Relaxor Ferro-electrics:
A baby problem for thinking about electrolytes and Batteries.

Based on Guzman-Verri, CMV arXiv:1212.13402 - PRB 2015.
Guzman Verri, Littlewood, CMV , PRB-2013

Relaxor Ferro-electrics:

A baby problem for thinking about electrolytes and Batteries.

1. Some general issues in theory of local fields.

   Physics of the Onsager Cavity method
   for local fields in terms of Statistical mechanics.

   Application of the generalized Onsager method
   to problems with disorder and local and long-range interactions

2. Application to Relaxor Ferro-electrics.

   Dielectric constant and Structure factor
   as a function of temperature and disorder.

   Relaxor in finite electric fields.

3. Speculations towards application to electrolytes, etc.

Simplest local field method : Clausius-Mosotti, Lorentz.

Onsager (1937): For a collection of interacting dipoles
Lorentz local field gives completely wrong answers:
For example Water is calculated to turn into a ferro-electric
at about 200 degrees centigrade.

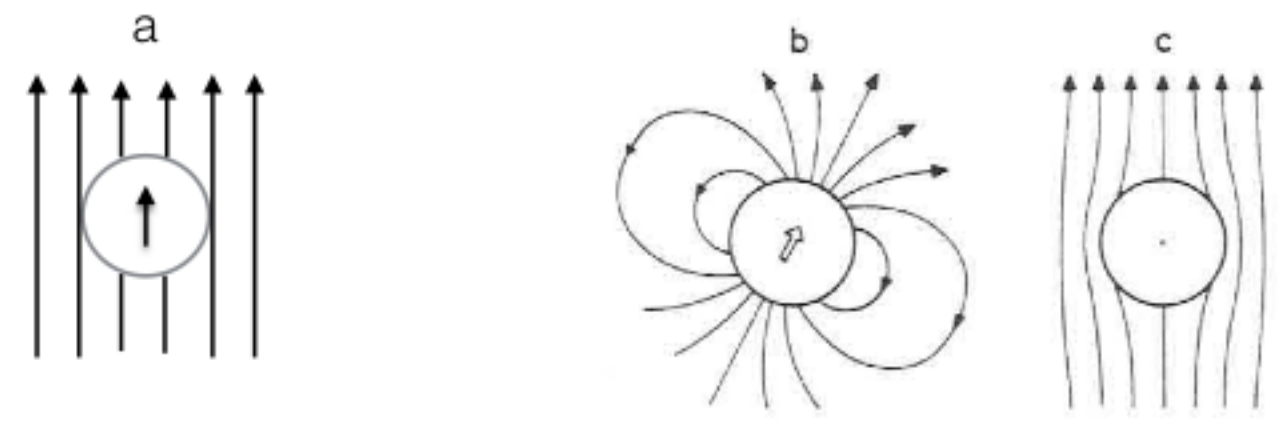
Whereas in a model with purely dipolar interactions,
there should (probably) be no order down to 0 K.
This is due to the frustrating nature of the dipolar interaction.

Luttinger and Tisza (1948):
Exact results on lack of ordering of
dipoles in square and cubic lattice.

These ideas were (among other things) essential in
formulating a model for ferro-electrics in terms of
short-range anharmonic forces giving condensation of
soft TO phonon modes, leading to formation of interacting dipoles
(Cochran 1952, Anderson 1952).

Onsager Cavity Method

Onsager Cavity Method.



Lorentz Local Field

b: Reaction Field
Always parr. to dipole.
So cannot orient dipole

c: Cavity Field=
Lorentz filed - React. Field.

Onsager calculated Cavity field by continuum electrostatics.
We want to use it more generally and in a problem with disorder.

van Vleck: (1937): Onsager fields are obtained from the leading terms in high temperature expansion about Mean-Field or Curie Law.
Brout: (1968) Onsager exact in the Spherical model.

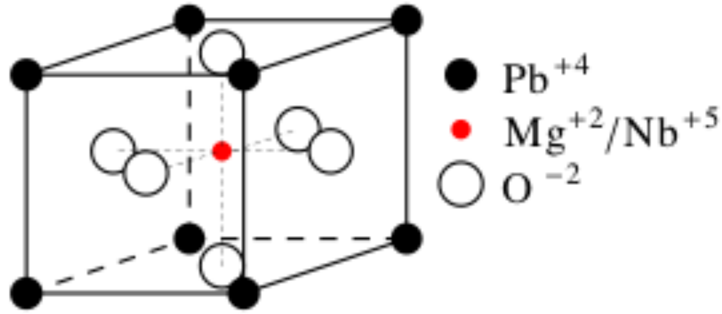
In more general problems: the Onsager cavity field may be obtained by calculating the response to E(q, ω) and fixing it to satisfy fluctuation - dissipation theorem.

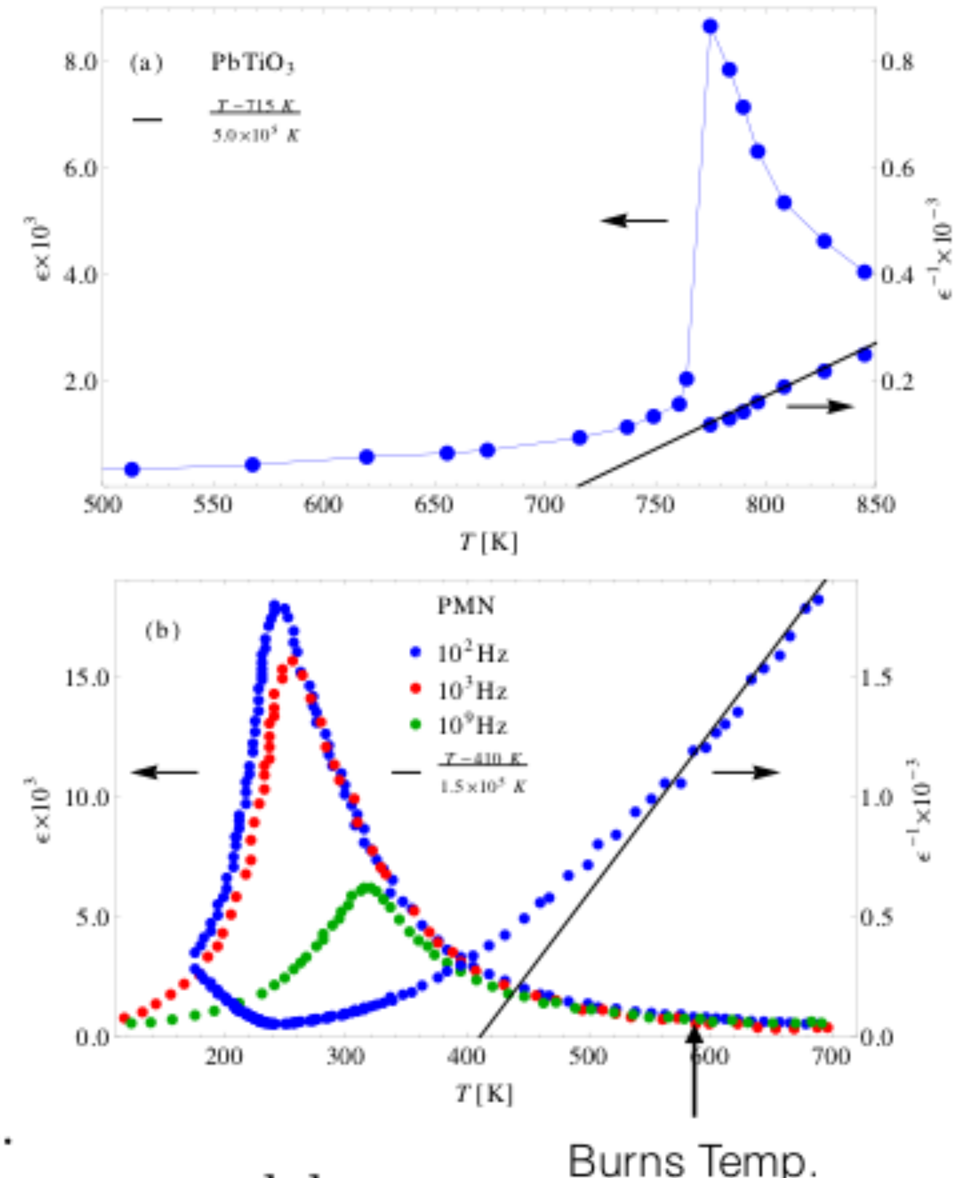
Alternately by a variational calculation of the Self-consistent dynamical kind.
Guzman-Verri, CMV (2012);
Guzman-Verri, Littlewood, CMV (2013).

Properties of Relaxor Ferro-electrics.

Properties of Relaxor Ferro-electrics.

PMN: $Pb(Mg_{1/3}Nb_{2/3})O_3$: perovskite with disorder (Mg^{2+}), (Nb^{5+})





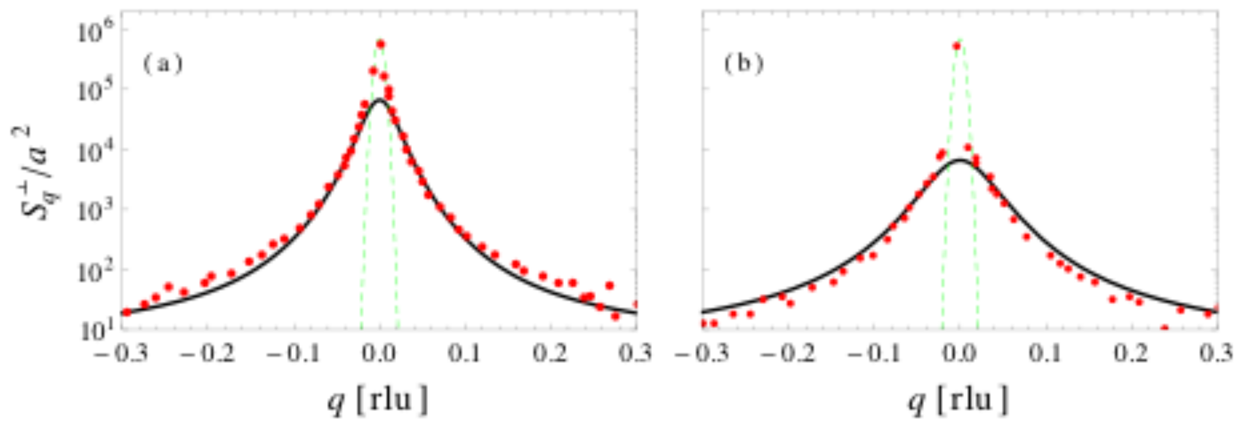
Bovtun et al.,
Ferroelectrics, 298, 23 (2004)

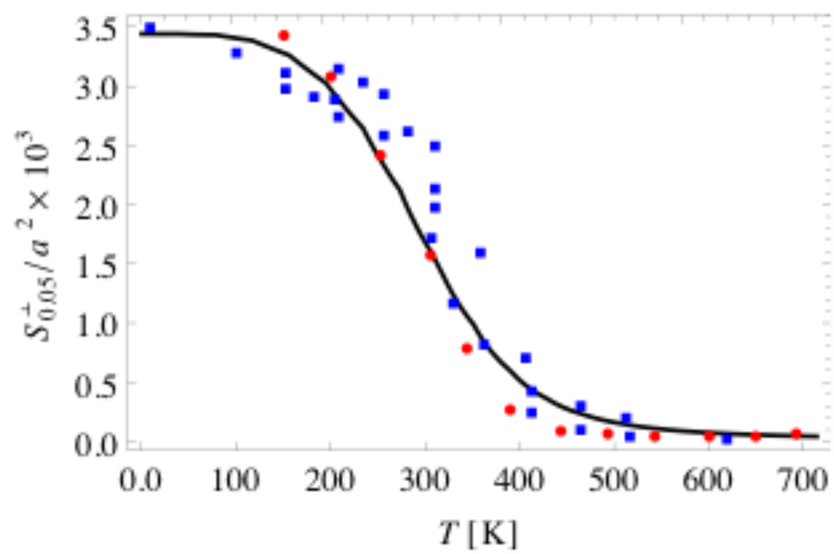
Cowley et al. (2011):
This problem is not understood.

Most approaches;
Short-range random field models.
Some recent numerical work on better models.

Dynamical Structure factor S(q,ω)

A clear indication of an unusual fluctuation regime is provided by measurement of S(q,ω) ; Cowley et al.





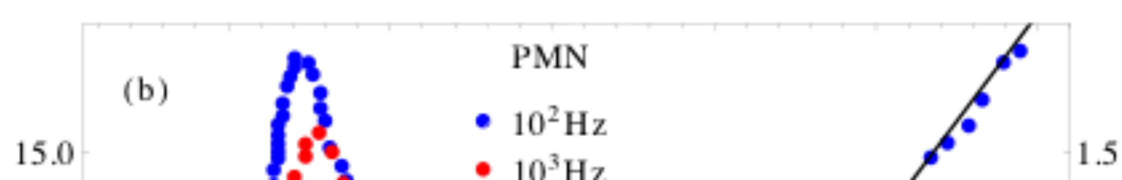
Unusual Features in Static Structure factor.

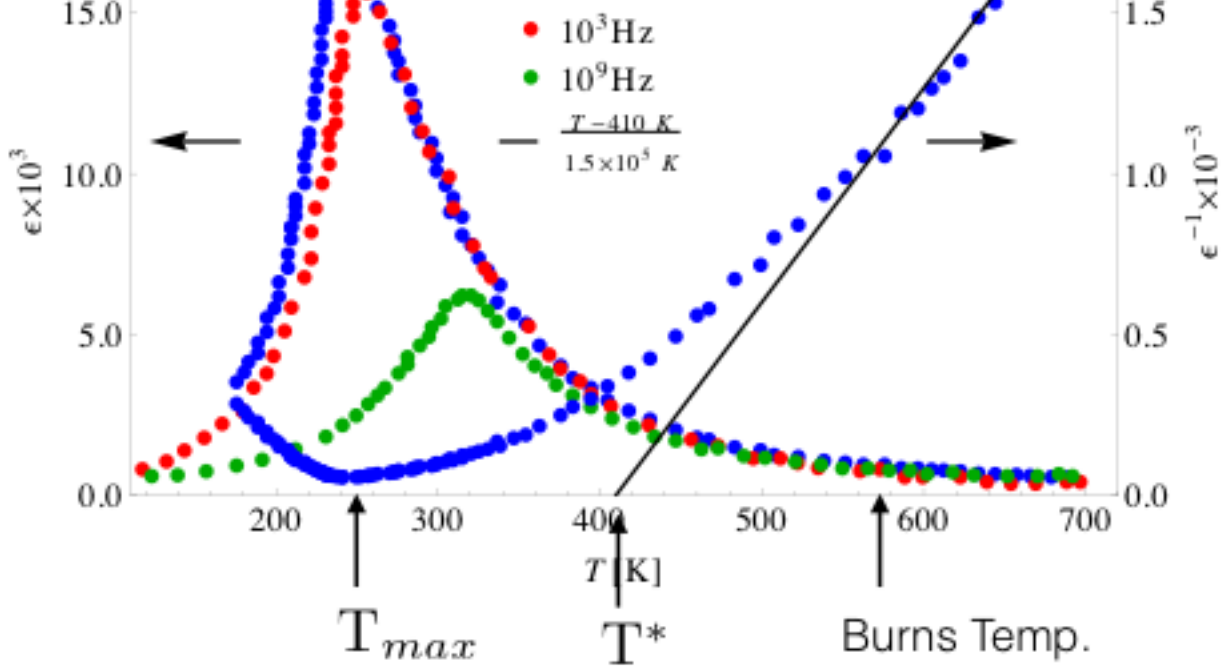
Unusual Features in Static Structure factor.

Correlations have power law behavior at large distance for all tempertues below about T* and a characteristic short-range cut-off.

S(q $\rightarrow$ 0) saturates below T_{max}.

These are characteristic of extended region of Fluctuations.





A rounded response of this kind
is a signature of a wide Fluctuation regime.

Theory must include frustrating nature of dipole interactions (at least at the level of Onsager) and random fields also beyond mean-field - in order to characterize phenomena with characteristic scales T_B, T^*, T_{max}.

Model and Principles of Solution

u_i : TO phonon displacement or dipole.

$$H = \sum_i \left[\frac{\Pi_i^2}{2M} + V(u_i) \right] - \frac{1}{2} \sum_{i,j} v_{ij} u_i u_j - \sum_i E_i^{ext} u_i - \sum_i h_i u_i.$$

Kinetic energy	Dipole interactions	Random fields

Short-range random pot. $V(u_i) = \frac{\kappa}{2} u_i^2 + \frac{\gamma}{4} u_i^4$

Some numerical results (Molecular dynamics) on this model are available, Burton et al. (2006).

Generalized Onsager Soln.

$$\mathrm{H}_{eff} = \sum H_i^{Onsager} = \sum \left(H_i^0 - h_i u_i - E_i^{cavity} u_i \right).$$

$$\mathrm{H}_{eff} = \sum_i H_i^{Onsager} = \sum_i \left(H_i^0 - h_i u_i - E_i^{cavity} u_i \right).$$

$$H_i^0 = \frac{\Pi_i^2}{2M} + V(u_i) - \frac{\lambda}{2} u_i^2,$$

$$E_i^{cavity} = \sum_j v_{ij} \langle u_j \rangle_{th} - \lambda \langle u_i \rangle_{th} + E_i^{ext}.$$

Lorentz local field approx: $\lambda = 0$

How to determine λ?

Onsager did it in the simpler problem using continuum electro-statics.

We must generalize the procedure.

How to determine λ?

Two procedures:

1. Satisfy Fluctuation dissipation theorem

1. Satisfy Fluctuation dissipation theorem.
2. Use a varaitional scheme at the level of the Self-consistent harmonic approx.

1 :

$$\chi(q,\omega) = \frac{\partial u(q,\omega)}{\partial E_{ext}(q,\omega)}$$

Satisfy: $\left\langle \langle u_i^2 \rangle_{th}^0 \right\rangle_c - \left\langle {\langle u_i \rangle_{th}^0}^2 \right\rangle_c = \frac{1}{N} \sum_{\boldsymbol{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth\left(\frac{\beta\hbar\omega}{2}\right) \mathrm{Im}\left[\chi_{\boldsymbol{q}}(\omega)\right]$

2 :

Variational method:

$$\rho^{\mathrm{tr}} = \frac{1}{Z^{\mathrm{tr}}} e^{-\beta H^{\mathrm{tr}}}, \qquad H^{\mathrm{tr}} = \sum_i \frac{\Pi_i^2}{2M} + \frac{1}{2}\sum_{i,j}(u_i - p)G_{i-j}(u_j - p) - \sum_i h_i u_i,$$

G_{ij} and p are variational parameters.

An interesting analytical result:

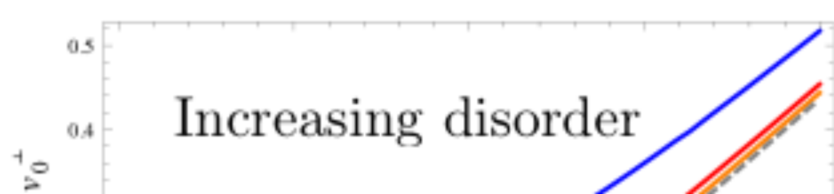
For weak disorder: $< \Delta^2 > /(T_c^0 v_0^\perp) << 1,$

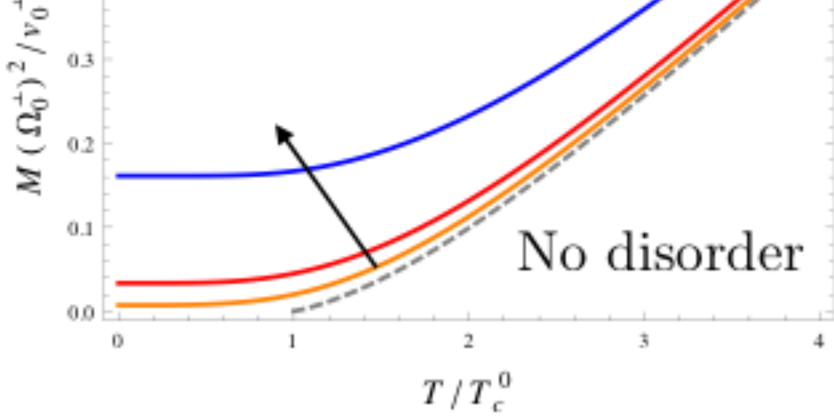
$$M(\Omega_0^\perp)^2 \simeq (4B^2 Q^2 v_0^\perp e^{-1})\, e^{-2B^2 Q^2 \frac{k_B T_c^0}{(\Delta^2/v_0^\perp)}}$$

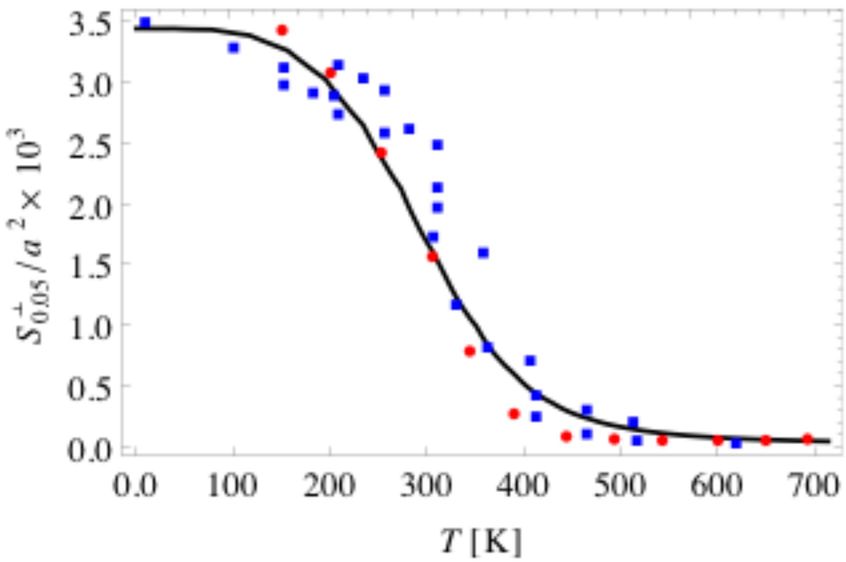
No ordered state ever in zero external field.
All is fluctuations.

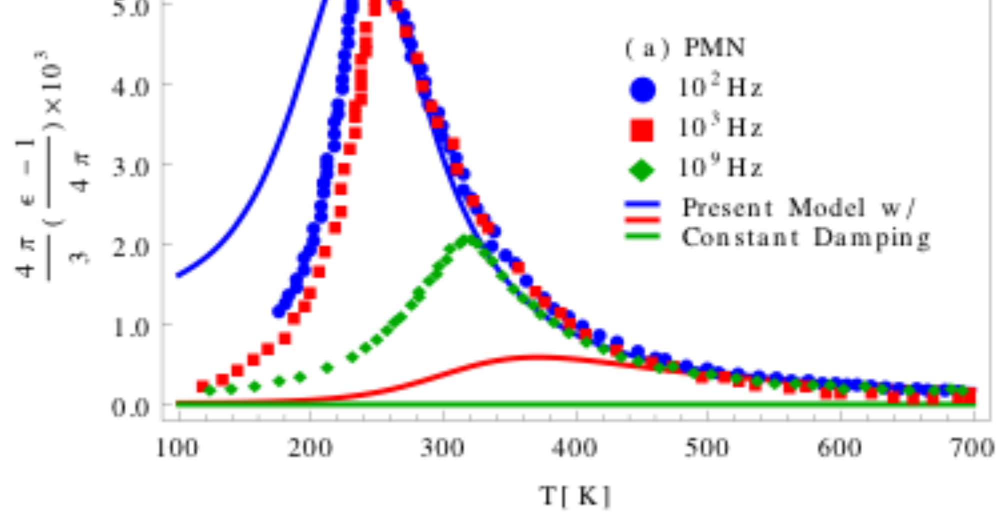
The complete Free-energy landscape calculable in the Gaussian Fluctuation approximation.

Results:

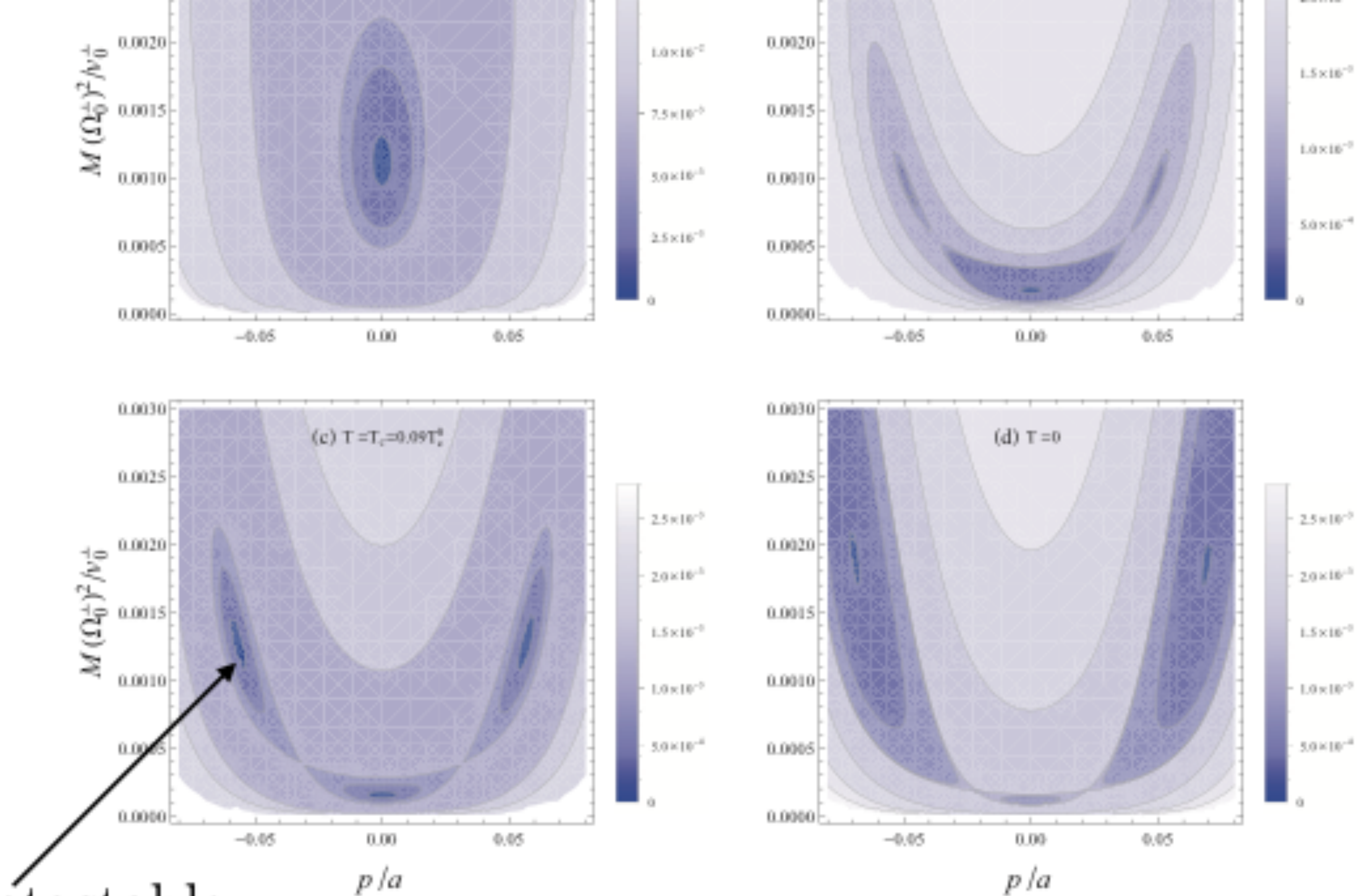



No disorder
T / T_c^0
$M\,(\Omega_0^{\perp})^2 / v_0^{\perp}$


$S^{\perp}_{0.05} / a^2 \times 10^3$
T [K]

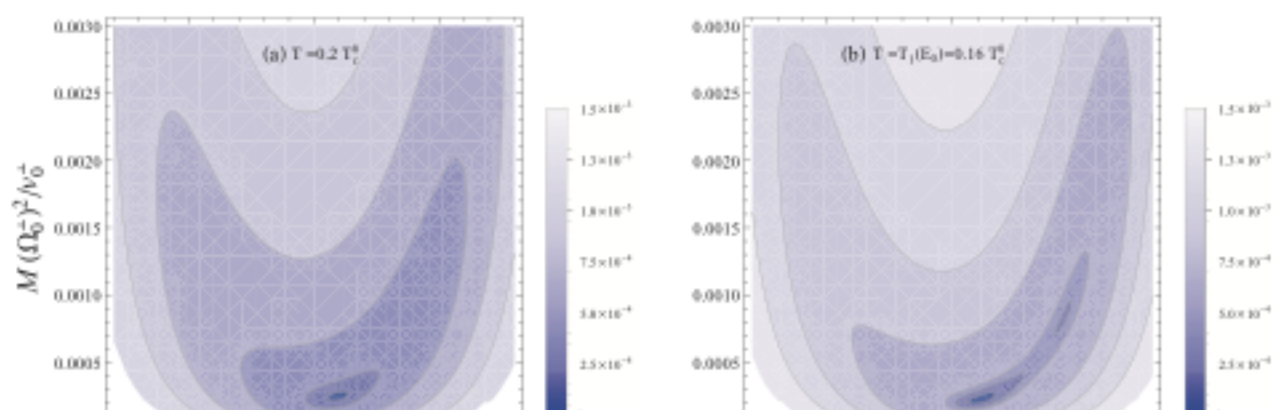


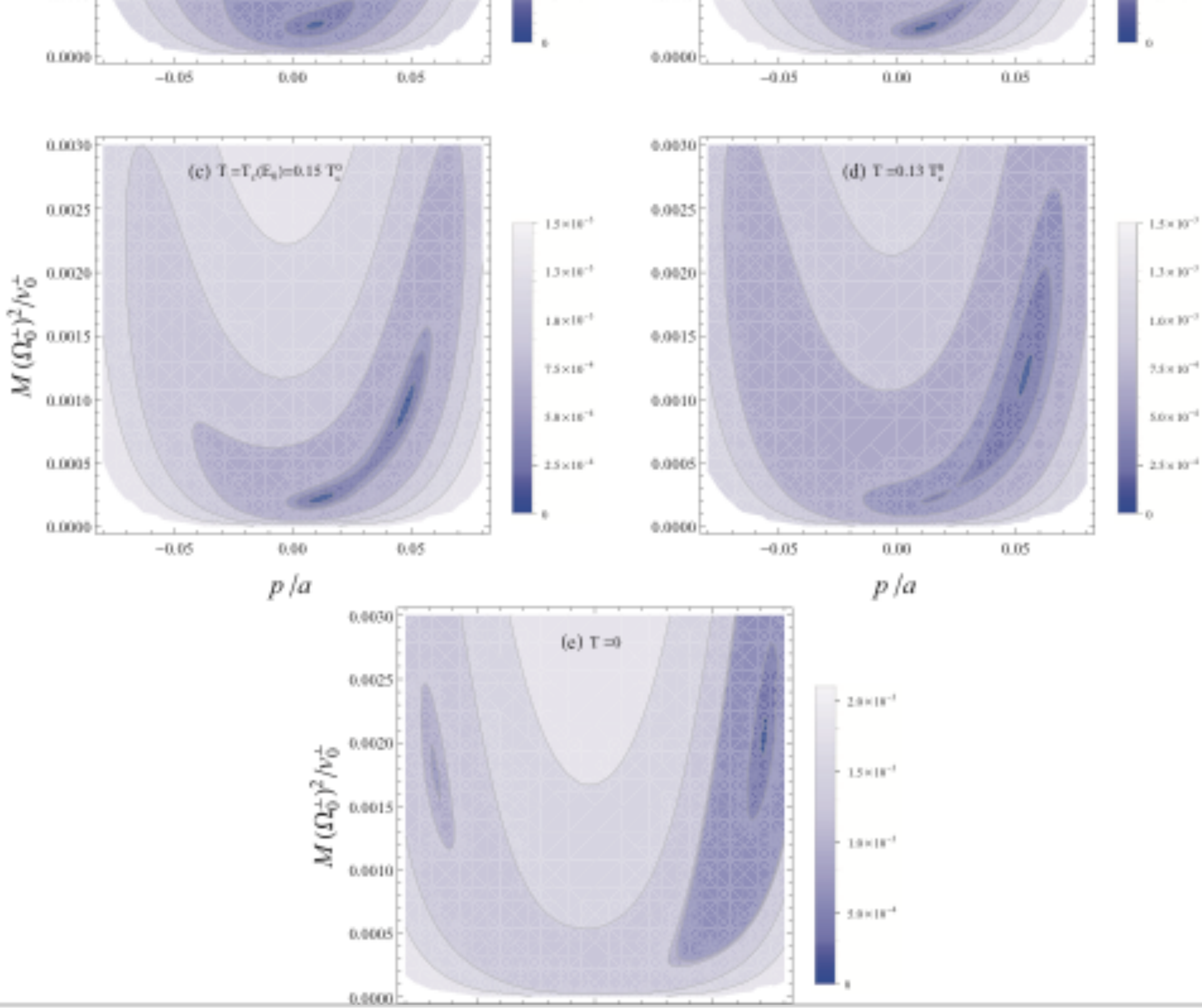
Free-energy landscape in $E_{ext} = 0$.



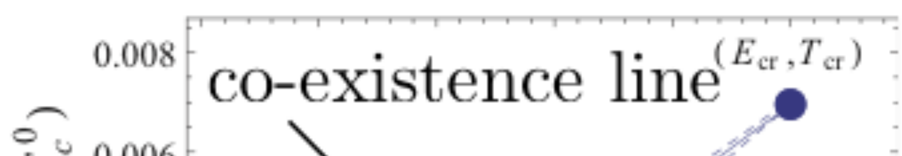
Metastable
ferro-electric regions.

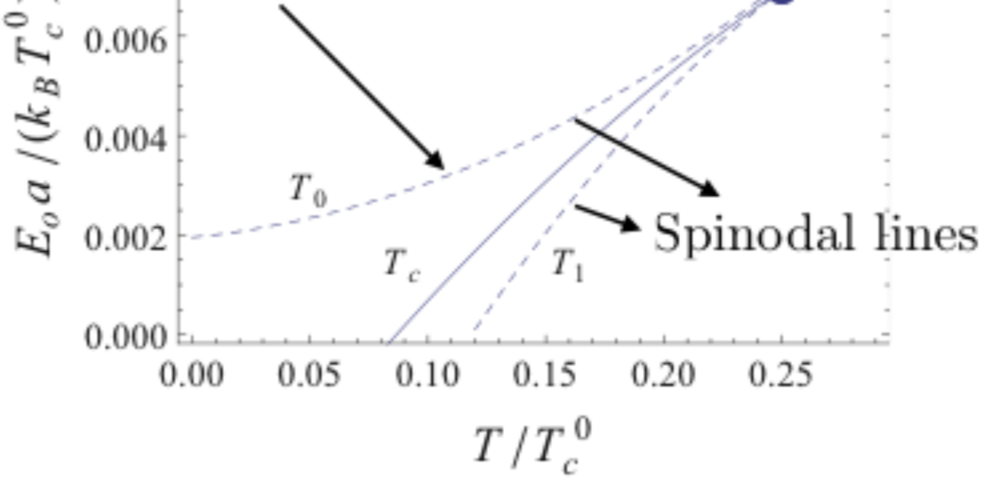
Free-energy landscape in E_{ext}.





Field (E_0)-induced first order transition





Other applications of the Method?

i.e. for problems of generalized fluctuations
not well treatable by mean-field approximations.

Straightforward to consider contact of a

Straightforward to consider contact of a disordered dipolar model with a metal.

Generalization to model containing free-ions besides dipole?

Water as a set of dipoles on a lattice vacancies, with averages over random pair distribution function of vacancies?

Principal Points of the talk:
In problems of dipole interactions, probably including solvation and strong electrolytes, the physics is in the fluctuation regime due to frustration of dipole interactions and disorder.

disorder.

A general method has been devised to analytically get good answers for one such problem, which allows application of Onsager's ideas more generally.

Application to harder problems, inclduing those with ion motion may be possible.