A short introduction to the phase field approach

Benoît Appolaire

LEM – Onera/CNRS

2016, feb. 3rd

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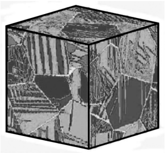
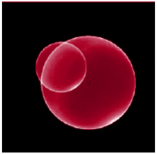
Karma et al.



Khatchaturyan et al.

Casademunt et al.



Du et al.

For all free boundary problems (potentially)

- Phase transformations (solidification, solid states, fluid . . .)
- Fluid flow (free surfaces)
- Membranes (biology)
- Cracks . . .

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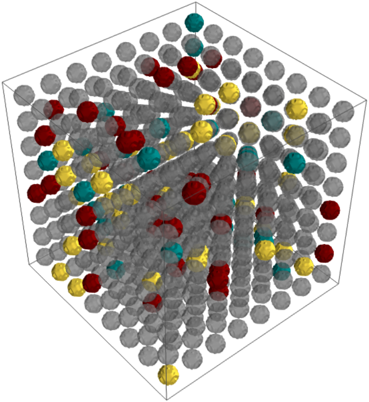

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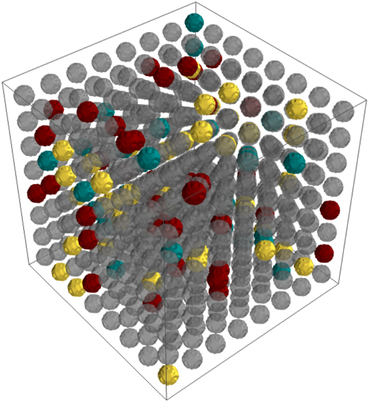

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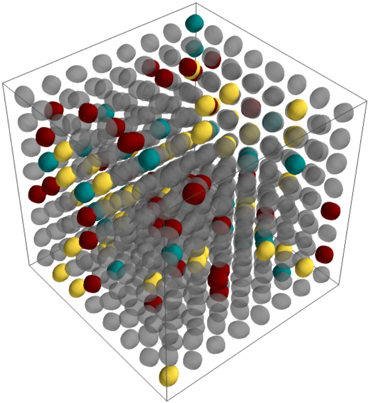

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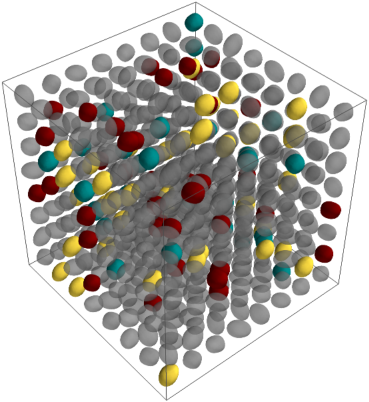

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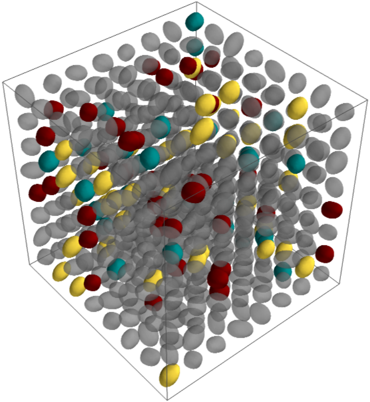

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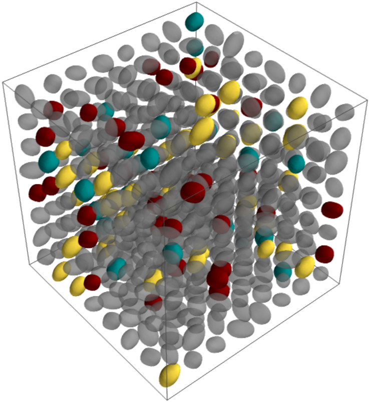

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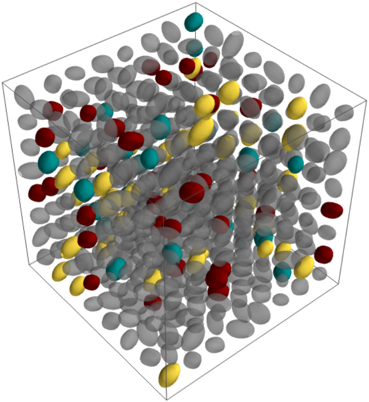

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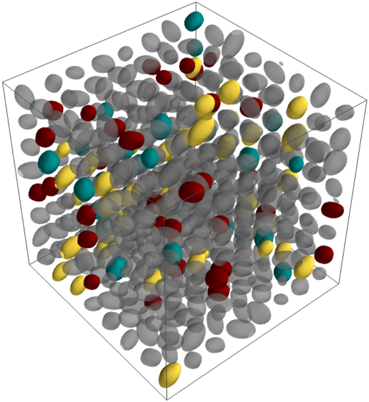

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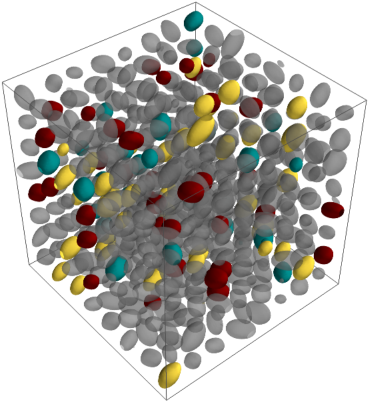

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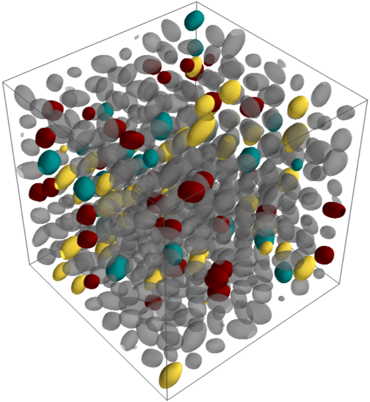

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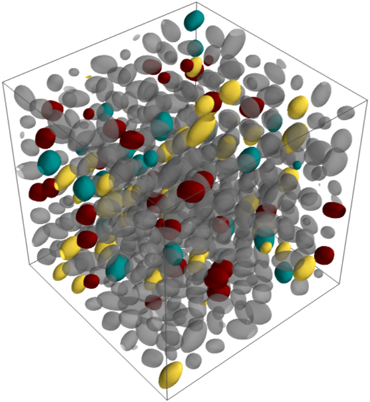

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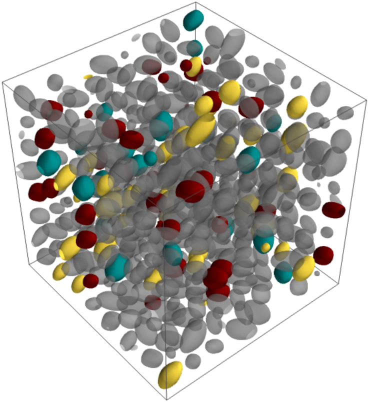

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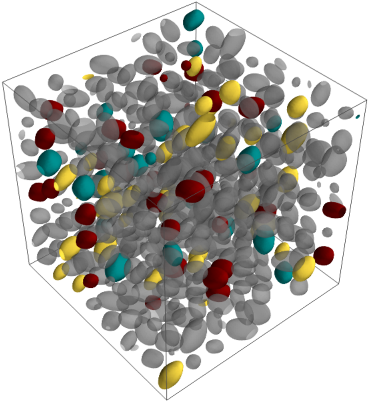

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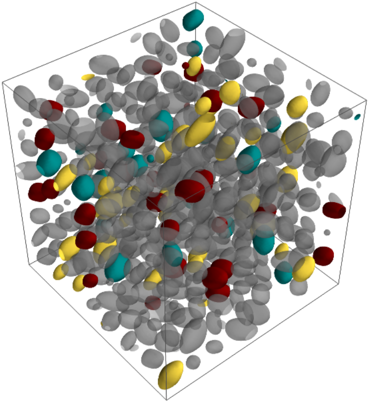

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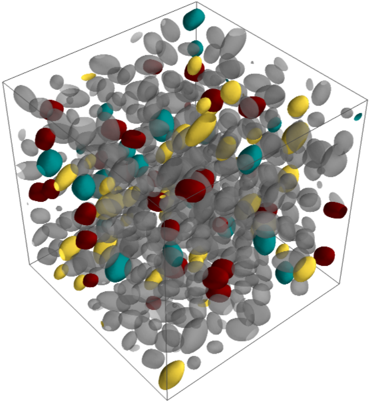

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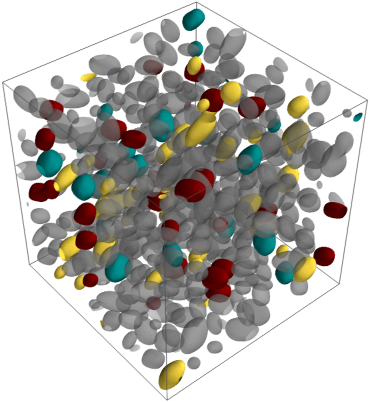

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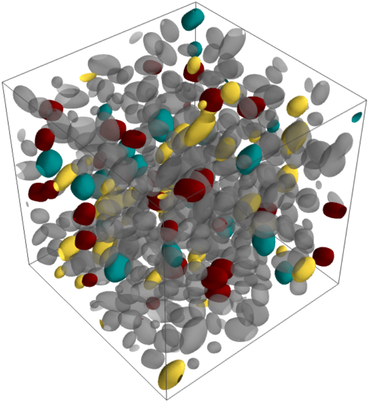

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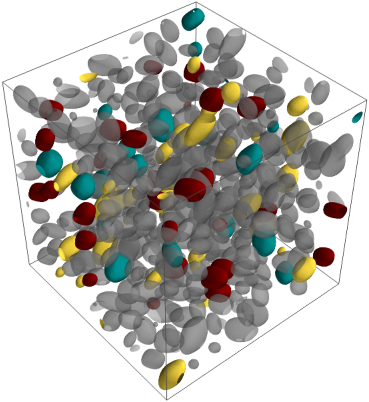

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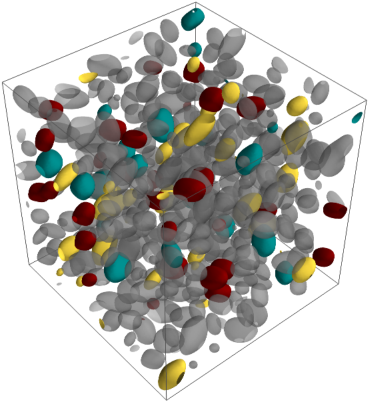

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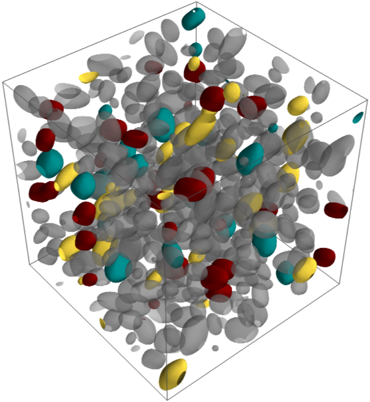

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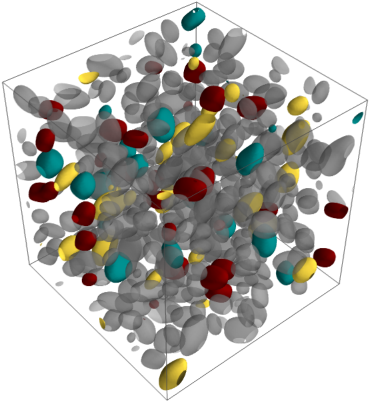

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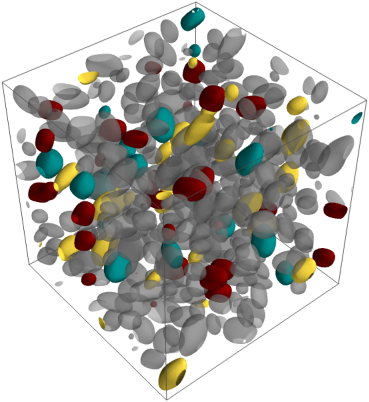

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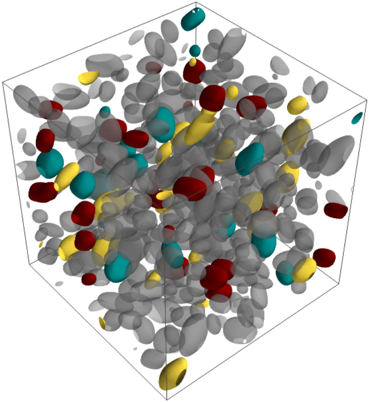

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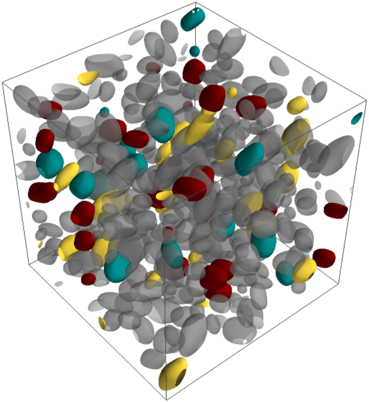

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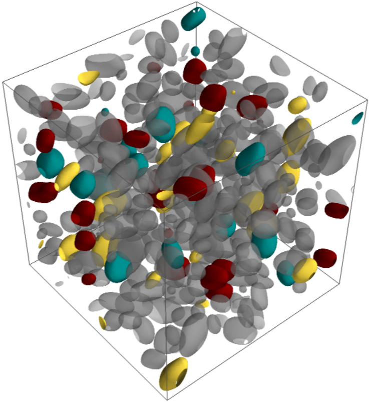

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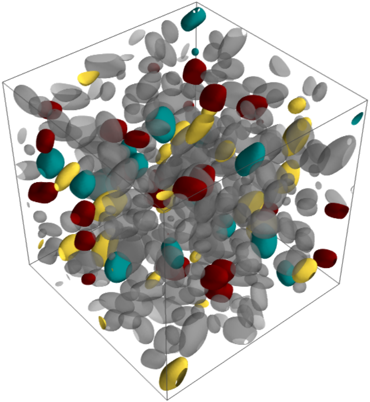

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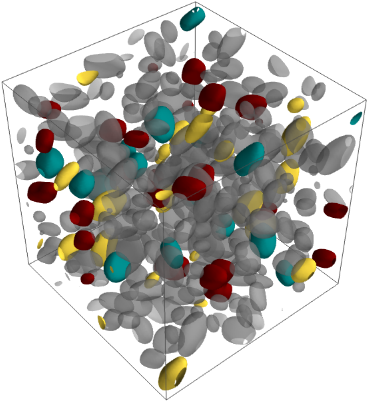

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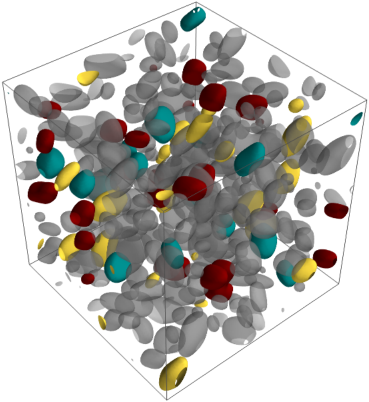

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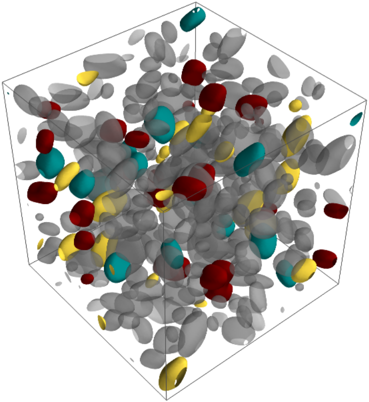

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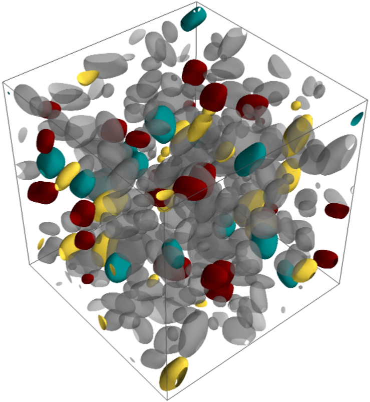

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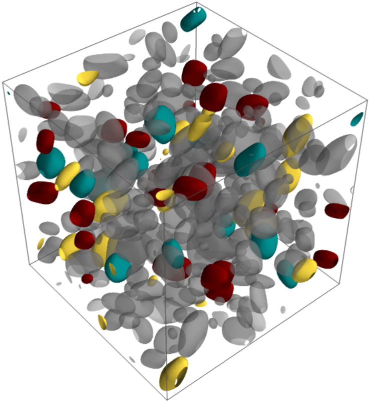

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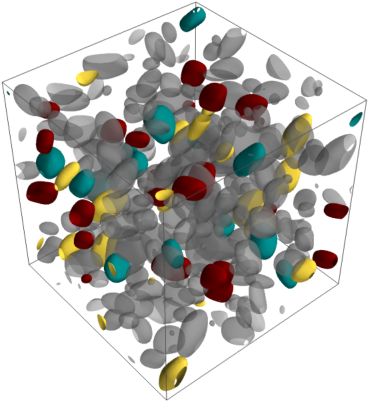

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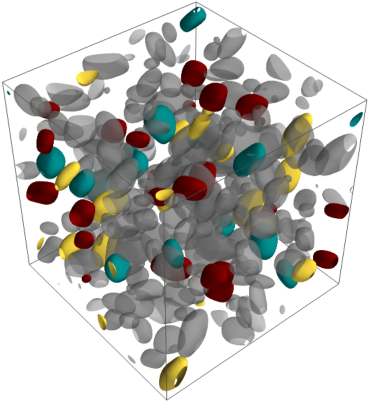

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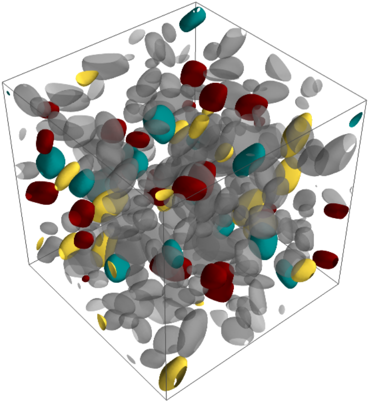

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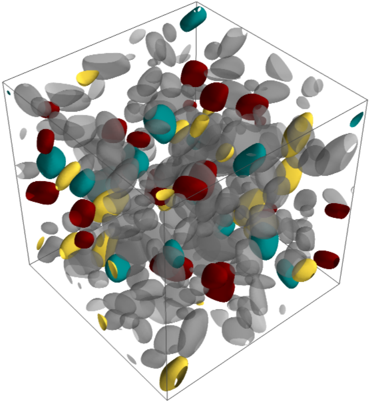

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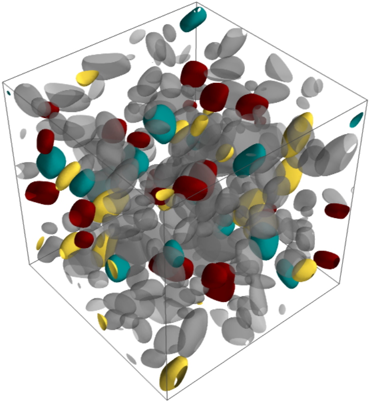

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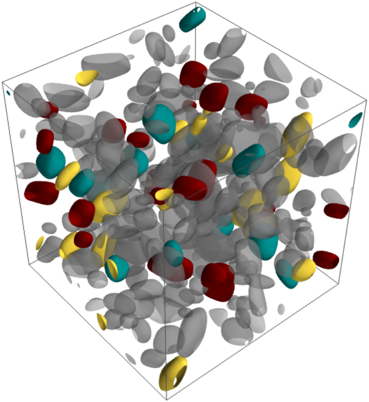

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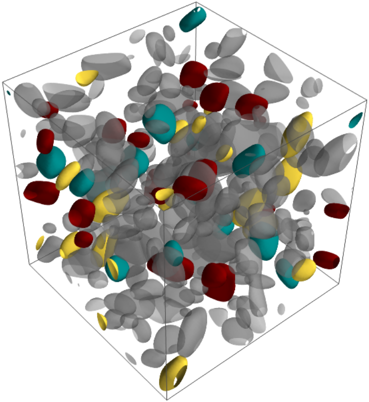

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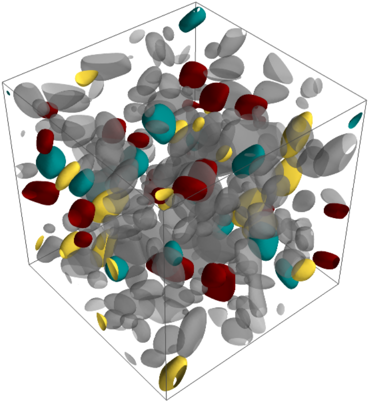

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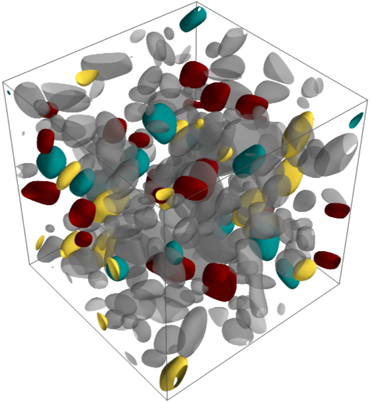

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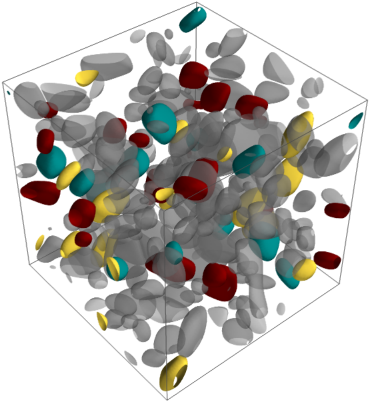

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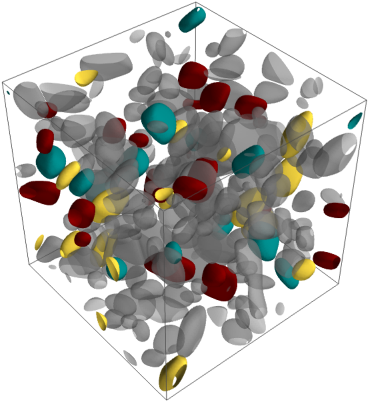

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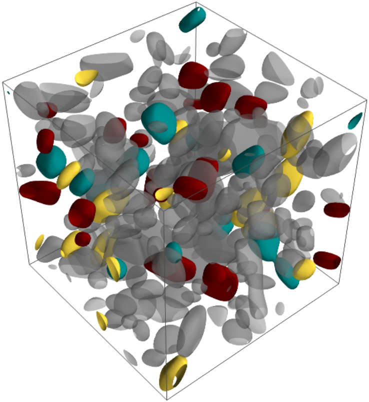

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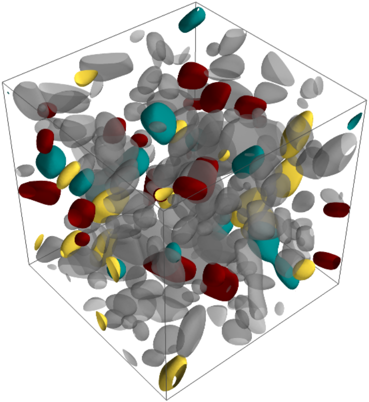

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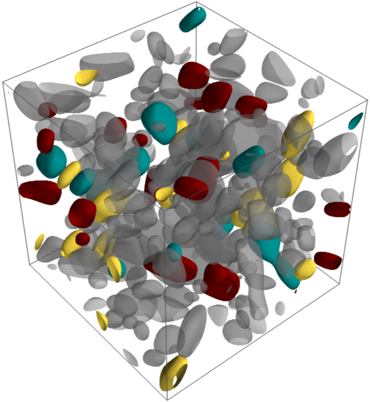

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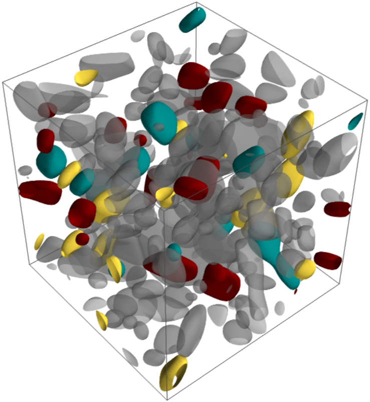

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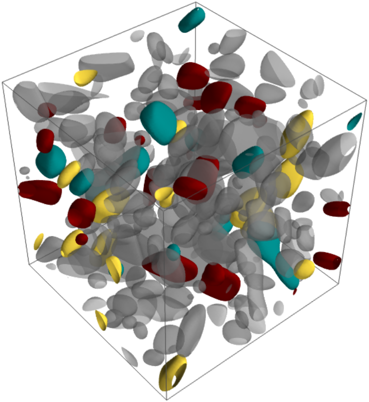

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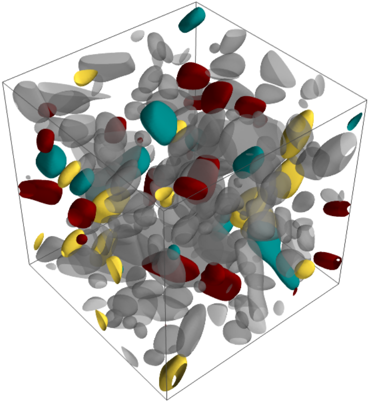

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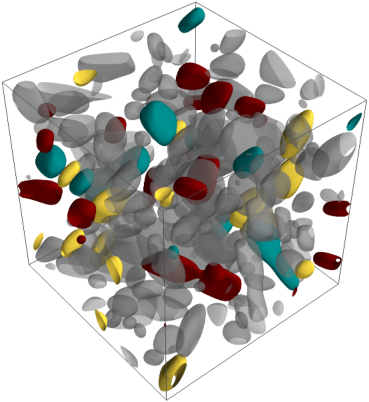

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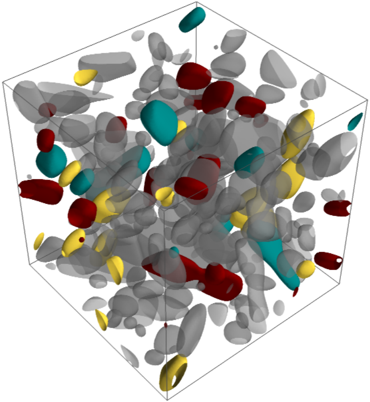

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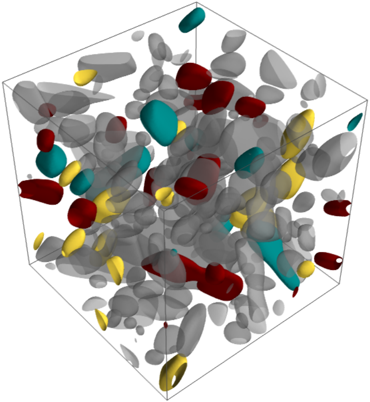

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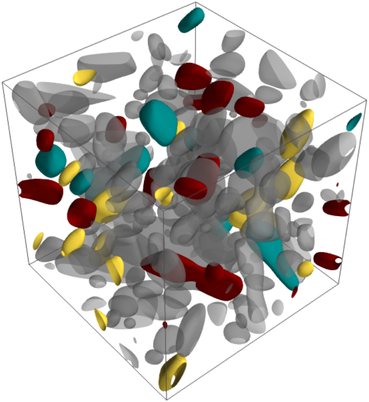

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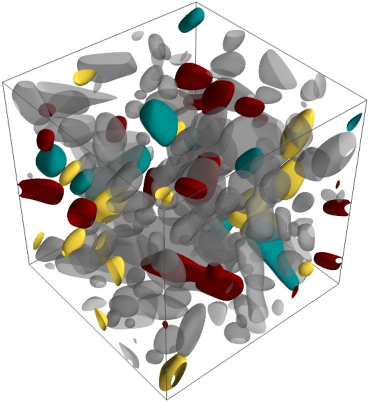

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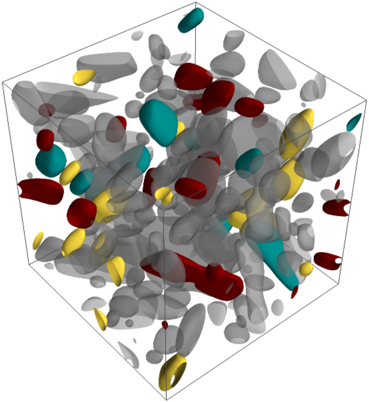

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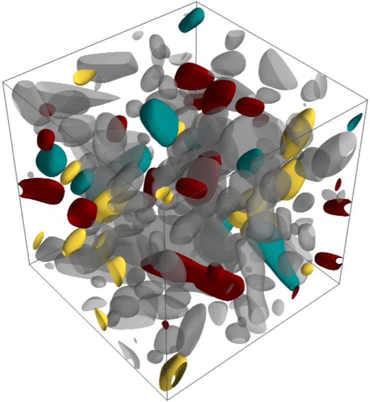

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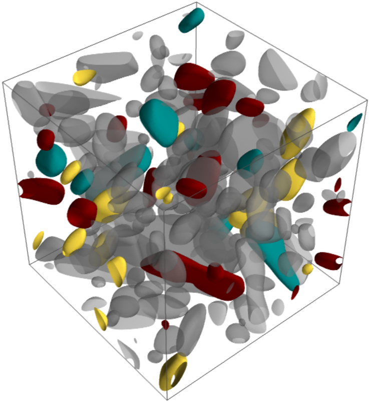

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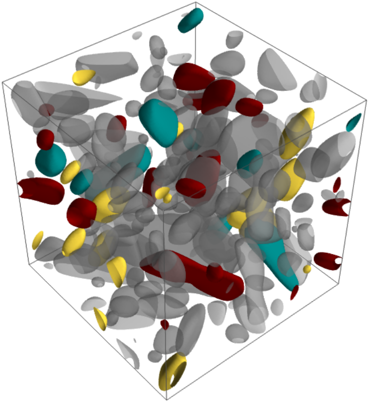

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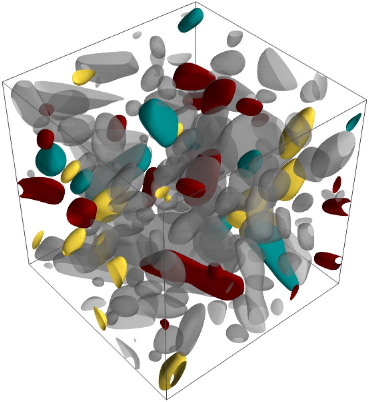

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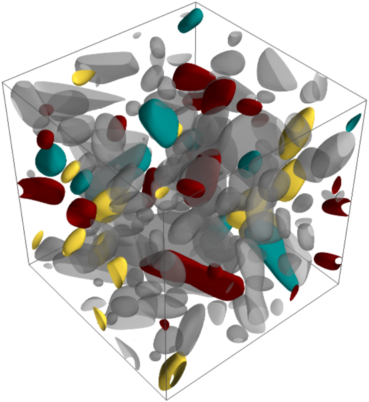

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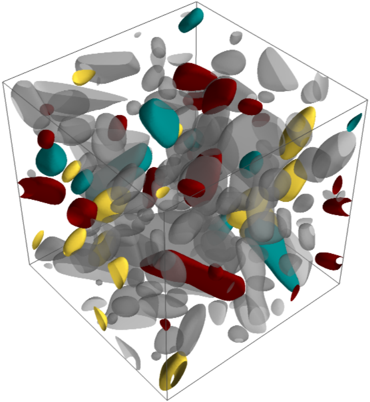

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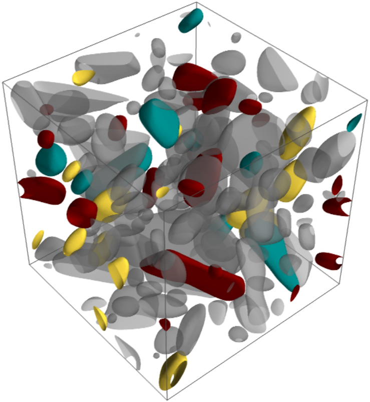

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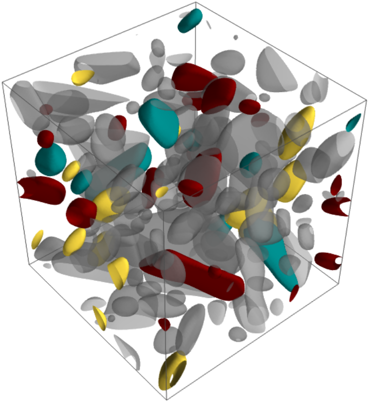

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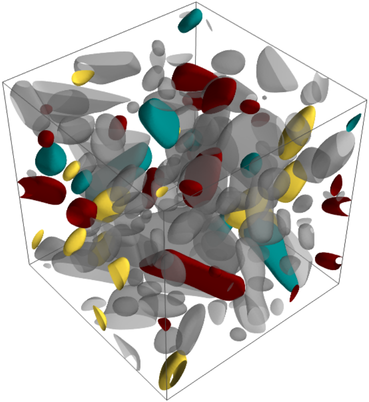

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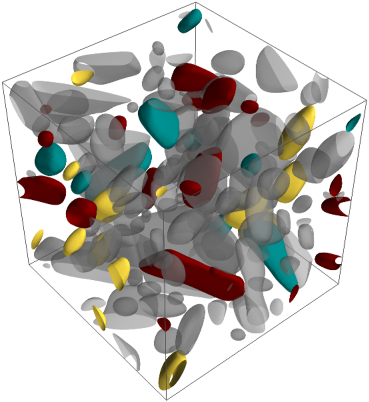

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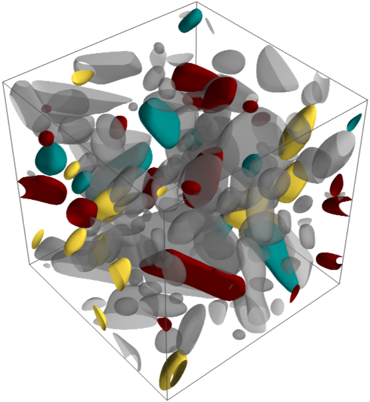

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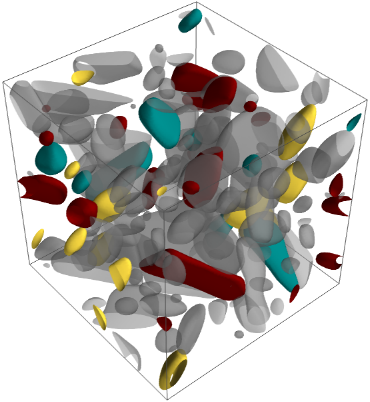

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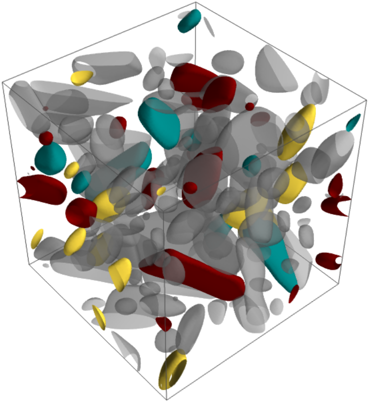

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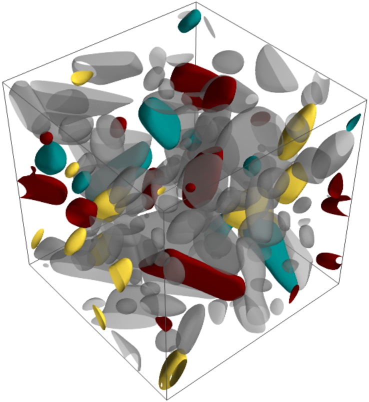

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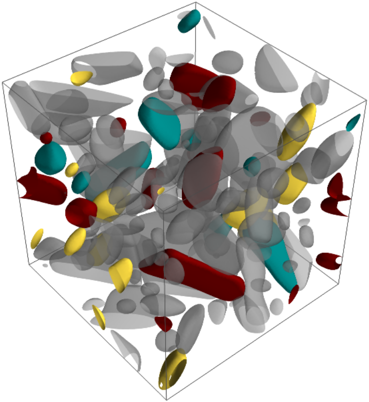

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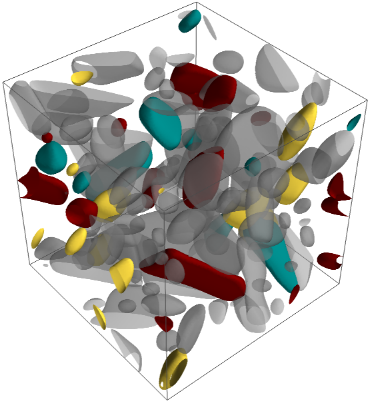

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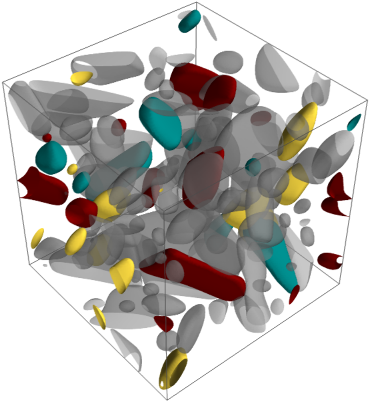

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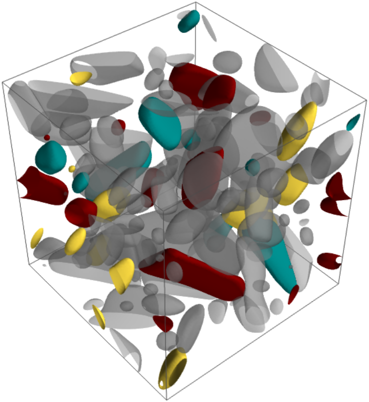

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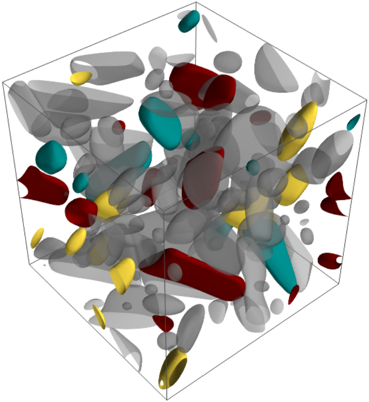

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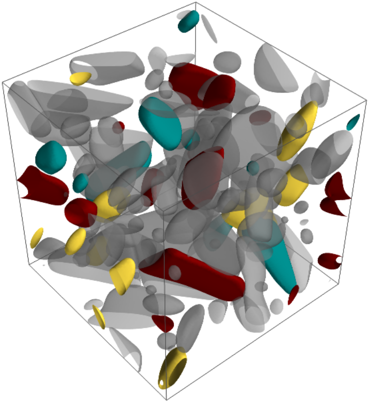

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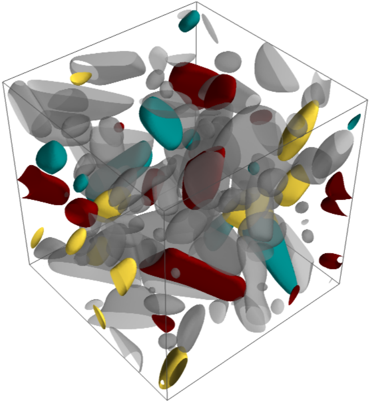

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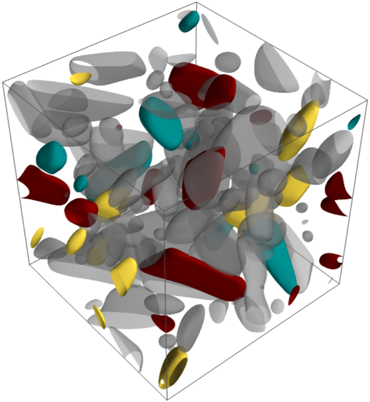

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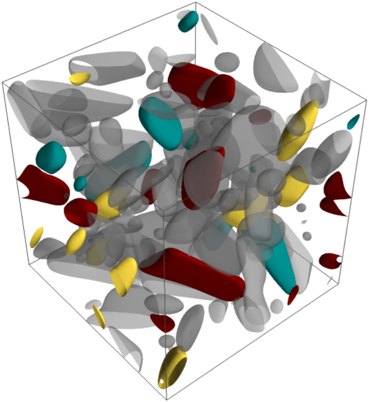

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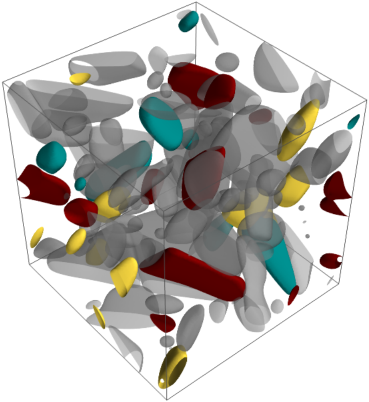

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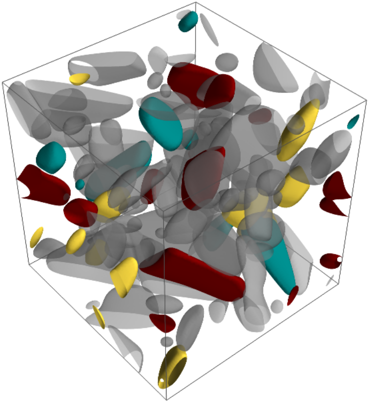

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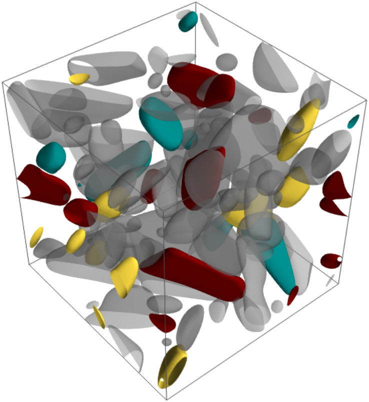

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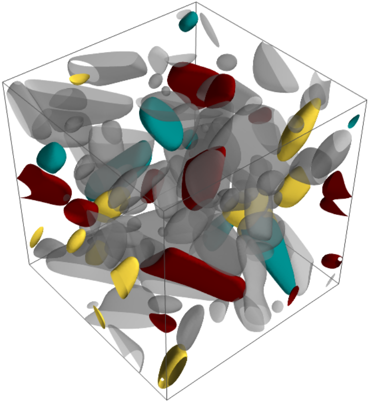

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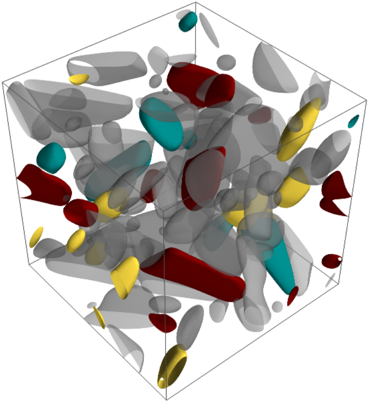

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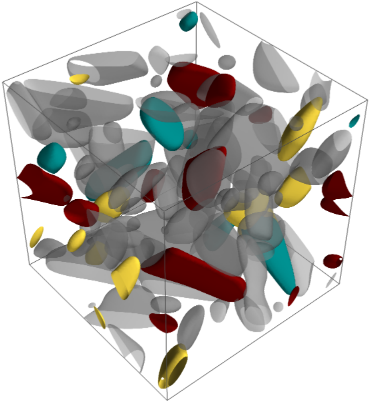

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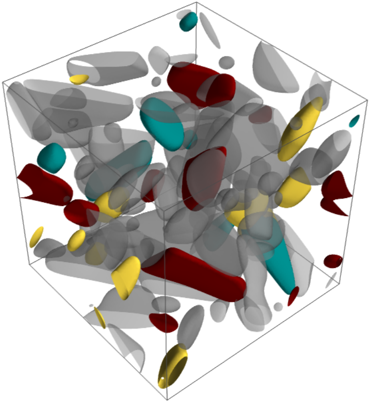

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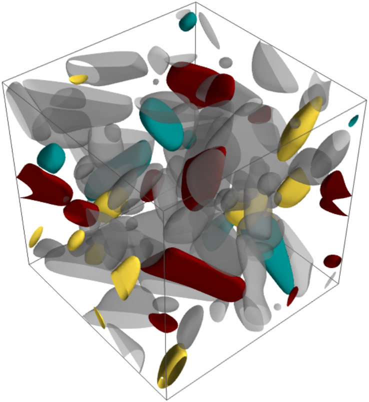

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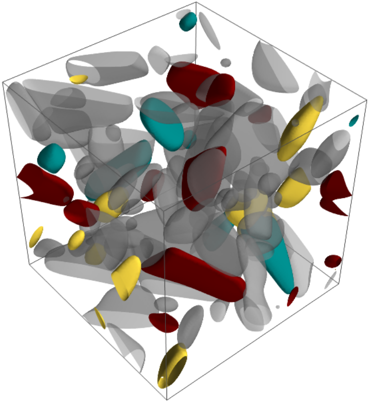

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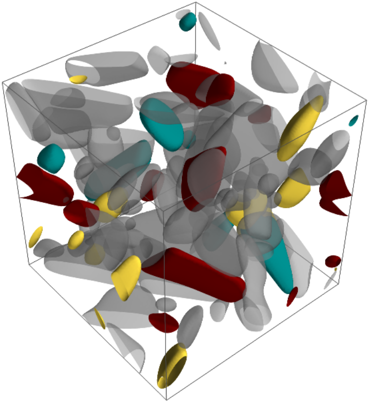

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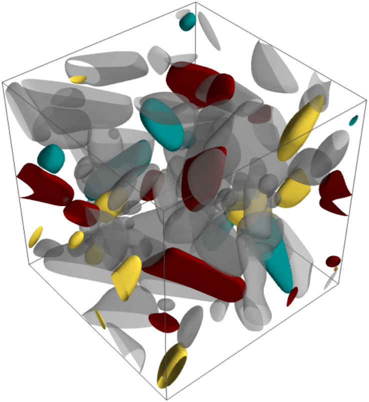

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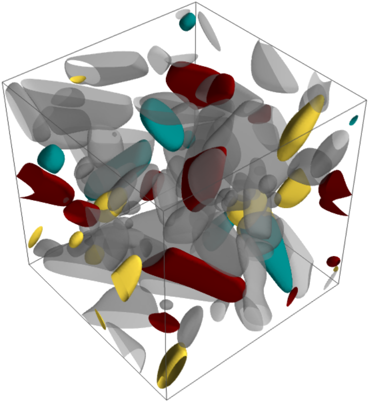

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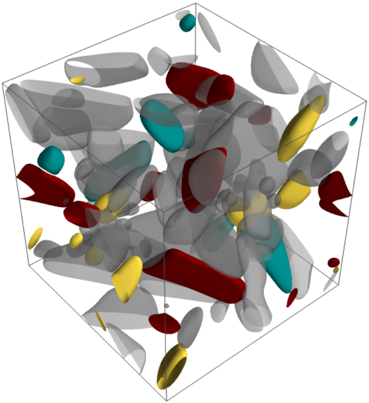

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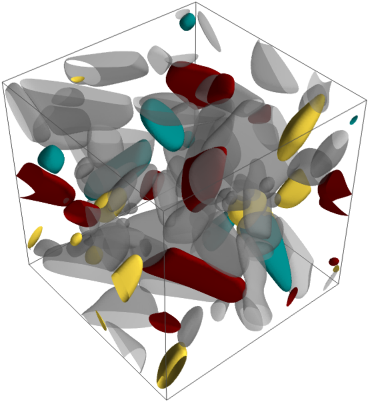

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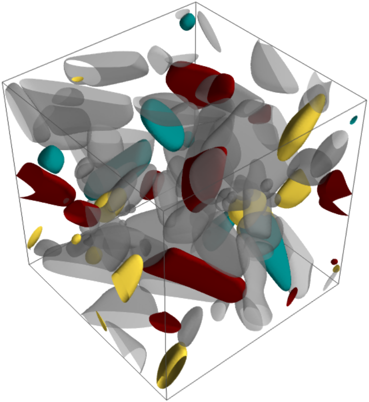

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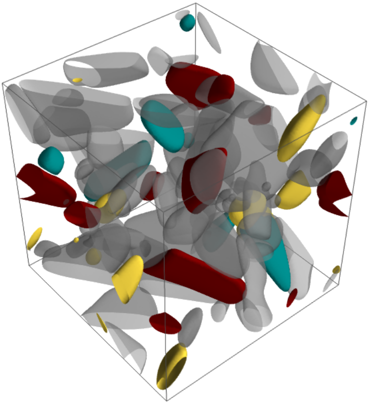

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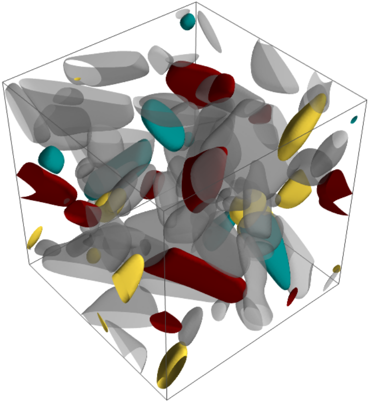

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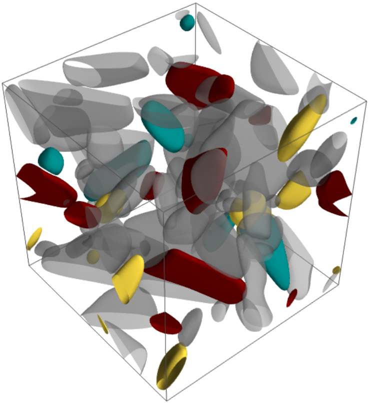

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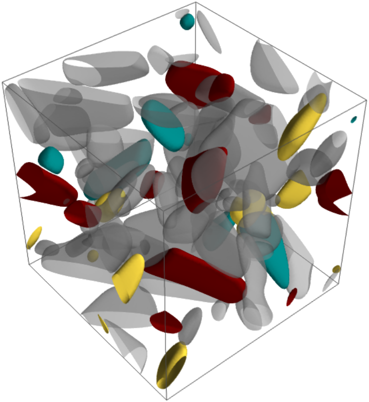

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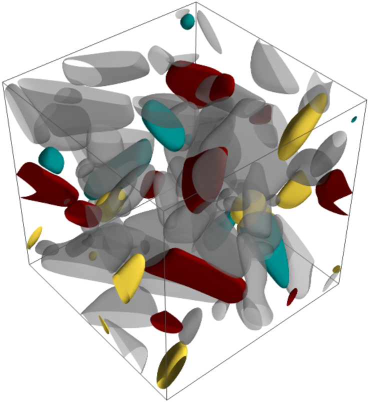

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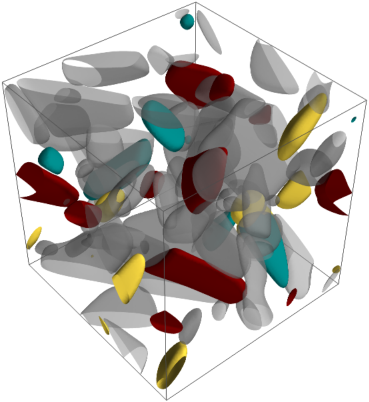

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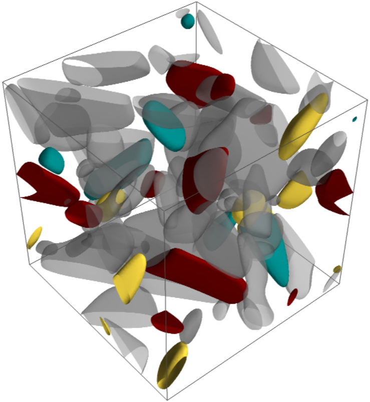

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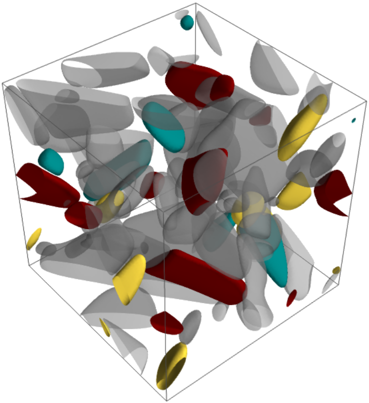

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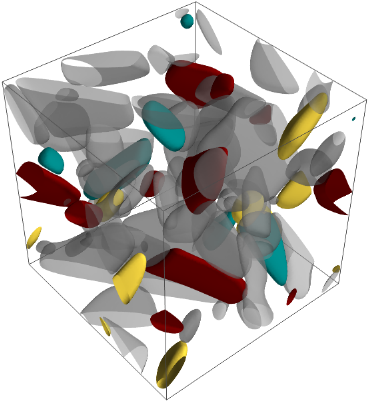

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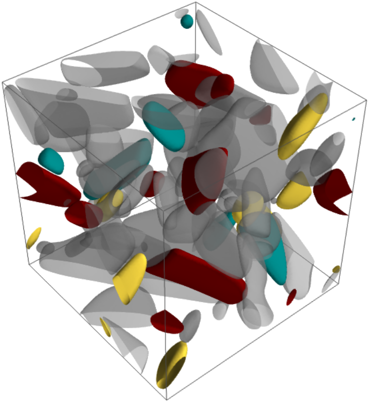

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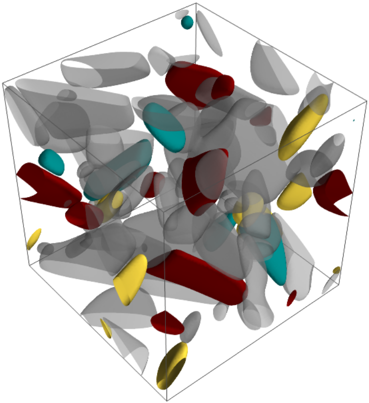

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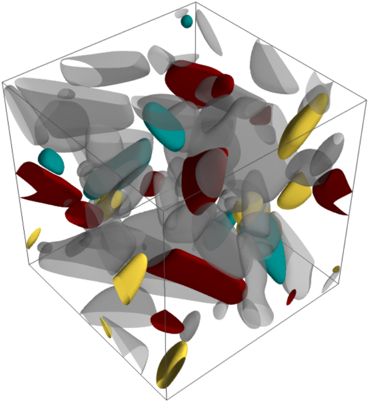

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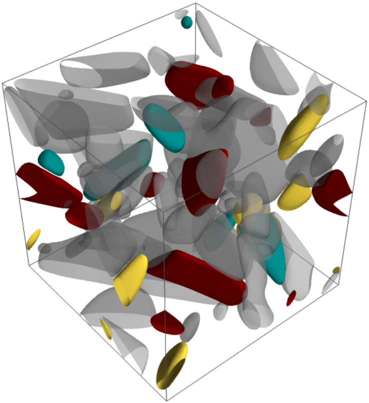

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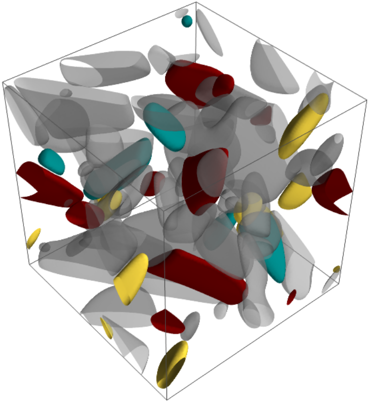

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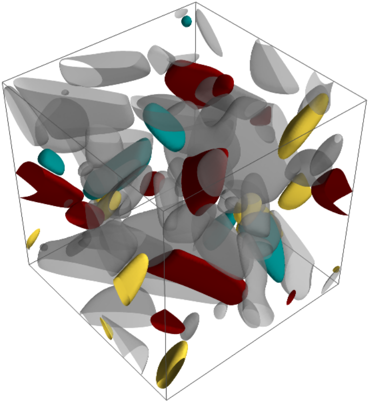

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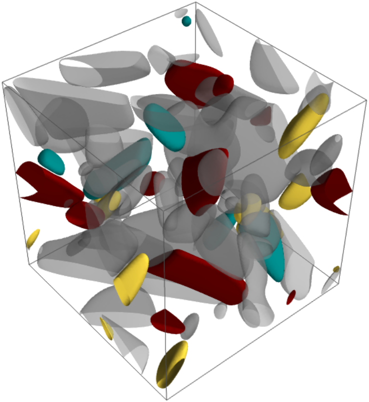

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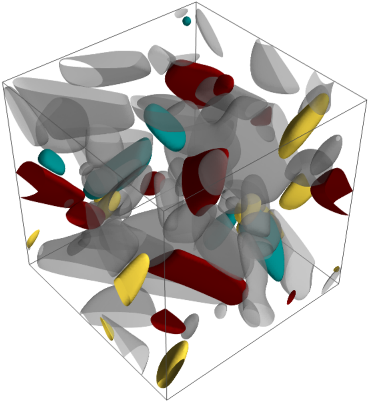

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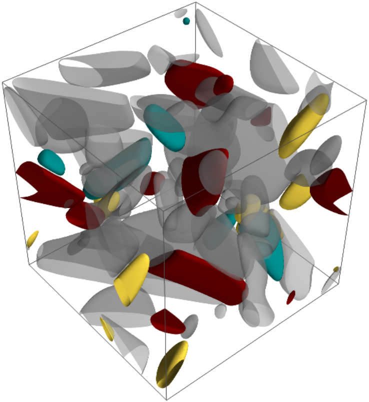

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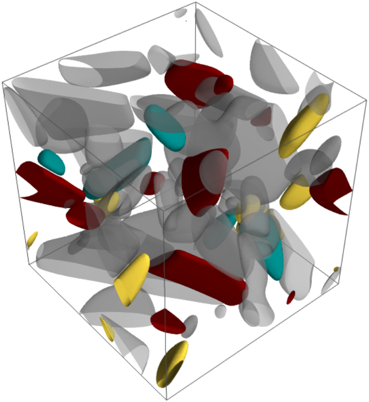

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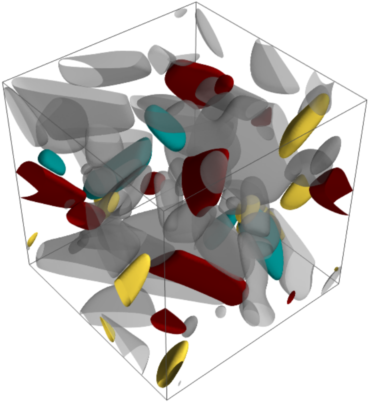

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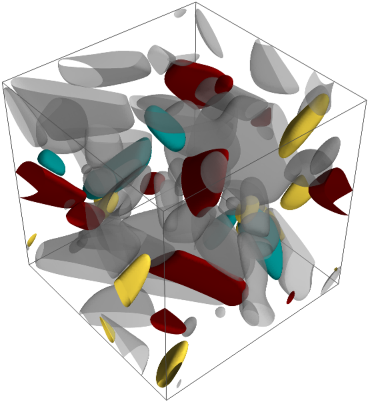

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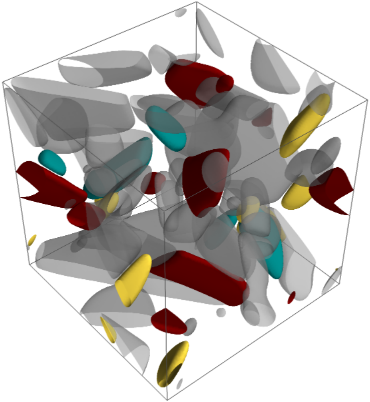

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What is it for?

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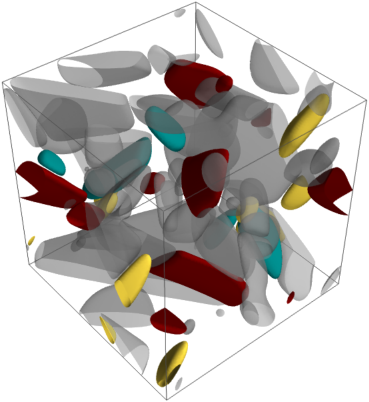

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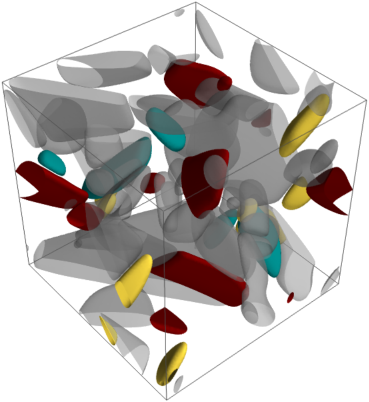

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The recipe

1. Identify the order parameter(s)
2. Build the most relevant thermodynamic functional
3. Derive the evolution equations
4. Relate the parameters to physical quantities
5. Solve (this afternoon)
6. Post-process (this afternoon)

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1. Introduced in the context of phase transition (not only for phase field)
   Physical quantity that discriminates different physical states (gas, liquid, solid, paramagnetic, ferromagnetic . . .)
2. Related to choice of phase diagram to display the different states

- Gas/liquid *[Van der Waals, 1873!]*: density
- Ferromagnetic/paramagnetic *[Weiss, 1907]*: magnetization
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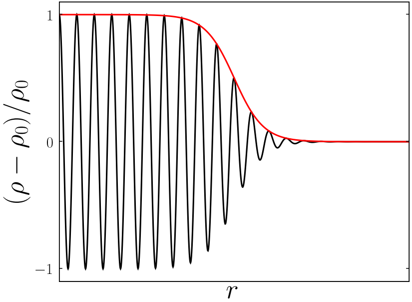
Co-existence of two different states: the order parameter is a field (heterogeneous)

Two visions of the problem

- Either interface are sharp (macroscopic), so discontinuities of the field
- Or diffuse, as proposed very early by van der Waals, 1893



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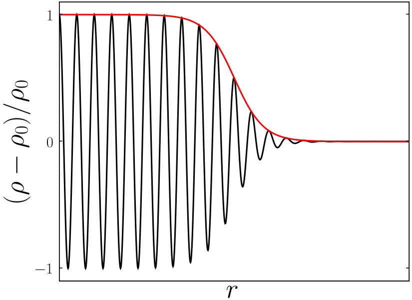

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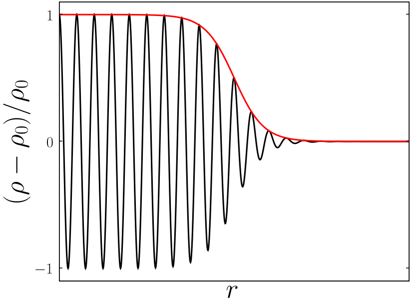

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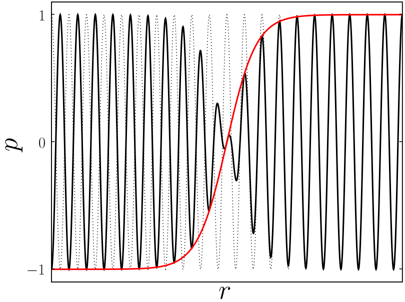

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Same as usual macroscopic thermodynamics, with functionals rather than functions because variables are fields (depend on space . . . and time)

- Isothermal condition and cst volume: Free energy $\mathcal{F}$
  - J.D. Van der Waals,
    The thermodynamic theory of capillarity under the hypothesis of a continous variation of density
  - V.L. Ginzburg, L.D. Landau,
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Starting with the easiest model: Allen-Cahn

Oversimplified version (parameter free but unrealistic)

$$\mathcal{F}(\varphi_{(t,\underline{x})}) = \int_V \left[\varphi^4_{(t,\underline{x})} - \varphi^2_{(t,\underline{x})} + |\nabla\varphi_{(t,\underline{x})}|^2\right] \mathrm{d}V$$

Where does all these terms come from?

1. Homogeneous system $\nabla\varphi = 0$: homogeneous free energy density
   I will consider two examples

2. What is this gradient term?

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1.1. Homogeneous part: Van der Waals fluid

Equation of state for simple fluids: improvement wrt the ideal gas $pv_\mathrm{m} = RT$ by accounting for finite volume of atoms/molecules and interactions (liquid can sustain negative pressures)

$$(p - a/v_\mathrm{m}^2)(v_\mathrm{m} - b) = RT$$

Features a transition between liquid and gas below a critical point given by $\partial P/\partial v_\mathrm{m} = 0$ and $\partial^2 P/\partial v_\mathrm{m}^2 = 0$

2. Build the relevant thermodynamic functional

1.1. Homogeneous part: Van der Waals fluid

Critical point

$$p^c = \frac{a}{27b^2}$$
$$T^c = \frac{8a}{27bR}$$
$$v_{\mathrm{m}}^c = 3b$$

Reduced form

$$\pi = \frac{8\tau}{3v-1} - \frac{3}{v^2}$$

with $\tau = T/T^c$, $\pi = p/p^c$
and $v = v_{\mathrm{m}}/v_{\mathrm{m}}^c$

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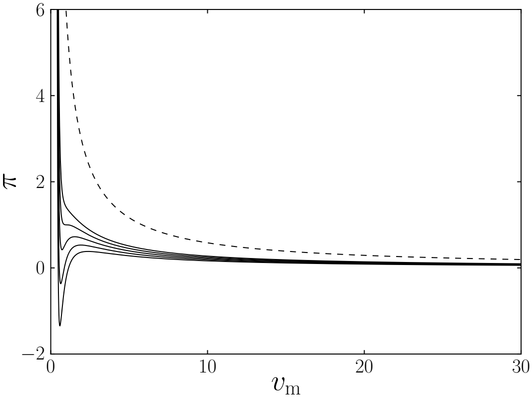

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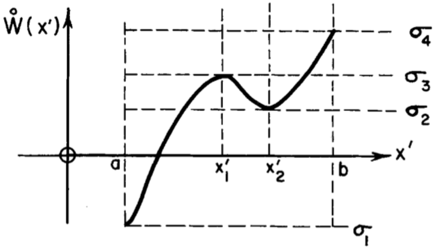

[J. Ericksen, Equilibrium of bars, 1975]

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Free energy: integration of the law of state at constant temperature

$$\frac{1}{RT_c} \frac{\partial f_{\mathrm{m}}}{\partial v}\bigg|_{\tau} = -\pi$$

Below the critical point, f_{m} features a non-convex part: corresponds to states that cannot be observed

Liquid $\leftrightarrow$ Gas transitions

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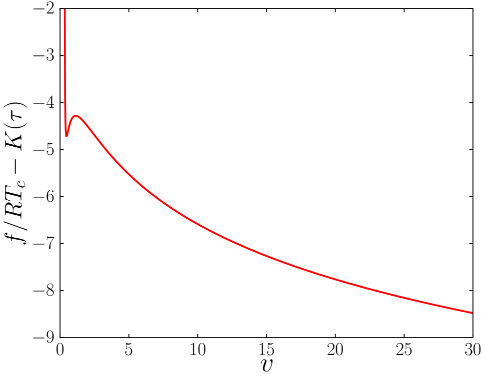

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Equilibrium between liquid and gas: variational calculus

Minimum of $\mathcal{F}$ with constant total number of atoms (constraint)
Miminize the Lagrangian $\mathcal{L} = \mathcal{F} - \lambda\left(\int_V \rho \mathrm{d}V - N\right)$ with $\rho = 1/v_\mathrm{m}$

$$\delta\mathcal{L} = \int_V \left[\delta(\rho f_\mathrm{m}) - \lambda\delta\rho\right]\mathrm{d}V = 0$$

$$\delta\mathcal{L}$$

This is valid $\forall\,\delta\rho$

$$f_\mathrm{m} + \rho\frac{\partial f_\mathrm{m}}{\partial\rho} = \lambda$$

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This is valid $\forall\,\delta\rho$

$$f_\mathrm{m} + \rho\,\frac{\partial f_\mathrm{m}}{\partial \rho} = \lambda$$

2. Build the relevant thermodynamic functional

1.1. Homogeneous part: Van der Waals fluid

Equilibrium between liquid and gas: variational calculus

Minimum of $\mathcal{F}$ with constant total number of atoms (constraint)
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Equilibrium between liquid and gas: variational calculus

$$f_{\mathrm{m}} + \rho \frac{\partial f_{\mathrm{m}}}{\partial \rho} = \lambda$$

Thus, if liquid L and gas G are coexisting, they must feature the same value for their respective Gibbs energies:

$$f_{\mathrm{m}}^{\mathrm{L}}(v_{\mathrm{m}}^{\mathrm{L}}) + p^{\mathrm{L}} v_{\mathrm{m}}^{\mathrm{L}} = f_{\mathrm{m}}^{\mathrm{G}}(v_{\mathrm{m}}^{\mathrm{G}}) + p^{\mathrm{G}} v_{\mathrm{m}}^{\mathrm{G}}$$

Moreover, more involved variational calculus considering two co-existing liquid and gas extending over volumes V^{L} and V^{G} respectively would prove that for a flat interface $p^{\mathrm{L}} = p^{\mathrm{G}}$.

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Equilibrium between liquid and gas: variational calculus

- Maxwell rule: both phases (Gibbs energies of both phases are equal)
- Amounts to find the common tangent which convexifies the free energy

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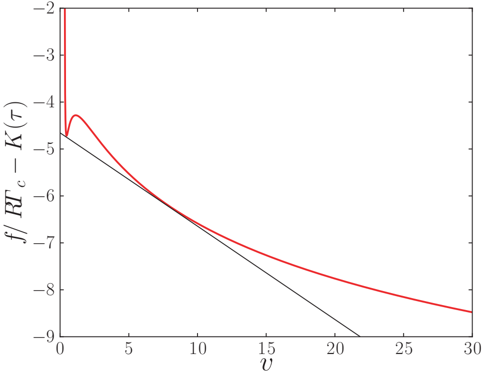

2. Build the relevant thermodynamic functional

1.1. Homogeneous part: Van der Waals fluid

Most important feature: non-convexity of free energy

Expansion with respect to the relevant order parameter $\phi = (v_\mathrm{m} - v_\mathrm{m}^c)/v_\mathrm{m}^c$

$$\pi = \frac{8\tau}{3\phi + 2} - \frac{3}{(1+\phi)^2}$$

$$\pi \sim 4\tau - 3 + 6(1-\tau)\phi$$
$$+ 9(\tau - 1)\phi^2 + 3(4 - 9/2\tau)\phi^3$$

$$f(\phi) = f_0 + A\phi + B\phi^2 + C\phi^3 + D\phi^4$$

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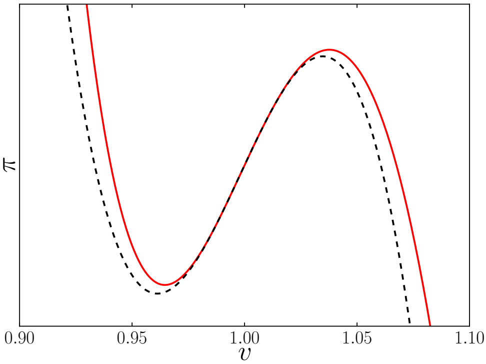

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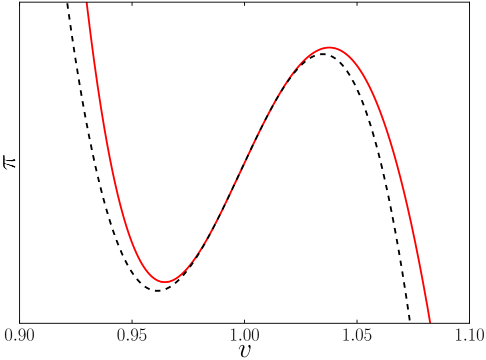

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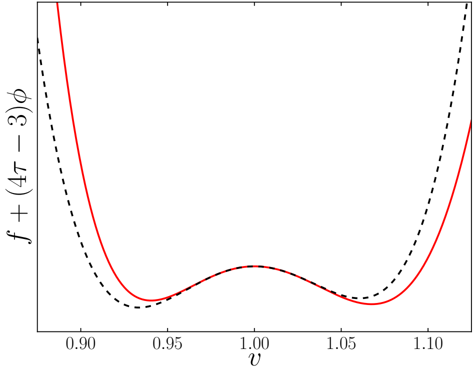

2. Build the relevant thermodynamic functional

1.2. Homogeneous part: Weiss molecular field for magnetism

A bit of statistical physics

In the canonical ensemble $\mathcal{F}$
At equilibrium, the configurations follow the Boltzmann distribution

$$\mathcal{P}_i = \frac{1}{\mathcal{Z}} \exp\big(-\beta E_i\big)$$

$$\mathcal{Z} = \sum_i \exp\big(-\beta E_i\big) \qquad \text{with } \beta = 1/(k_\mathrm{B}T)$$

$$\mathcal{F} = -k_\mathrm{B} T \ln \mathcal{Z}$$

Most simple model for magnetism: Ising
N atoms with spins $s_i = \pm 1$ interacting with nearest neighbors

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i$$

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Let's consider a single atom: can display only two states with probabilities

$$\mathcal{P}_+ = \frac{1}{\mathcal{Z}} \exp(+\beta h) \qquad \mathcal{P}_- = \frac{1}{\mathcal{Z}} \exp(-\beta h)$$

Partition function

$$\mathcal{Z} = \exp(+\beta h) + \exp(-\beta h)$$

Magnetization: average spin

$$m = \langle s \rangle = (+1)\mathcal{P}_+ + (-1)\mathcal{P}_-$$
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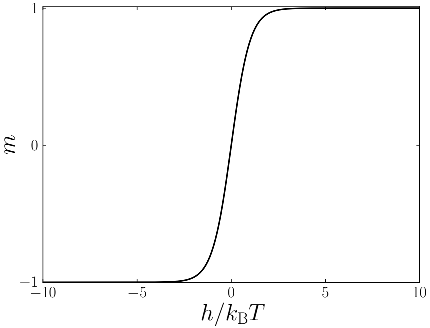

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1.2. Homogeneous part: Weiss molecular field for magnetism

Now, let's consider N atoms: there are 2^N different configurations
Hard to calculate $\mathcal{Z}$ and so the probability of a given configuration (aka microstate)

- Brute force: Monte Carlo with Metropolis algorithm
- Mean field approximation
  Reducing the N bodies problem into a problem involving a single body in an effective field
  Neglect correlations between fluctuations

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- Mean field approximation

  Then, it is easy to compute the averages

$$\mathcal{E} = \langle \mathcal{H} \rangle = -J \sum_{\langle ij \rangle} \langle s_i s_j \rangle - h \sum_i \langle s_i \rangle$$

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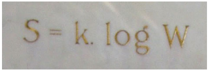
- Mean field approximation

  Bolztmann has related entropy to combinatorics:



Simple when there is no correlation.

Indeed reduces to count how many configurations with N_+ indistinguishable positive spins over the N atoms

$$W = \binom{N}{N_+} = \frac{N!}{N_+!N_-!}$$

with $N_+ = N(1+m)/2$ and $N_- = N(1-m)/2$

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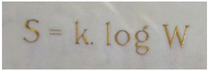

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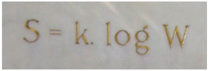

  Stirling formula: $n! \sim \sqrt{2\pi} n^{n+1/2} \exp(-n)$ or $\ln n! \sim n \ln n - n$
  (very good for $n > 10$)

$$\ln W = N \ln N - N - \left(N_+ \ln N_+ - N_+ + N_- \ln N_- - N_- \right)$$

  Of course $N_+ + N_- = N$, then

$$\ln W = -(N_+ \ln(N_+/N) + N_- \ln(N_-/N))$$

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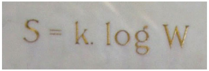

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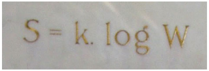

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- Mean field approximation

  Bolztmann has related entropy to combinatorics:

  $$S = k.\log W$$

  Introducing m: $N_+ = N(1+m)/2$ and $N_- = N(1-m)/2$

  $$\ln W = -N\Big(\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2}\Big)$$

  Find a polynomial expansion!

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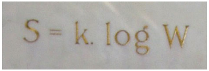

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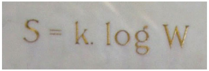

Expanding not far from the critical point, i.e. $m \sim 0$:

$$\ln W \sim -N\Big[-\ln 2+\frac{1+m}{2}\Big(m-\frac{m^2}{2}+\frac{m^3}{3}\Big)+\frac{1-m}{2}\Big(-m-\frac{m^2}{2}-\frac{m^3}{3}\Big)\Big]$$

$$\ln W \sim -N\Big(-\ln 2+\frac{1}{2}m^2+\frac{1}{12}m^4\Big)$$

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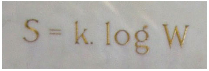

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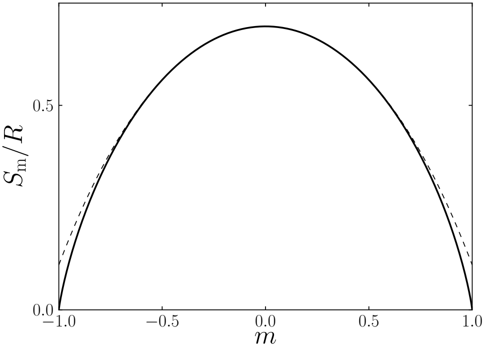
$$\mathcal{S} \sim -k_{\mathrm{B}} N\Big(-\ln 2 + \frac{1}{2} m^2 + \frac{1}{12} m^4 \Big)$$



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  End up with some $-\phi^2 + \phi^4$ potential

  Indeed the free energy now reads:

$$n f_{\mathrm{m}} = \mathcal{F} = \mathcal{E} - T\mathcal{S}$$

$$\frac{f_{\mathrm{m}}}{\mathcal{N}_a} = -\frac{zJ}{2} m^2 - hm + k_{\mathrm{B}} T\left(-\ln 2 + \frac{1}{2} m^2 + \frac{1}{12} m^4\right)$$

At the critical temperature $\frac{\partial^2 f_{\mathrm{m}}}{\partial m^2}\Big|_{m=0} = 0$, then $k_{\mathrm{B}} T_c = zJ$, so that:

$$\frac{f_{\mathrm{m}}}{\mathcal{N}_a} + \mathrm{cste} = -hm + \frac{k_{\mathrm{B}}}{2}(T - T_c)\, m^2 + \frac{k_{\mathrm{B}} T}{12} m^4$$

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$$
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\frac{f_{\mathrm{m}}}{\mathcal{N}_a} + \mathrm{cste} = -hm + \frac{k_{\mathrm{B}}}{2}(T - T_c)\,m^2 + \frac{k_{\mathrm{B}}T}{12}m^4
$$

2. Build the relevant thermodynamic functional

1.2. Homogeneous part: Weiss molecular field

- Mean field approximation

  End up with some $-\phi^2 + \phi^4$ potential

  Indeed the free energy now reads:

$$
\begin{aligned}
n f_{\mathrm{m}} &= \mathcal{F} = \mathcal{E} - T\mathcal{S} \\
\frac{f_{\mathrm{m}}}{\mathcal{N}_a} &= -\frac{zJ}{2}\, m^2 - hm + k_{\mathrm{B}}T\left(-\ln 2 + \frac{1}{2}m^2 + \frac{1}{12}m^4\right)
\end{aligned}
$$

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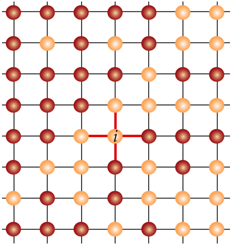
2. Build the relevant thermodynamic functional

2.1. Gradient: spinodal decomposition *[Hillert 1956]*

Equivalent to the mean field approximation of Ising model



- Mean field neglects fluctuations

$$G(\underline{r}, \underline{r}') = \left\langle \delta\psi(\underline{r})\, \delta\psi(\underline{r}') \right\rangle = 0$$

$$\left\langle \psi(\underline{r})\, \psi(\underline{r}') \right\rangle = \langle \psi(\underline{r}) \rangle \left\langle \psi(\underline{r}') \right\rangle$$

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2. Build the relevant thermodynamic functional

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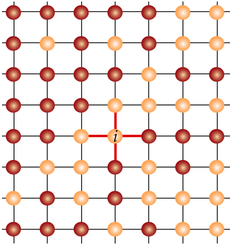

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$$\mathcal{H} = \frac{1}{2} \sum_{ij} V^{\alpha\beta} p_i^{\alpha}\, p_j^{\beta}$$

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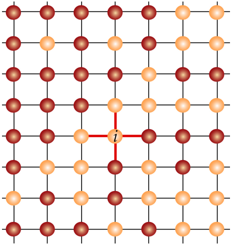

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$$\mathcal{E} = \langle \mathcal{H} \rangle = \frac{1}{2} \sum_{ij} V^{\alpha\beta} \langle p_i^\alpha p_j^\beta \rangle$$

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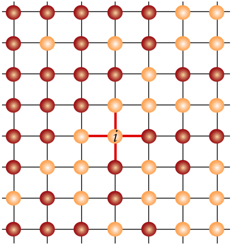

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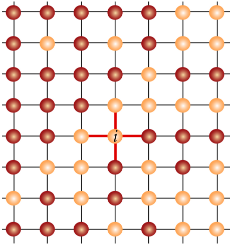

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2. Build the relevant thermodynamic functional

2.1. Gradient: spinodal decomposition *[Hillert 1956]*

Mean field

- Energies of first nearest neighbors ij

$$\mathcal{E}_{ij} = -c_i(1-c_j)\,V + (1-c_j)\,V^{\mathrm{AA}} + c_i\,V^{\mathrm{BB}} + (c_j - c_i)\,V^{\mathrm{AB}}$$

with $V = V^{\mathrm{AA}} + V^{\mathrm{BB}} - 2V^{\mathrm{AB}}$

Proove it (better to know what to get)

- Internal energy becomes

$$\mathcal{E} =$$

2. Build the relevant thermodynamic functional

2.1. Gradient: spinodal decomposition *[Hillert 1956]*

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$$\mathcal{E} = \frac{1}{2}\sum_{ij}\mathcal{E}_{ij}$$

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Proove it (better to know what to get)

- Internal energy becomes

$$\mathcal{E} = N\,V^{\mathrm{AA}} + \left(V^{\mathrm{BB}} - V^{\mathrm{AA}}\right)\sum_i c_i - \frac{1}{2}\sum_{ij} c_i\,(1-c_j)\,V$$

2. Build the relevant thermodynamic functional

2.1. Gradient: spinodal decomposition *[Hillert 1956]*

Mean field

- Entropy of a random assembly (ideal solution)

$$\mathcal{S} = -k_{\mathrm{B}} \sum_i \left[c_i \, \ln c_i + (1 - c_i) \, \ln(1 - c_i) \right]$$

2. Build the relevant thermodynamic functional

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$$\mathcal{S} = -k_{\mathrm{B}} \sum_i \left[c_i \ln c_i + (1 - c_i) \ln(1 - c_i)\right]$$

- Free energy

$$\mathcal{F} = N\, V^{\mathrm{AA}} + (V^{\mathrm{BB}} - V^{\mathrm{AA}}) \sum_i c_i + k_{\mathrm{B}}T \sum_i \left[c_i \ln c_i + (1 - c_i) \ln(1 - c_i)\right] - \frac{1}{2} \sum_{ij} c_i\,(1 - c_j)\, V$$

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- Free energy with respect to pure A & B

$$\Delta \mathcal{F} = k_{\mathrm{B}} T \sum_i \left[c_i \, \ln c_i + (1 - c_i) \, \ln(1 - c_i) \right] - \frac{1}{2} \sum_{ij} c_i \, (1 - c_j) \, V$$

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- Then the density for an homogeneous solution (i.e. $c_i = c \quad \forall \, i$)

$$\Delta f_0 = k_{\mathrm{B}} T \left[c \, \ln c + (1 - c) \, \ln(1 - c) \right] - \frac{1}{2} c \, (1 - c) \, V$$

- Demixing possible for $V < 0$ such as $\frac{\partial^2}{\partial c^2} \Delta f_0 < 0$

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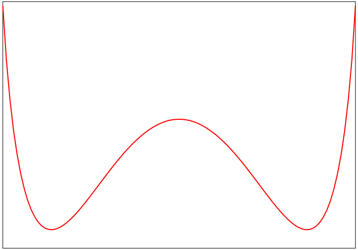

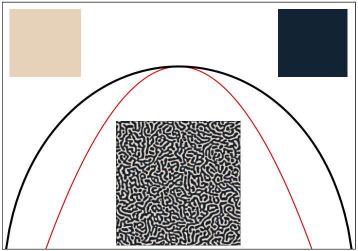

2. Build the relevant thermodynamic functional

2.1. Gradient: spinodal decomposition *[Hillert 1956]*

Mean field

- At equilibrium

$$\frac{\partial}{\partial c_i}\mathcal{F} = \mu \quad \forall\, i$$

- Using the homogeneous free energy density (do it!)

2. Build the relevant thermodynamic functional

2.1. Gradient: spinodal decomposition *[Hillert 1956]*

Mean field

- At equilibrium

$$\frac{\partial}{\partial c_i}\Delta\mathcal{F} = \mu' \quad \forall\, i$$

- Using the homogeneous free energy density (do it!)

2. Build the relevant thermodynamic functional

2.1. Gradient: spinodal decomposition *[Hillert 1956]*

Mean field

- At equilibrium (symetrical case $V^{\mathrm{AA}} = V^{\mathrm{BB}}$ and $\mu = 0$)

$$\frac{\partial}{\partial c_i}\Delta\mathcal{F} = k_{\mathrm{B}}T \, \ln\left(\frac{c_i}{1-c_i}\right) + \sum_j c_j \, V - \frac{V}{2} = 0$$

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$\sum_j (c_j - c_i)$ is the Laplacian discretized at the scale of the first neighbors spacing: may have something to do with the gradient term

2. Build the relevant thermodynamic functional

2.2. Gradient: spinodal decomposition by Cahn-Hilliard

- Lowest order expansion (continuum limit of a mean field model with first neighbor approximation [Hillert, 1956, 1961])

$$f(c, \nabla c, \nabla^2 c \dots) \approx f_0(c) + \sum_i \left.\frac{\partial f}{\partial(\partial_{x_i} c)}\right|_c \partial_{x_i} c + \sum_{ij} \left.\frac{\partial f}{\partial(\partial^2_{x_i x_j} c)}\right|_c \partial^2_{x_i x_j} c + \frac{1}{2}\sum_{ij} \left.\frac{\partial^2 f}{\partial(\partial_{x_i} c)\partial(\partial_{x_j} c)}\right|_c (\partial_{x_i} c)(\partial_{x_j} c) + \dots$$

- In an isotropic medium, f is invariant wrt $x_i \to -x_i$ and $x_i \to x_j$

$$f(c, \nabla c, \nabla^2 c, \dots) = f_0(c) + \kappa_1 \nabla^2 c + \kappa_2 |\nabla c|^2$$

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$$+ \frac{1}{2} \sum_{ij} \left. \frac{\partial^2 f}{\partial\left(\partial_{x_i} c\right) \partial\left(\partial_{x_j} c\right)} \right|_c \left(\partial_{x_i} c\right)\left(\partial_{x_j} c\right) + \dots$$

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The gradient terms can be gathered

$$\int_V \left[\kappa_1 \nabla^2 c + \kappa_2 |\nabla c|^2\right] \mathrm{d}V = \int_V \left[\nabla \cdot (\kappa_1 \nabla c) - d\kappa_1/dc\, |\nabla c|^2 + \kappa_2 |\nabla c|^2\right] \mathrm{d}V$$

$$= \int_V (\kappa_2 - d\kappa_1/dc) |\nabla c|^2 \mathrm{d}V + \int_{\partial V} \kappa_1 \nabla c \cdot \underline{n}\, \mathrm{d}S$$

Generally, no prescription at the boundaries for different reasons:

- Periodic boundary conditions
- Surfaces can be described by diffuse interfaces

Then

$$\int_{\partial V} \kappa_1 \nabla c \cdot \underline{n}\, \mathrm{d}S = 0$$

and the gradient term involves only $|\nabla c|^2$

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3. Evolution equations

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Following usual non-equilibrium thermodynamics

- Considering some "Allen-Cahn" free energy functional

$$\mathcal{F} = \int_V \psi \, \mathrm{d}V = \int_V \left[f_0(\varphi) + \frac{\alpha}{2} |\nabla \varphi|^2 \right] \mathrm{d}V$$

  where φ is not conserved (e.g. order, magnetization. . .) and where f_0 displays two minima separated by a non convex part

- Second principle implies at cst temperature:

$$\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}t} = -T\,\dot{S}_i + \mathcal{P}_{\text{ext}} \quad \text{with } \dot{S}_i \geq 0$$

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$$\nabla\varphi \cdot \nabla \frac{\partial \varphi}{\partial t} = -\frac{\partial \varphi}{\partial t}\,\nabla \cdot \nabla\varphi + \nabla \cdot \left(\frac{\partial \varphi}{\partial t}\nabla\varphi\right)$$

$$\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}t} = \int_V \left[\frac{\partial f_0}{\partial \varphi}\frac{\partial \varphi}{\partial t} - \alpha\,\frac{\partial \varphi}{\partial t}\,\nabla \cdot \nabla\varphi\right] \mathrm{d}V + \alpha \int_S \frac{\partial \varphi}{\partial t}\,\nabla\varphi \cdot \underline{n}\ \mathrm{d}S$$

$$T\,\dot{\mathcal{S}}_i = \int_V \left[-\frac{\partial f_0}{\partial \varphi}\frac{\partial \varphi}{\partial t} + \alpha\,\frac{\partial \varphi}{\partial t}\,\Delta\varphi\right] \mathrm{d}V$$

$$\mathcal{P}_{\mathrm{ext}} = \alpha \int_S \frac{\partial \varphi}{\partial t}\,\nabla\varphi \cdot \underline{n}\,\mathrm{d}S$$

Discard subtleties of alternative routes (in part. entropy flows)

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- Dissipation $T\,\dot{\mathcal{S}}_i$

$$\int_V \left[-\frac{\partial f_0}{\partial \varphi}\,\frac{\partial \varphi}{\partial t} + \alpha\,\frac{\partial \varphi}{\partial t}\Delta\varphi\right] \mathrm{d}V \geq 0$$

- Local dissipation $T\,\dot{s}_i$

$$\frac{\partial \varphi}{\partial t}\left(-\frac{\partial f_0}{\partial \varphi} + \alpha\Delta\varphi\right) \geq 0$$

- Usual argument (linear regime) *[I. Prigogine, E. Guggenheim]*

$$\dot{s}_i = J\,F \geq 0 \quad \longrightarrow \quad J \propto F$$

$$\dot{\varphi} = M\left(\alpha\Delta\varphi - \frac{\partial f_0}{\partial \varphi}\right) \qquad \text{with } M > 0$$

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- Second principle implies at cst temperature:

$$\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}t} = -T\,\dot{S}_i - T\,\dot{S}_{\mathrm{ext}} + \mathcal{P}_{\mathrm{ext}} \quad \text{with } \dot{S}_i \geq 0$$

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The solute balance must be accounted for

$$T\,\dot{\mathcal{S}}_i + T\,\dot{\mathcal{S}}_{\text{ext}} = \int_V \mu\,\nabla\cdot J\,\mathrm{d}V - \alpha \int_S \nabla\cdot J\,\nabla c \cdot \underline{n}\,\mathrm{d}S$$

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- So we proceed to a second integration by parts

$$\mu \, \nabla \cdot J = \nabla \cdot \big(\mu J\big) - J \cdot \nabla \mu$$

Then

$$T\,\dot{S}_i + T\,\dot{S}_{\text{ext}} = \int_S \mu J \cdot \underline{n}\,\mathrm{d}S - \int_V J \cdot \nabla \mu \,\mathrm{d}V - \alpha \int_S \nabla \cdot J \,\nabla c \cdot \underline{n}\,\mathrm{d}S$$

and we identify

$$T\,\dot{S}_i = -\int_V J \cdot \nabla \mu \,\mathrm{d}V \geq 0$$

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Following usual non-equilibrium thermodynamics

- The dissipation reads

$$T\,\dot{\mathcal{S}}_i = -\int_V J\cdot\nabla\mu\,\mathrm{d}V \geq 0$$

In the linear regime

$$J = -L\,\nabla\mu = -L\,\nabla\left(\frac{\partial f_0}{\partial c} - \alpha\Delta c\right) \qquad \text{with } L > 0$$

Inserting the full expression of J into the solute balance gives the famous Cahn-Hilliard equation

$$\frac{\partial c}{\partial t} = \nabla\cdot\left[L\,\nabla\left(\frac{\partial f_0}{\partial c} - \alpha\Delta c\right)\right]$$

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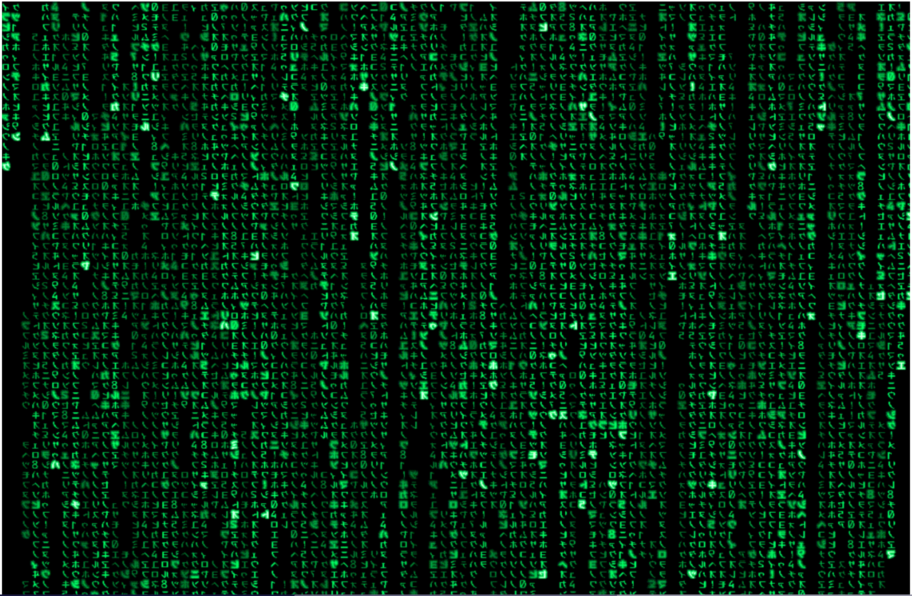

4. Parameters

Equilibrium profile of φ in a simple Allen-Cahn

1D system with a flat interface perpendicular to x and

$$\varphi(-\infty) = 1 \qquad \mathrm{d}\varphi/\mathrm{d}x(-\infty) = 0$$

$$\varphi(+\infty) = 0 \qquad \mathrm{d}\varphi/\mathrm{d}x(+\infty) = 0$$

The equilibrium condition reads

$$\delta\mathcal{F} = \delta \int_V \left[f_0(\varphi) + \frac{\alpha}{2}|\nabla\varphi|^2 \right] \mathrm{d}V = 0 \quad \Leftrightarrow \quad \alpha \frac{d^2\varphi}{dx^2} = \frac{df_0}{d\varphi}$$

Integration of this ODE is elementary calculus.

Recognize that $d\varphi/dx$ is an integrating factor, the previous ODE becomes:

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Complying with the boundary conditions (sign)

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In the general case (f_0 non-convex but cumbersome function), integrate numerically: the profile features a sigmoidal shape (smooth step function)

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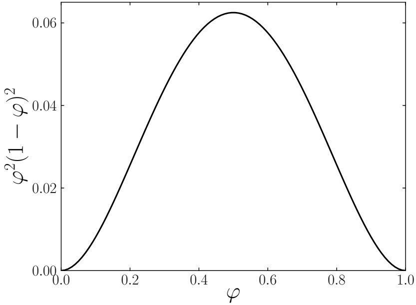
When
$f_0(\varphi) = W\, g(\varphi) = W \varphi^2 (1-\varphi)^2$,
the sigmoidal shape can be computed analytically and displays nice features



$$\frac{d\varphi}{dx} = -\sqrt{2W/\alpha}\,\varphi(1-\varphi)$$

Just basic calculus

$$\frac{d\varphi}{\varphi(1-\varphi)} = -4\,\frac{dx}{\delta} \quad \text{with} \quad \delta = 4\sqrt{\alpha/(2W)}$$

Just do it!

Hint: substitute $\psi = \varphi/(1-\varphi)$ and use symmetry

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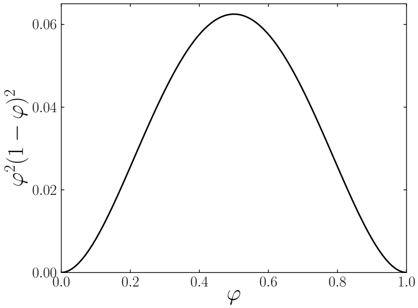

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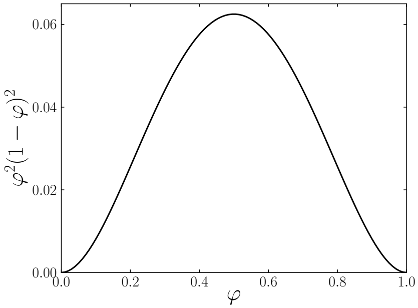

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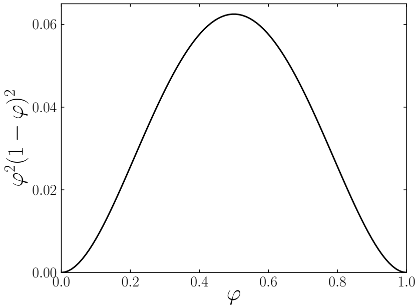

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$$\ln\left(\frac{\psi}{\psi_{(x=0)}}\right) = -4\,\frac{x}{\delta}$$

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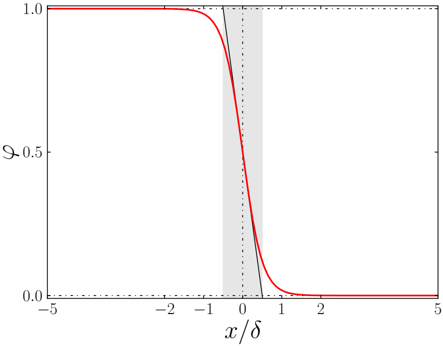

$$\varphi_{(x)} = \frac{1}{2}\left(1-\tanh(2\,x/\delta)\right)$$

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Interface energy in a simple Allen-Cahn

The interface energy is the excess of the relevant potential:
free energy in Allen-Cahn $(f_0(\varphi_{(-\infty)}) = f_0(\varphi_{(+\infty)}))$

$$\gamma = \int_{-\infty}^{+\infty} \left[\Delta f_0 + \frac{\alpha}{2}\left|\frac{d\varphi}{dx}\right|^2\right]\mathrm{d}x$$

with $\Delta f_0 = f_0(\varphi_{(x)}) - f_0(\varphi_{(-\infty)})$

Let's recall that at equilibrium (cf. Eq.(1)):

$$\frac{\alpha}{2}\left(\frac{d\varphi}{dx}\right)^2 = \Delta f_0$$

Thus

$$\gamma = \int_{-\infty}^{+\infty} 2\,\Delta f_0(\varphi_{(x)})\,\mathrm{d}x = \int_{-\infty}^{+\infty} \alpha\left|\frac{d\varphi}{dx}\right|^2\mathrm{d}x$$

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Rather than integrating wrt x, better to integrate wrt φ

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Try!

Using again Eq.(1)

$$\gamma = \int_0^1 \sqrt{2\alpha\Delta f_0}\,\mathrm{d}\varphi$$

For $f_0(\varphi) = W\,g(\varphi) = W\,\varphi^2(1-\varphi)^2$

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4. Parameters

Interface energy in a simple Allen-Cahn

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4. Parameters

Allen-Cahn: equilibrium

$$\varphi_0 = \frac{1}{2}\left[1 - \tanh\left(\frac{r}{2\delta}\right)\right] \qquad \delta \propto \frac{\varepsilon}{\sqrt{W}}$$

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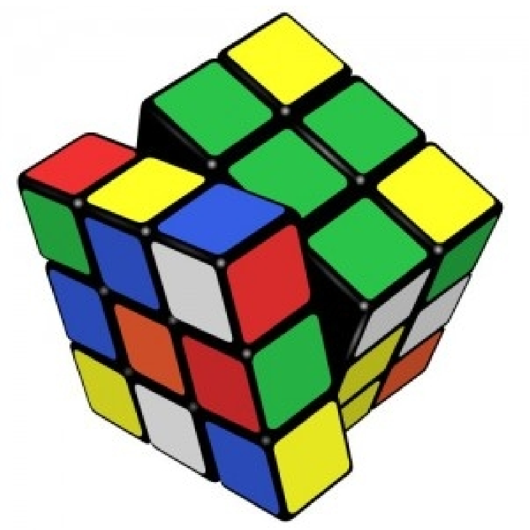
5. Solving

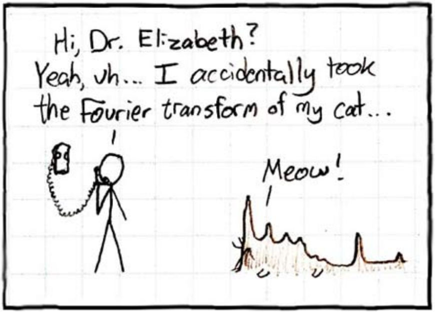


4. Solving

A few words on the spectral method used this afternoon

Use Fourier transforms for periodic microstructures

- Spatial differential operators become algebraic operations
- Very fast algorithms for performing the transforms back and forth: FFT *[Cooley,Tukey]*
- Scale as $N \log N$ rather than N^2
- Small memory footprints: 3D!!



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I will not give any rigorous definitions and proofs

More like a quick and (very) dirty recipes

$$\hat{\varphi}(\underline{k}) = \int_V \varphi(\underline{x}) \exp\left(-\,\mathrm{i}\underline{k}\cdot\underline{x}\right) \mathrm{d}^3x$$

$$\varphi(\underline{x}) = \frac{1}{(2\pi)^3} \int_K \hat{\varphi}(\underline{k}) \exp\left(+\,\mathrm{i}\underline{k}\cdot\underline{x}\right) \mathrm{d}^3k$$

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$$\widehat{\frac{\partial \varphi}{\partial x_i}} = \mathrm{i}k_i\,\hat{\varphi}$$

(proof: integration by parts, considering that the functions are well behaved such that the integrals are convergent)

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Apply to Allen-Cahn equation