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

Interaction:

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

Dipolar fluids:

- no external field
- applied external field

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

Interaction:

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

ER/MR fluids:

- no external field
- weak external field
- strong external field
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
Magnetofection

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

\[ \text{drug is delivered by an activated trigger molecule} \]

\[ \text{aC. Plank et al., Biological Chemistry} \]

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*)

Electrorheological plasmas

- discovery of electrorheological plasmas in PK-3²
- 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:

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

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

- a reference system for classical solids: Einstein-Model

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

$$F_0 = 3Nk_B T \ln \left( \frac{\Lambda}{\sigma} \sqrt{\frac{\alpha}{\pi}} \right) \quad \alpha = \frac{m\Omega^2\sigma^2}{2k_B T}$$
A Perturbation theory... Variational free energy:

\[ \tilde{F} = F_0 + \frac{1}{2} \epsilon \sum_{i \neq j} \tilde{W}(x_{ij}^0) - \frac{3}{2} N k_B T \]

\[ \tilde{W}(x_{ij}^0) = \int d\mathbf{x}_i d\mathbf{x}_j \ \varphi_\alpha(\mathbf{x}_i) \phi(\mathbf{x}_{ij}) \varphi_\alpha(\mathbf{x}_j) \]

\[ \varphi_\alpha(\mathbf{x}_i) = \left( \frac{\alpha}{\pi} \right)^{3/2} e^{-\alpha(\mathbf{x}_i - \mathbf{x}_0^i)^2} \]

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

\[ \tilde{W}(\mathbf{x}_i) = \left( \frac{\alpha}{2\pi} \right)^{3/2} \exp\left(-\frac{1}{2} \alpha x_i^2 \right) \times \int d\mathbf{x} \ \phi(\mathbf{x}) \exp\left(-\frac{1}{2} \alpha x^2 + \alpha \mathbf{x} \cdot \mathbf{x}_i \right). \]
### Approximated interaction

- **binary particle-particle interaction separation:**
  
  \[ V(r) = \epsilon [\phi_I(r) + \xi \phi_A(r, \theta)] \]

- **sophisticated: dipol-dipol interaction** \( \propto r^{-3} \)

(conditionally convergent lattice sums, divergences \( r \to 0 \)) requires an approximation (chosen here GCM):

\[
\phi_I(r) = \frac{\sigma}{r} e^{-\kappa (r/\sigma - 1)} \quad (1) \\
\phi_A(r, \theta) = \exp\left(-\left(\frac{r}{\sigma R}\right)^2\right) P_2(\cos \theta) \quad (2)
\]

\[
\tilde{W}_A(x_i) = (\alpha Q^2)^{3/2} \left[ \left(1 - \frac{3}{\alpha^2 Q^2 x_i^2}\right) \exp\left(-\frac{\alpha x_i^2}{2 + \alpha R^2}\right) + \sqrt{\frac{\pi}{2}} \frac{3}{\alpha^3 Q^3 x_i^3} \text{erfi}\left(\frac{\alpha Q x_i}{\sqrt{2}}\right) \exp\left(-\frac{\alpha x_i^2}{2}\right) \right] P_2(\cos \theta).
\]
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: $\mathcal{V} = \sqrt{\frac{a_y}{a_x}} \geq 1$, $\mathcal{Z} = \sqrt{a_xa_y/a_z}$
- chosen here: two classes of lattices bco
  (including fcc, bct, bcc), and hcp

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Variational approach | Variation

A toy variation: \((Z)\) only

- fcc \(Z = 1/\sqrt{2}\)
- bcc \(Z = 1\)
- bct \(Z = \sqrt{3/2}\)

\[
\begin{align*}
\xi &= 0 &\quad \text{black dashed line} \\
\xi &= 0.5 &\quad \text{blue solid line} \\
\xi &= 1.0 &\quad \text{dotted line} \\
\xi &= 1.5 &\quad \text{light blue solid line} \\
\xi &= 2.0 &\quad \text{dotted line} \\
\xi &= 2.5 &\quad \text{green solid line}
\end{align*}
\]
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 \(\kappa\) of the isotropic core \(\phi_I\) at least three different regimes of phase diagrams exist: here named as soft, medium and hard
- additional parameters
  - \(\rho\): particle number density
  - \(\xi\): anisotropic strength (viz. strength of the external field)
  - \(\epsilon\): strength of interaction
Ornstein-Zernike equation

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

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

→ open integral equation
→ closure relation required

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

appropriate choice $B(1, 2) = 0$ (hypernetted chain closure)
Ornstein-Zernike equation

- simple approximation: spherical symmetric interaction:
  \[ \phi(1, 2) = \phi_I(r) \quad (\phi_A(r): \text{ignored}) \]

- solved using Picards iteration (in Fourier space)
- free excess energy (per particle, virial route)
  \[ f_{\text{ex}} = \frac{2\pi}{3} \int_0^\rho d\rho' \int_0^\infty drr^3 g(r)|_{\rho'} \phi'(r) \]

- approximative closure relations may cause thermodynamic inconsistencies (cross checks required, Percus-Yevick)
Medium regime

$(\kappa = 7)$ sequence of phases: fcc $\rightarrow$ hcp $\rightarrow$ bct $\rightarrow$ bco

three fluid-solid-solid-solid triple points
Medium regime | \( \lambda \)-line candidate

- a candidate for a second order (continuous) transition?
- continuous phase transition \( \rightarrow \) critical phenomena
Medium regime | $\lambda$-line candidate

specific “heat”: $c(\tau) = -\xi \frac{\partial^2 \tilde{f}}{\partial \xi^2}$

note: $\xi$ is just a temperature
Medium regime | $\lambda$-line candidate

critical phenomena

- critical exponents: (universality class)
  
  \[
  w(\xi) \propto (\tau_c)^{\beta_c} \\
  c(\xi) = -\xi \partial^2_\xi f \propto (\tau_c)^{\alpha_c}
  \]

- $\alpha = 0$, $\beta = \frac{1}{2}$ (main field theory)

- anisotropic critical phenomena...
  
  - anisotropic $\phi^4$ renormalization group (V. Dohm, et al.)
    
    $\rightarrow$ 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. $\kappa = 35$
- $\text{fcc}(\ast)$ is almost wiped out ($\xi \leq 4 \times 10^{-3}$)
- dominating phase: hcp
- new topology for high values of $\kappa$ “bco-lens”
- likely bco is eliminated for even higher values of $\kappa$ (i.e. hard spheres)
phase diagram for $\kappa = 1$
- only two phases bct (bcc for $\xi = 0$) and bco
- here: first-order transition
- speculative: tri-critical point in $1 < \kappa < 4$?
- no other structures observed (i.e. hcp)
- diagram for \( \kappa = 1, \bar{\epsilon} = 25, \bar{\rho} = 0.7 \)
- precisely tunable bct and bco structures (PhoC)
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: precisely tunable bct
  - medium regime: miscalleny of phases (fcc, hcp, bct, bco)
    each (within limits) tunable
Thank you for your attention!