Solid-solid phase transitions in electro- and magnetorheological Systems

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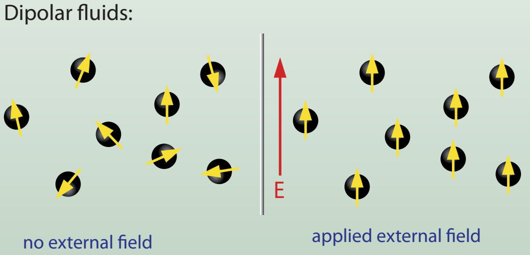
Tunable crystal structures

- buzzword: *smart materials*: materials with properties that can be changed in a controlled fashion
  - well known: liquid crystals (tunable property: isotropic, nematic, smectic, . . .)
  - electro- and magnetorheological systems (ERMR)
    tunable property: **structure**
- found at various scales
  colloids, complex plasmas, nano-sized particles (proteins, polymers), mesoscopic level, . . .
- a toy system for critical phenomena

Electro- and magnetorheological Systems (ERMR)

A short retrospection:
permanent dipoles (embedded in media) (also called: Stockmayer-fluids)
Interaction:

$$u_{dipol}(i,j) = \frac{(\vec{\mu}_i \cdot \vec{r})(\vec{\mu}_j \cdot \vec{r}) - (\vec{\mu}_i \cdot \vec{\mu}_j) r^2}{r^5}$$

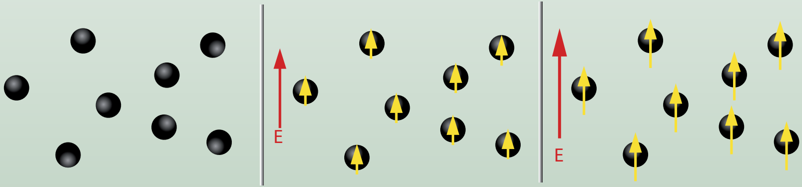


Electro- and magnetorheological Systems (ERMR)

Electro- or magnetorheological fluids: particles with *induced* moments (may be both magneto or electrostatic) in media:
Interaction:

$$u_{rheo}(i,j) = -m^2 \frac{(\vec{e}_z \cdot \vec{e}_r)^2 - 1}{r^3} = -d\frac{1}{r^3}P_2(cos\theta)$$

ER/MR fluids:



no external field weak external field strong external field

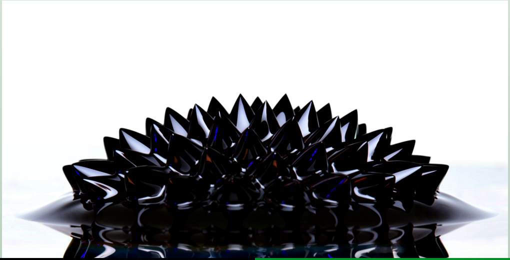
Applications | Mechanics

Tunable mechanical properties (colloids)

ERMR systems can be switched to fluid or solid state:

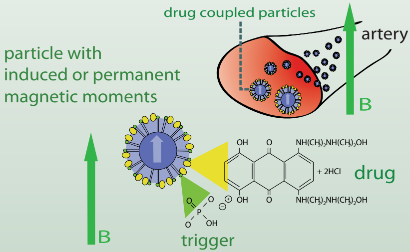
- adaptive shock absorbers[a]
- electrostatic switchable valves and hydraulic flow control
- lock-less breaks (hydraulic bridge circuits)[b]

[a] R. Stanway et al. , Smart Materials 5 (1996) 464
[b] S.B. Choi et al., Smart Materials 14 (2005) 1483



Applications | Medical Science

Magnetofection



drug is delivered by an activated trigger molecule

- a tool for biological chemistry and medicine [a]
- intention: place drugs only in affected tissues
- uses nano-sized particles as a vehicle(+tigger) (colloidial MR-fluid)
- affected tissue is exposed to external magnetic fields

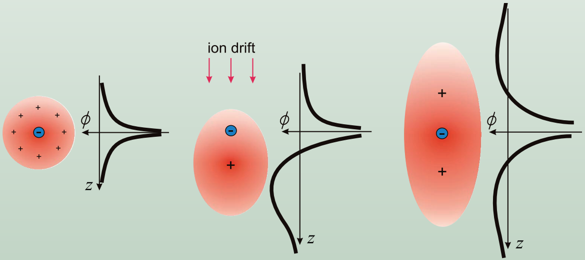
[a] C. Plank et al.,Biological Chemistry 384 (2003) 737

Electrorheological plasmas

- basic principle: Application of RF-discharges: (PK-3 experiment)[1]
- applied RF-amplitude: *tunable* dipolar-dipolar interaction:

$$W(r,\theta) = Q^2 \left(\frac{\exp(-r/\lambda)}{r} - d\,\frac{M_T^2 \lambda^2}{r^3} P_2(\cos\theta) \right)$$

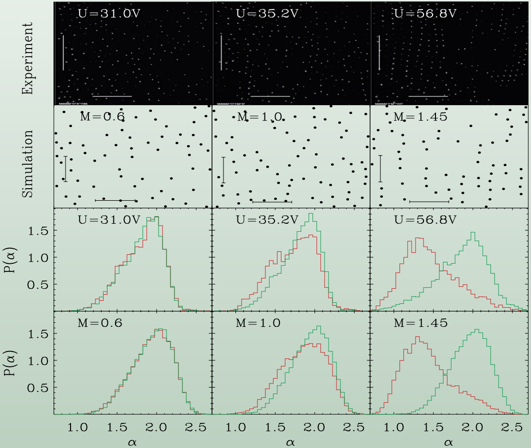
- also higher multipoles possible (next-gen experiment *plasmalab*



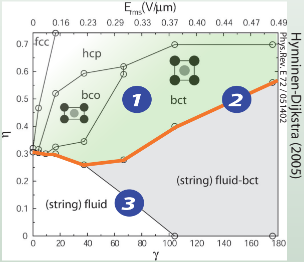
[1] R. Kompaneets, PhD Thesis (2007)

Electrorheological plasmas

- discovery of electrorheological plasmas in PK-3[2]
- advantage: interaction is determined by plasma parameters
- experimental results: String fluids, observations on the kinetic level



Simulation of ERMR systems



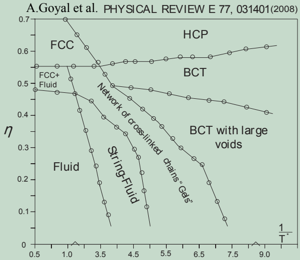
Simulations

until now: molecular dynamics and Monte-Carlo simulations

- MC-Simulation with strong dipol-dipol interactions are hindered by pitfalls...
- lattice sums are just **conditionally** convergent
- solution: for each sweep an Ewald-Summation is calculated (FFT)
- Hynninen-Dijkstra: MC with 256 particles

Simulation of ERMR systems (ctd.)

Molecular dynamics



- fast, using step potentials[a]
- provides dynamics and kinetics

[a] A. Goyal et al., PRE 77, 031401

Drawbacks

MC and MD tell you **What?, When?, How?**
but do not reveal the driving mechanisms

Variational approach

An alternative approach : Bogoliubov-Inequality

- Bogoliubov inequality provides an upper limit for the Helmholtz free energy F
- assuming the free energy F_0 of a reference system H_0 is known:

$$F = -\beta^{-1} \int d\Gamma \exp(-\beta H) \qquad \beta = \frac{1}{k_B T}$$

$$F \leq F_0 + \langle H - H_0 \rangle_0$$

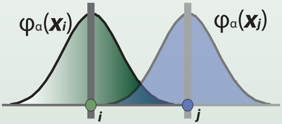
- a reference system for classical solids: Einstein-Model

$$H_0 = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} m\Omega^2 \left(\mathbf{r}_i - \mathbf{r}_i^0 \right)^2 \right]$$

$$F_0 = 3Nk_B T \ln \left(\frac{\Lambda}{\sigma} \sqrt{\frac{\alpha}{\pi}} \right) \qquad \alpha = \frac{m\Omega^2 \sigma^2}{2k_B T}$$

Variational approach

A Perturbation theory... Variational free energy:



$$\tilde{F} = F_0 + \frac{1}{2}\epsilon \sum_{i \neq j}^{N} W(\mathbf{x}_{ij}^0) - \frac{3}{2} N k_{\mathrm{B}} T$$

$$W(\mathbf{x}_{ij}^0) = \int d\mathbf{x}_i d\mathbf{x}_j \; \varphi_\alpha(\mathbf{x}_i) \, \phi(\mathbf{x}_{ij}) \, \varphi_\alpha(\mathbf{x}_j)$$

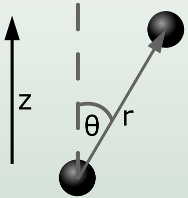
$$\varphi_\alpha(\mathbf{x}_i) = \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(\mathbf{x}_i - \mathbf{x}_i^0)^2}$$

⟶ free energy per particle:

$$\tilde{f} = \tilde{f}_0 + \frac{\epsilon}{2} \sum_{i \neq 0} \tilde{W}(\mathbf{x}_i) - \frac{3}{2} k_B T$$

$$\tilde{W}(\mathbf{x}_i) = \left(\frac{\alpha}{2\pi}\right)^{3/2} \exp(-\tfrac{1}{2}\alpha x_i^2) \times \int d\mathbf{x} \, \phi(\mathbf{x}) \exp(-\tfrac{1}{2}\alpha x^2 + \alpha \mathbf{x} \cdot \mathbf{x}_i).$$

Variational approach | Model



Approximated interaction

- binary particle-particle interaction separation:

$$V(\mathbf{r}) = \epsilon\,[\phi_I(r) + \xi\phi_A(r,\theta)]$$

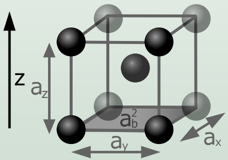
- sophisticated: dipol-dipol interaction $\propto r^{-3}$ (conditionally convergent lattice sums, divergences $r \longrightarrow 0$) requires an approximation (chosen here GCM):

$$\phi_I(r) = \frac{\sigma}{r} e^{-\kappa(r/\sigma-1)} \quad (1)$$

$$\phi_A(r,\theta) = \exp(-(\tfrac{r}{\sigma R})^2) P_2(\cos\theta) \quad (2)$$

$$\tilde{W}_\mathrm{A}(\mathbf{x}_i) = (\alpha Q^2)^{3/2}\left[\left(1-\frac{3}{\alpha^2 Q^2 x_i^2}\right)\exp\left(-\frac{\alpha x_i^2}{2+\alpha R^2}\right) + \sqrt{\frac{\pi}{2}}\frac{3}{\alpha^3 Q^3 x_i^3}\mathrm{erfi}\left(\frac{\alpha Q x_i}{\sqrt{2}}\right)\exp\left(-\frac{\alpha x_i^2}{2}\right)\right] P_2(\cos\theta).$$

Variational approach | Variation

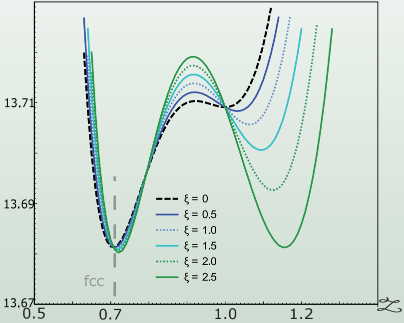


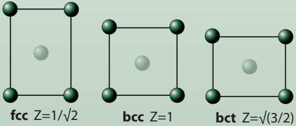
Approximated interaction

- W_I and W_A can be evaluated analytically
- hence: for a given lattice structure F viz. f can be evaluated using lattice sums (by variation)
- variational parameters: $\mathcal{Y} = \sqrt{\frac{a_y}{a_x}} \geq 1$, $\mathcal{Z} = \sqrt{a_x a_y}/a_z$
- chosen here: two classes of lattices bco (including fcc, bct, bcc), and hcp

Variational approach | Variation

A *toy* variation: ($\mathcal{Z}$ only)





Variational approach | Phase diagrams

Phase diagrams

- variation in the full parameter space $(\alpha, \mathcal{Y}, \mathcal{Z})$: phases and regimes
- numerical minimization: downhill-simplex algorithm & quadratic optimization
- depending on the *hardness* κ of the isotropic core ϕ_I at least three different regimes of phase diagrams exist: here named as soft, medium and hard
- additional parameters
  - ρ: particle number density
  - ξ: anisotropic strength (viz. strength of the external field)
  - ϵ: strength of interaction

Variational approach | Fluids

Ornstein-Zernike equation

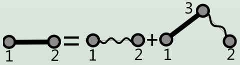
defines a basic relation for *direct* $c(1,2)$ and *total* h(1,2) correlation function
(total correlation function: $h(\vec{r}) = g(\vec{r}) - 1$)

$$h(1,2) = c(1,2) + \rho \int d(3)c(1,3)h(3,2)$$

$\longrightarrow$ open intergral equation
$\longrightarrow$ closure relation required

$$g(1,2) = \exp\left(-\beta\phi(1,2) + h(1,2) - c(1,2) + B(1,2)\right)$$

appropriate choice $B(1,2) = 0$ (hypernetted chain closure)



Variational approach | Fluids

Ornstein-Zernike equation

- simple approximation: spherical symmetric interaction:

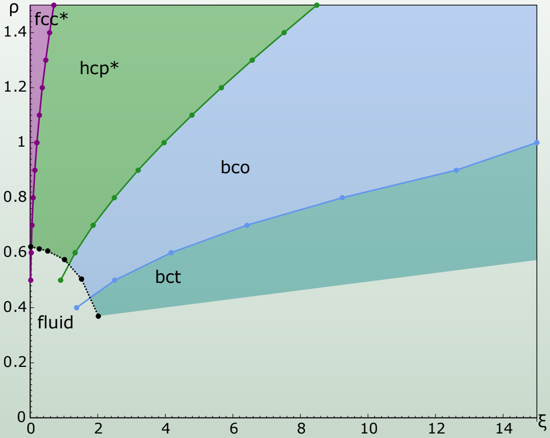
$$\phi(1,2) = \phi_I(r) \qquad (\phi_A(r)\text{: ignored})$$

- solved using Picards iteration (in Fourier space)
- free excess energy (per particle, virial route)

$$f_{ex} = \frac{2\pi}{3} \int_0^{\rho} d\rho' \int_0^{\infty} drr^3 \, g(r)|_{\rho'} \, \phi'(r)$$

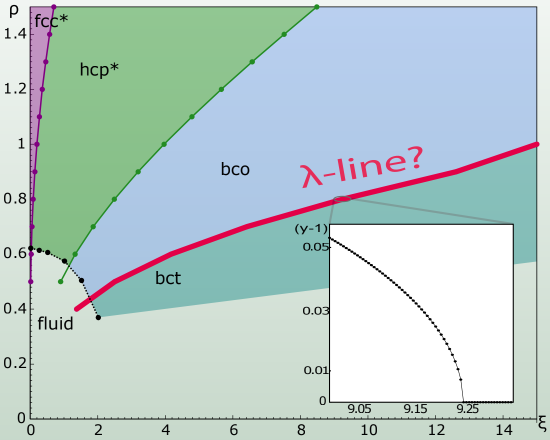
- approximative closure relations may cause thermodynamic inconsisties (cross checks required, Percus-Yevick)

Medium regime



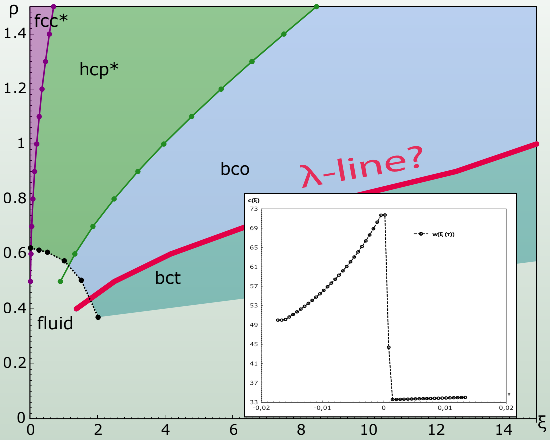
- ($\kappa = 7$) sequence of phases: fcc $\rightarrow$ hcp $\rightarrow$ bct $\rightarrow$ bco
- three fluid-solid-solid triple points

Medium regime | λ-line candidate



- a candidate for a second order (continuous) transition?
- continous phase transition → critical phenomena

Medium regime | λ-line candidate



- specific "heat": $c(\tau) = -\xi \frac{\partial^2 \tilde{f}}{\partial \xi^2}$
- note: ξ is just a temperature

Medium regime | λ-line candidate

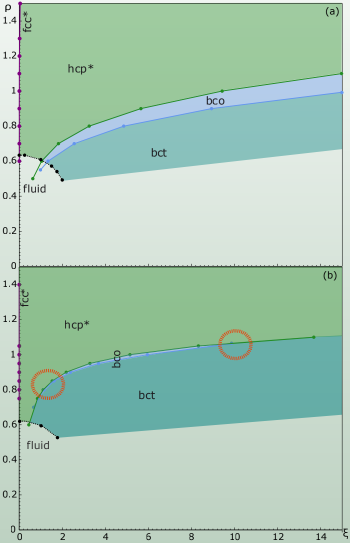
critical phenomena

- critical exponents: (universality class)

$$\begin{aligned} w(\xi) &\propto (-\tau_c)^{\beta_c} \\ c(\xi) &= -\xi\partial_\xi^2 f =\propto (-\tau_c)^{\alpha_c} \end{aligned}$$

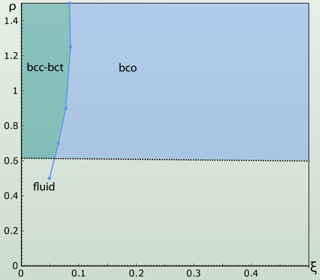
- $\alpha = 0$ $\beta = \frac{1}{2}$ (main field theory)
- anisotropic critical phenomena...
  - anisotropic ϕ^4 renormalization group (V. Dohm, *et al.*)
    $\longrightarrow$ critical exponents of anisotropic systems cannot be predicted by isotropic systems (i.e. via scaling)
  - prediction is compatible with mean field theory
  - open issue: universality class?

Hard regime



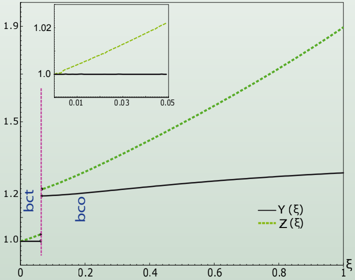
- phase diagrams for $\kappa = 15$ viz. $\kappa = 35$
- fcc(*) is almost wiped out ($\xi \leq 4 \times 10^{-3}$)
- dominating phase: hcp
- new topology for high values of κ “bco-lens”
- likely bco is eliminated for even higher values of κ (i.e. hard spheres)

Soft regime diagram



- phase diagram for $\kappa = 1$
- only two phases bct (bcc for $\xi = 0$) and bco
- here: first-order transition
- speculative: tri-crticial point in $1 < \kappa < 4$?
- no other structures observed (i.e. hcp)

Soft regime diagram | Applications?



- diagram for $\kappa = 1, \bar{\epsilon} = 25, \bar{\rho} = 0.7$
- precisely tunable bct and bco structrues (PhoC)

(Movie: tunable structure)

Results

Conclusions

- relevant phases are dependent on the hardness of the spherical symmetric core
- sequences in experimental & simulated phase diagrams (i.e. van Blaaderen, Hynninen-Dijkstra) can be explained
- masked phase transitions are possible (hcp vs. fcc-bct)
- switchable fluid-solid structures
- tunable crystal structures:
    - soft regime: precisley tunable bct
    - medium regime: miscalleny of phases (fcc, hcp, bct, bco) each (within limits) tunable

Questions

Open issues

- applications in „classical“ crystal groth?
- kinetics and universality class?
- higher multipol ERMR systems?
- self-organisation?

Thank you for your attention!