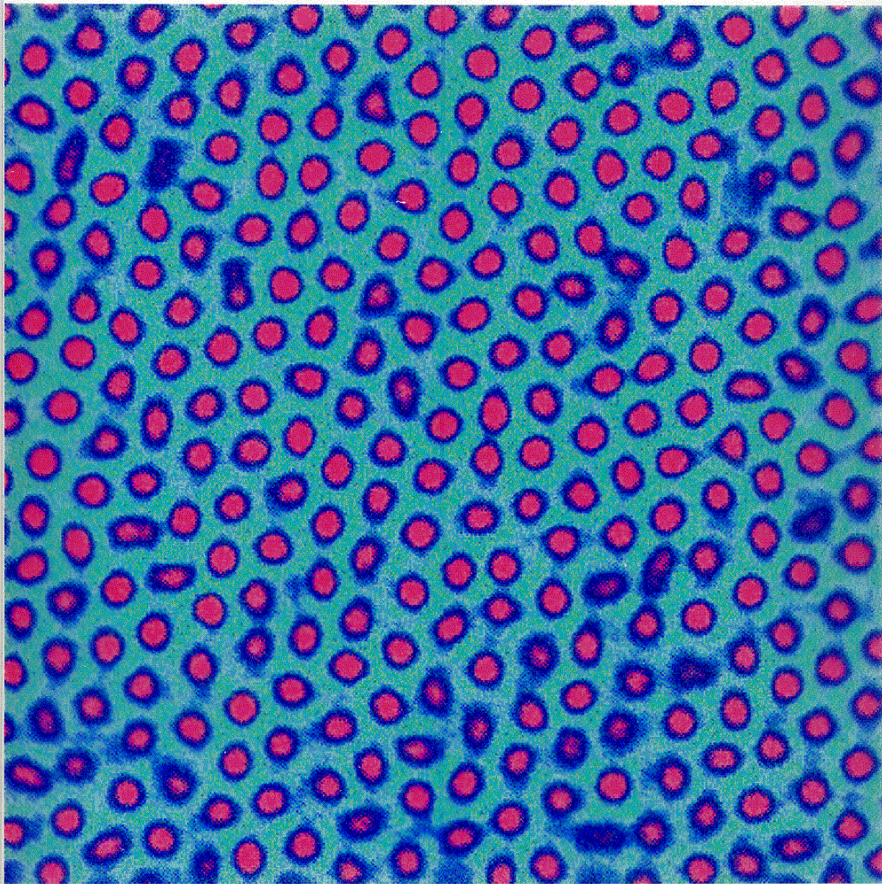


- Flux lines interact with the modified Bessel function of the first kind. This interaction is repulsive in nature. For short distances the interaction is logarithmic while for the bigger distances it decays exponentially.
- For the **pure system** a first order transition (FOT) from the **vortex solid** phase to the **vortex liquid** phase is seen both experimentally as well as numerically.

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Vortex lattice in NbSe₂ (Hess et al. Physica B 169, 4221 (1991))
 Scanning tunneling microscopy
 probes density of electrons attached to vortices



Vortex Lines

For small and intermediate values of the magnetic fields, we can write the following expression for the London free energy functional for YBCO:

$$\frac{\mathcal{F}}{kT} = \frac{1}{kT} \int_0^{Lz} dz \left\{ \sum_i \frac{\varepsilon_l}{2} \left(\frac{d\mathbf{R}_i}{dz} \right)^2 + \sum_{i < j} 2\varepsilon_0 K_0 \left(\frac{R_{ij}}{\lambda} \right) + \sum_i V(\mathbf{R}_i) \right\},$$

where $\mathbf{R}_i(z)$ is a two-dimensional vector, $\varepsilon_0 = \phi_0^2 / (4\pi\lambda)^2$ is the vortex line energy per unit length, the line tension is $\varepsilon_l \sim \varepsilon_0 / \gamma^2$. Average distance between FLs:

$$a_0 \sim \sqrt{\phi_0 / B}$$

A similar expression is used for BSCCO with some modifications.

Maps to a system of 2D Bosons with repulsive Coulomb interaction. (Nelson)

The cage model

$$E = \int_0^{L_z} dz \left\{ \frac{\epsilon_l}{2} \left(\frac{d\mathbf{R}(z)}{dz} \right)^2 + \frac{\mu}{2} \mathbf{R}^2(z) + V(\mathbf{R}(z)) \right\},$$

The harmonic part represents the cage which follows from the neighbor's repulsion.

$$\mu \approx d^2(-2\epsilon_0 \ln(r))/dr^2|_{r=a_0} \approx \epsilon_0/a_0^2.$$

$V(\mathbf{R}(z))$ represents random columnar defects. Assume first that $V=0$ (pure system).

Assume that the vortex requires a distance $z = \ell$ to sample the interior of its cage (Crabtree & Nelson). If the transverse deflection is denoted by r , the energy is

$$E \approx \frac{1}{2}(\epsilon_l/\ell + \mu\ell)r^2.$$

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optimizing with respect to ℓ one gets

$$\ell^* = \sqrt{\epsilon_l/\mu}, \quad E^* = \sqrt{\epsilon_l\mu} r^2.$$

The equipartition theorem gives

$$\langle r^2 \rangle = k_B T / \sqrt{\epsilon_l\mu} = k_B T \gamma a_0 / \epsilon_0.$$

The melting transition can be obtained from the Lindemann criterion $\langle r^2 \rangle \geq c_L^2 a_0^2$, with $c_L \sim 0.1 - 0.2$. Turning on columnar defects (random potential) has the effect of decreasing $\langle r^2 \rangle$, thus increasing the melting temperature (YYG 1997).

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Snapshots

In the figures below, snapshots of FLs, projected on a plane, at temperatures less than the transition temperature and at a temperature bigger than the transition temperature are shown.

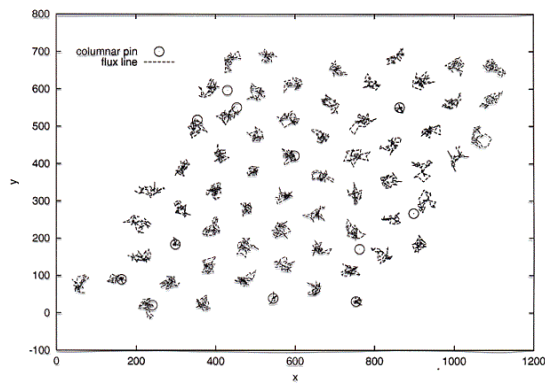


Figure 1: BSCCO: A typical configuration in the solid phase (low temperature) for $N = 64$ FLs for $B_\phi/B = 0.2$. FLs have been projected onto one plane.

From Fig. 1 it is easily seen that at low temperatures most columnar defects have captured

FLs. Also, the FLs make simple loops and have cleverly set themselves so as to make a hexagonal lattice and yet occupy as many defects as possible. The transverse fluctuations of the trapped FLs are greatly suppressed at low temperatures. At higher temperature beyond the transition point, we see that columnar defects are not occupied any more and a lot of FLs are entangled.

Inspection of snapshots like Fig. 1 gives support to the assertion of Sen *et al.* that the Bose glass consists of patches of ordered regions with only short range positional and orientational order. This phase is different from the Bragg-glass in systems with point pins which is characterized by quasi-long-range order.

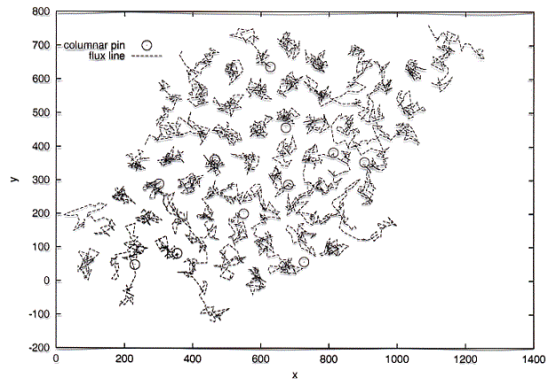


Figure 2: BSCCO: A typical configuration of FLs in the liquid phase (high temperature) for $N = 64$ and $B_\phi/B = 0.2$. FLs have been projected onto a single plane. Columnar defects are not drawn to scale. Some FLs on the boundary do not seem to make loops. That is only because virtual images of FLs outside the cell are not shown.

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Mapping of Parameters

Quantum Particle or System of bosons	Polymer chain(s)	Flux line(s)
τ (imaginary time)	u (monomer label)	z (plane label)
\hbar	kT	kT
\hbar/kT_B	L	L_z
m (mass)	dkT/b^2 b =bond length	$\epsilon_\ell = \epsilon_0/\gamma^2$ tilt modulus
g^2 (Coulomb repul.)		$2\epsilon_0$

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