

Magnetic Manipulation of Functional Molecular Materials

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Magnetic Tools & Materials

Homogeneous
magnetic fields



Orientation
(anisotropy required)

Magnetic field gradients



Levitation

polymers

peptides

proteins

molecular dyes

*biological
tissue*

*polymer
liquid crystals*

liquid crystals

*supramolecular
aggregates*

Outline

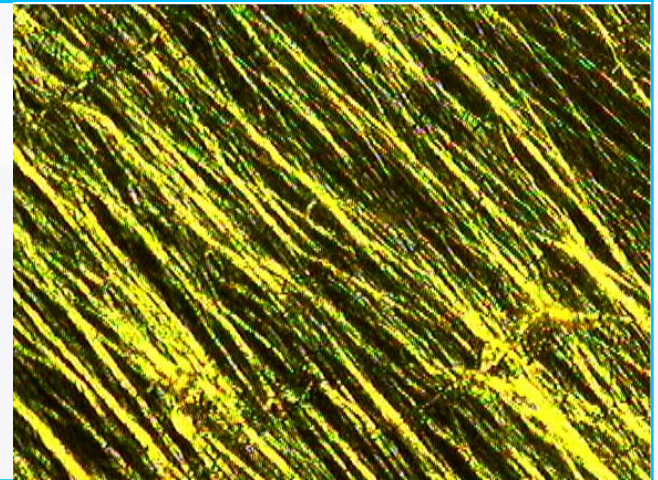
Part I: Magnetic Levitation

- Principle of Levitation
- Magneto-Archimedes effect
- Suppression of convection



Part II: Magnetic Orientation

- Principle of Orientation
- Liquid Crystals
- Supramolecular self-assemblies



Part I: Magnetic Levitation

Utilizing forces in gradient magnetic fields

Outline

- Explanation of principle
- Magneto-Archimedes effect
- Suppression of convection

Applications:

- magnetic separation
- tuning effective gravity
- microgravity
- crystal growth

Magnetic energy (isotropic objects)

$$E(B) = -\int_0^B \mathbf{m} \cdot d\mathbf{B} = -\frac{\chi V}{2\mu_0} B^2$$

$$\mathbf{m} = \frac{\chi V}{\mu_0} \cdot \mathbf{B}$$

m = induced magnetic moment
 χ = magnetic susceptibility
 B = magnetic field
 V = Volume object

Paramagnetism: $\chi \approx 10^{-3}$, χ positive

⇒ energy **decreases** with field

⇒ force **towards high fields**

Diamagnetism: $\chi \approx -10^{-5}$, χ negative

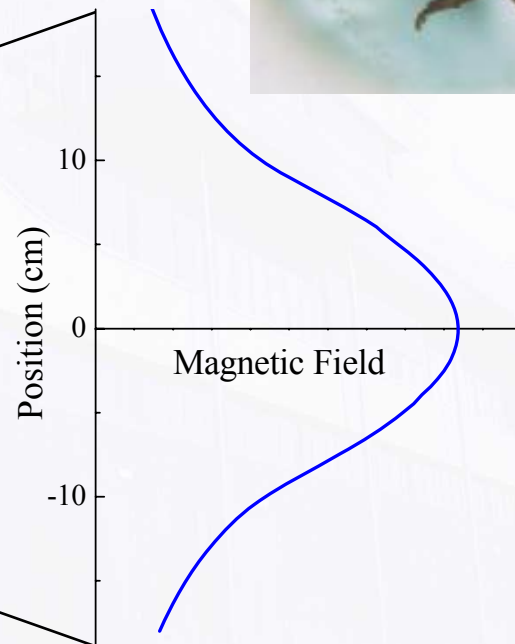
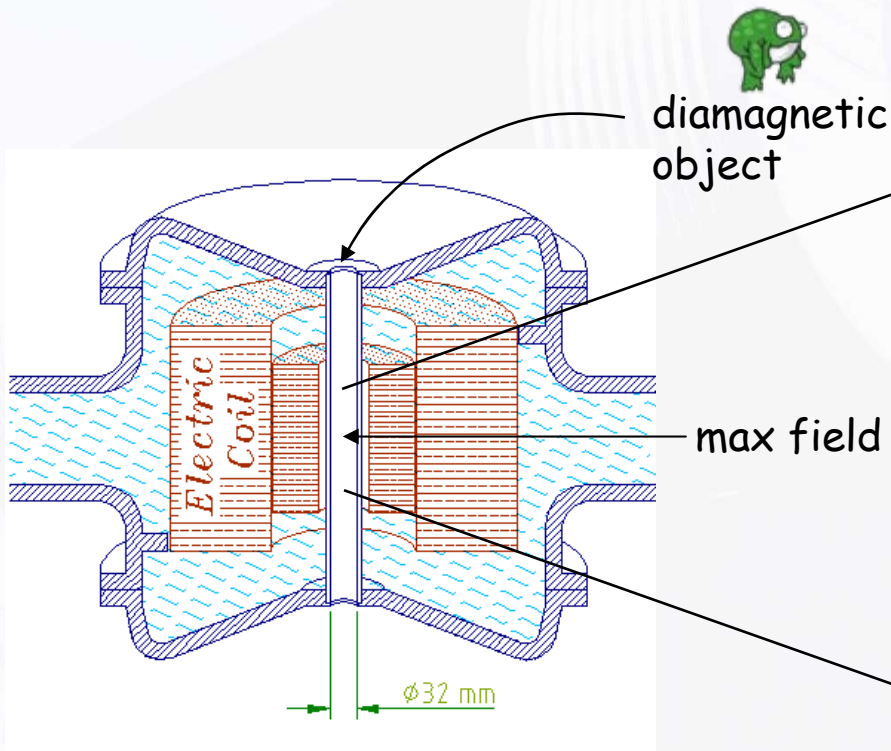
⇒ energy **increases** with field

⇒ force **towards low fields**



Diamagnetic levitation

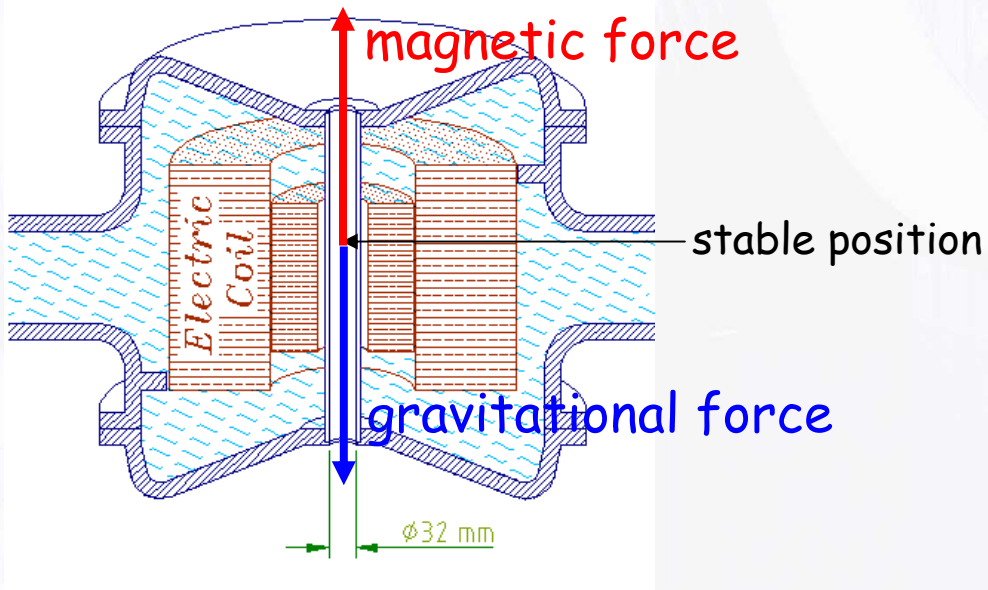
Magnetic levitation in a **field gradient**:



Beaugnon et al., Nature **349**, 470 (1991); J. Phys. III **1**, 1423 (1991)
Geim, Physics Today, Sept. 1998, 36-39

Diamagnetic levitation

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Diamagnetic levitation



diamagnetic
object

$$\mathbf{F}_g + \mathbf{F}_{mag} = \mathbf{0}$$

$$\begin{aligned} F_{mag} &= -\frac{\partial E(B)}{\partial z} = -\frac{\partial}{\partial z} \left(-\frac{\chi V B^2}{2\mu_0} \right) \\ &= \frac{V\chi}{\mu_0} B(z) \frac{dB(z)}{dz} \end{aligned}$$

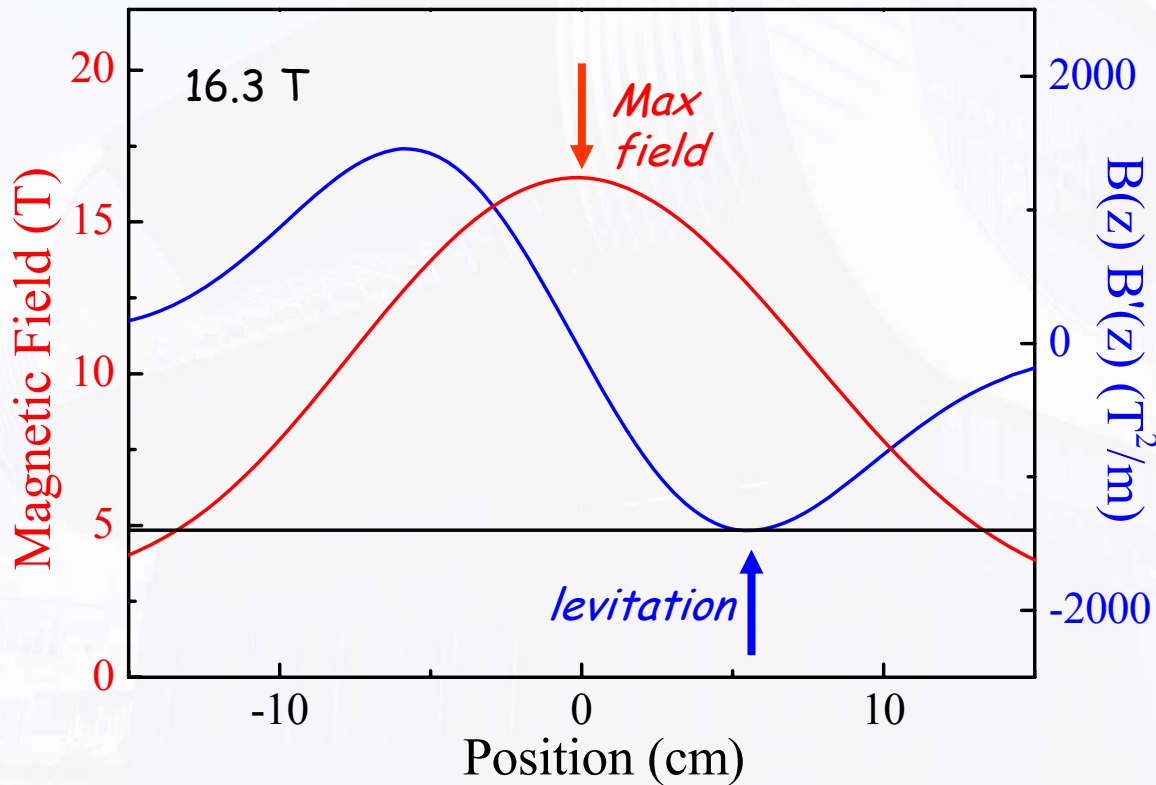
$$F_{gravity} = -V\rho g$$

levitation:

$$B(z) \frac{dB(z)}{dz} = \frac{\rho}{\chi} \mu_0 g$$

Diamagnetic levitation

$$B(z) B'(z) = \frac{\rho}{\chi} \mu_0 g$$



Water:

$$\rho = 10^3 \text{ kg/m}^3$$

$$\chi = -8.8 \cdot 10^{-6}$$



$$\frac{\rho}{\chi} = -1.14 \cdot 10^8 \text{ kg/m}^3$$



$$B(z)B'(z) \cong -1400 \text{ T}^2/\text{m}$$

Diamagnetic levitation

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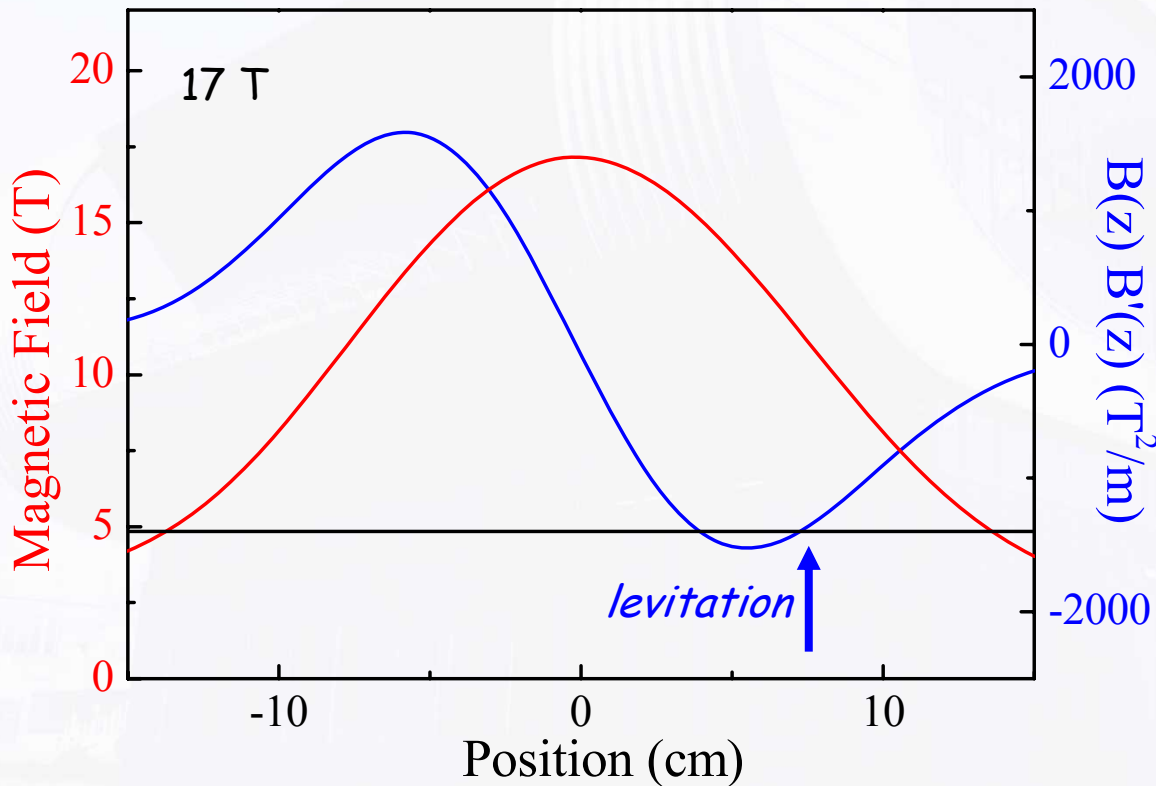
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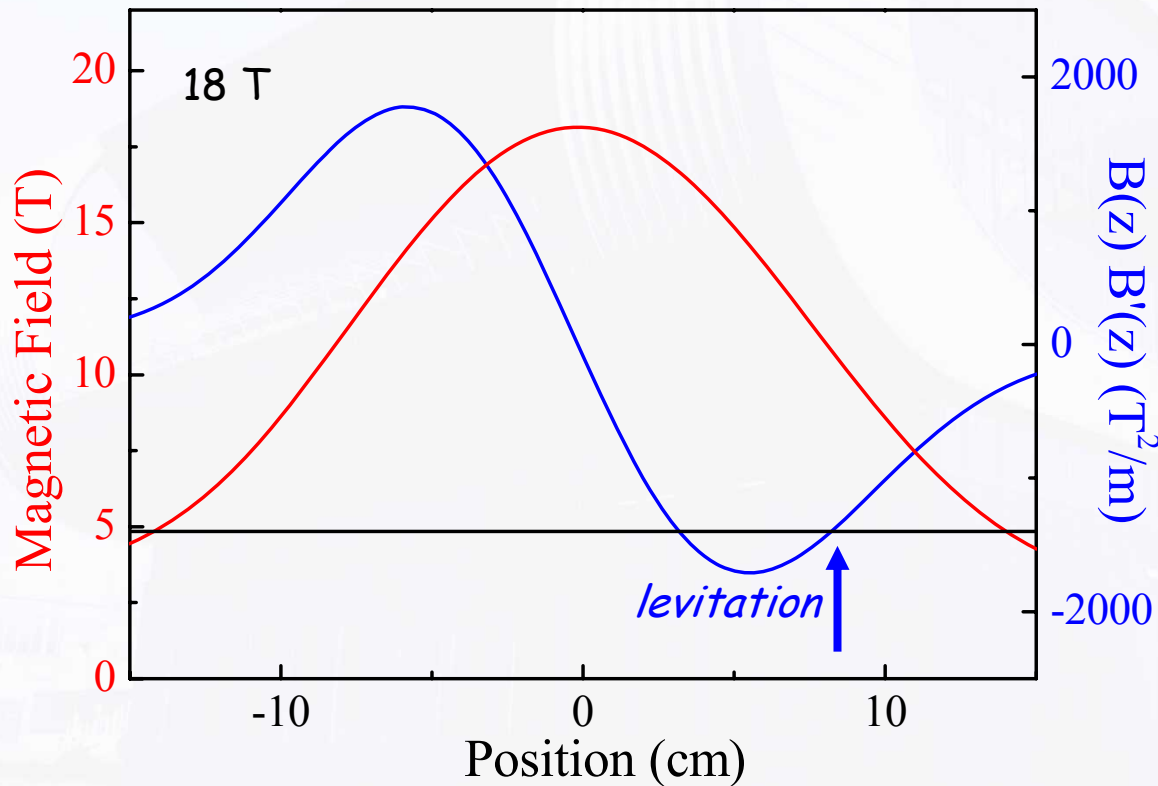
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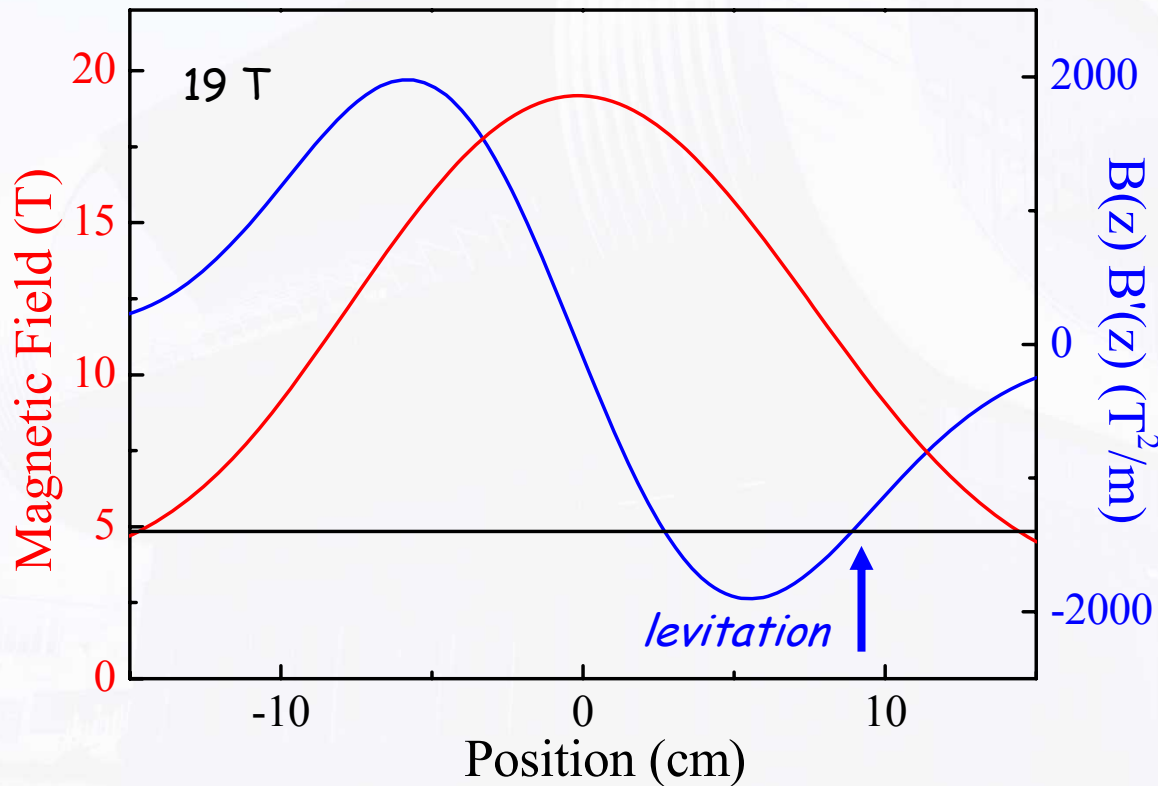
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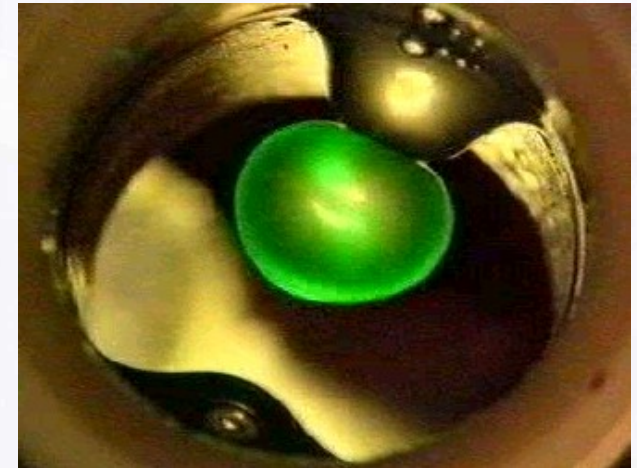
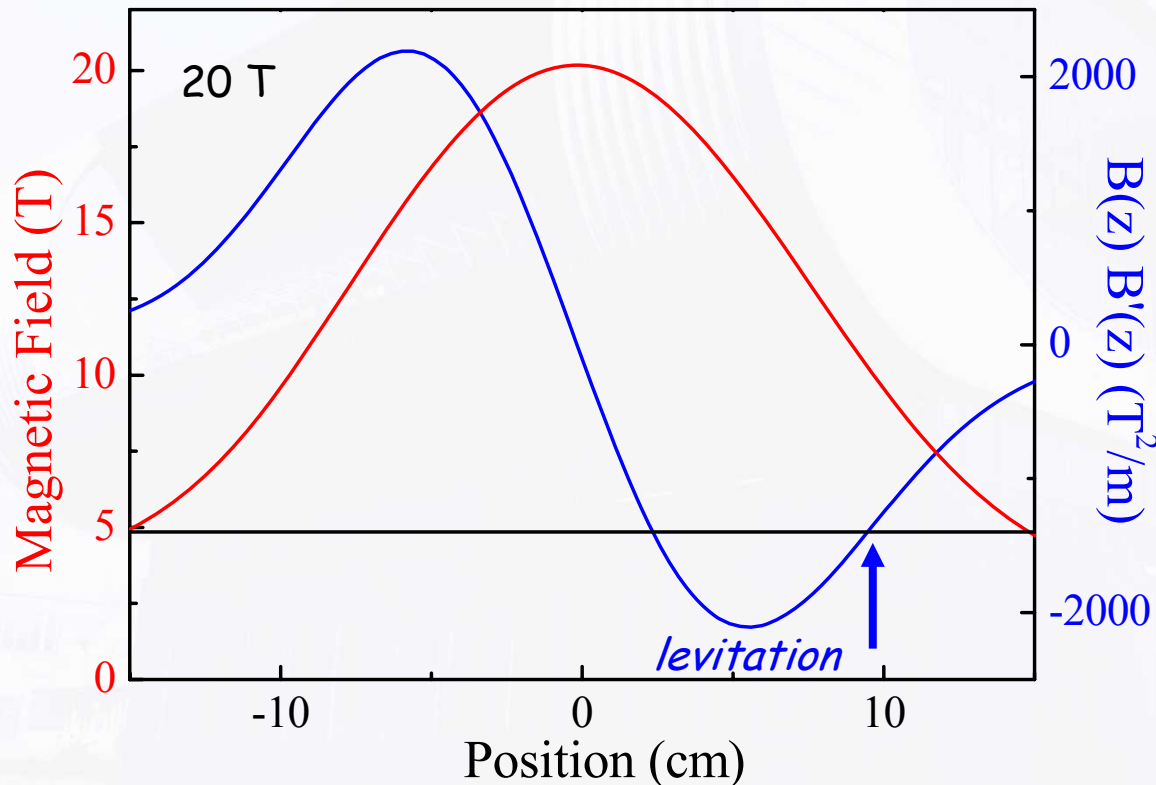
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See movies on HFML website: www.hfml.science.ru.nl

HFML

Science in High Magnetic Fields

Stability of levitation

Stable levitation requires a **restoring** force

$$E(\mathbf{r}) = mgz - \frac{\chi V}{2\mu_0} B^2(\mathbf{r})$$

$$\mathbf{F}(\mathbf{r}) = -\nabla E(\mathbf{r})$$

$$\oint \mathbf{F}(\mathbf{r}) \cdot d\mathbf{S} < 0 \quad \Rightarrow \quad \nabla \cdot \mathbf{F}(\mathbf{r}) < 0$$

for diamagnets: $\nabla^2 B^2(\mathbf{r}) > 0$

for paramagnets: ~~$\nabla^2 B^2(\mathbf{r}) < 0$~~

$$\nabla \cdot \mathbf{B} = 0 \quad \text{and} \quad \nabla \times \mathbf{B} = 0$$

$$\Downarrow$$
$$\nabla^2 B^2(\mathbf{r}) \geq 0$$

Stable levitation of paramagnets is impossible

Levitation: vertical and horizontal stability

Vertical stability: $\frac{\partial F(\mathbf{r})}{\partial z} < 0 \Rightarrow \frac{\partial^2 B^2(\mathbf{r})}{\partial z^2} > 0$

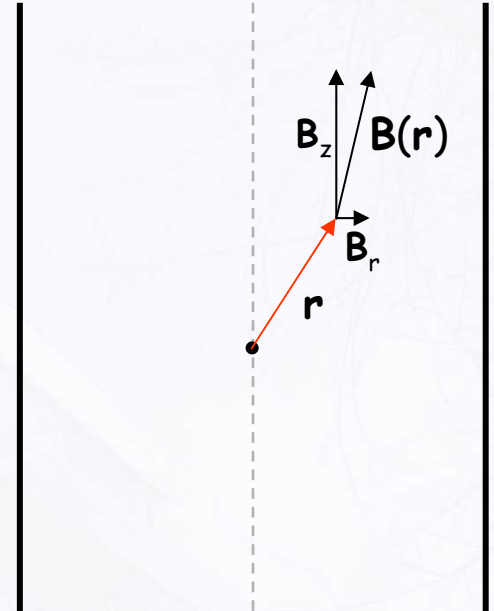
magnetic potential: $\mathbf{B}(\mathbf{r}) = \nabla \phi(\mathbf{r})$

on-axis terms: $\phi(0,0,z); \frac{\partial \phi(0,0,z)}{\partial z}; \frac{\partial^2 \phi(0,0,z)}{\partial z^2}; \dots$

$\nabla \cdot \mathbf{B}(\mathbf{r}) = 0 \Rightarrow \nabla^2 \phi(\mathbf{r}) = 0$

$\frac{\partial^2 \phi(0,0,z)}{\partial x^2} = \frac{\partial^2 \phi(0,0,z)}{\partial y^2} = -\frac{1}{2} \frac{\partial^2 \phi(0,0,z)}{\partial z^2}$

$\phi(\mathbf{r}) \approx \phi(0,0,z) - \frac{1}{4} (x^2 + y^2) \frac{\partial^2 \phi(0,0,z)}{\partial z^2} + \dots$



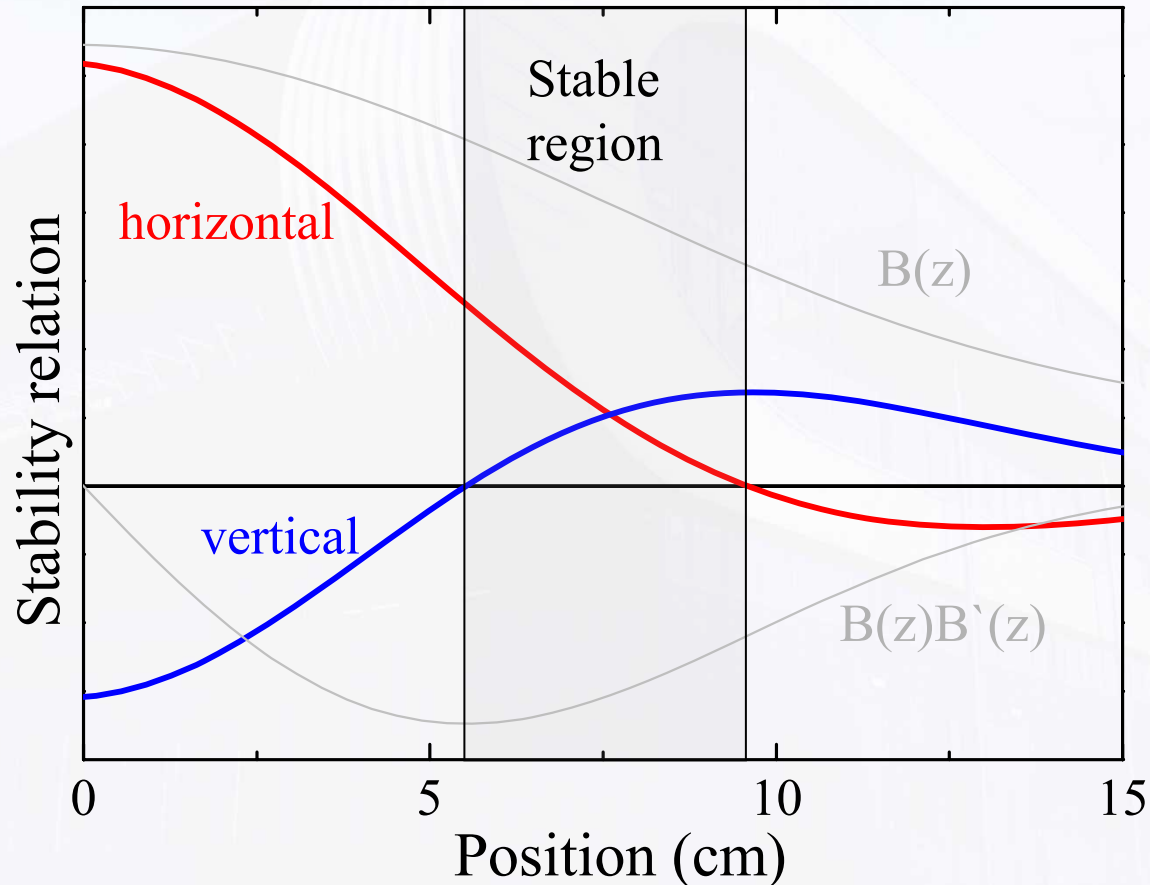
Vertical stability: $D_{vert.} = B'(z)^2 + B(z)B''(z) > 0$

Horizontal stability: $\frac{\partial^2 B^2(\mathbf{r})}{\partial r^2} > 0$

$D_{hor.} = B'(z)^2 - 2B(z)B''(z) > 0$

Levitation: vertical and horizontal stability

$$D_{\text{vert.}} = B'(z)^2 + B(z)B''(z) > 0 \quad \text{and} \quad D_{\text{hor.}} = B'(z)^2 - 2B(z)B''(z) > 0$$



Berry and Geim, *Eur. J. Phys.* **18**, 307 (1997)

Magneto-Archimedes effect



$$F_{\text{tot}} = \frac{V\chi}{\mu_0} B(z)B'(z) - V\rho g - \frac{V\chi_{\text{med}}}{\mu_0} B(z)B'(z) + V\rho_{\text{med}} g$$

magnetic and normal buoyancy forces

levitation:

$$\frac{V(\chi - \chi_{\text{med}})}{\mu_0} B(z)B'(z) - V(\rho - \rho_{\text{med}})g = 0$$



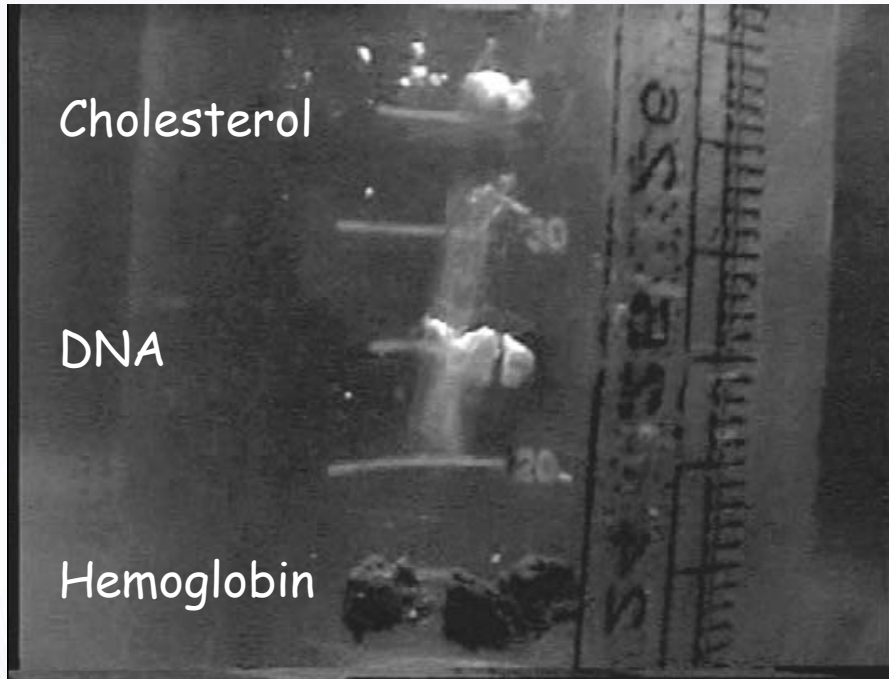
$$B(z)B'(z) = \frac{\rho - \rho_{\text{med}}}{\chi - \chi_{\text{med}}} \mu_0 g$$

$\chi_{\text{med}}, \rho_{\text{med}}$

Levitation enhanced in paramagnetic medium

For example in: *air, oxygen*
pressurized oxygen
liquid oxygen

Magneto-Archimedes separation

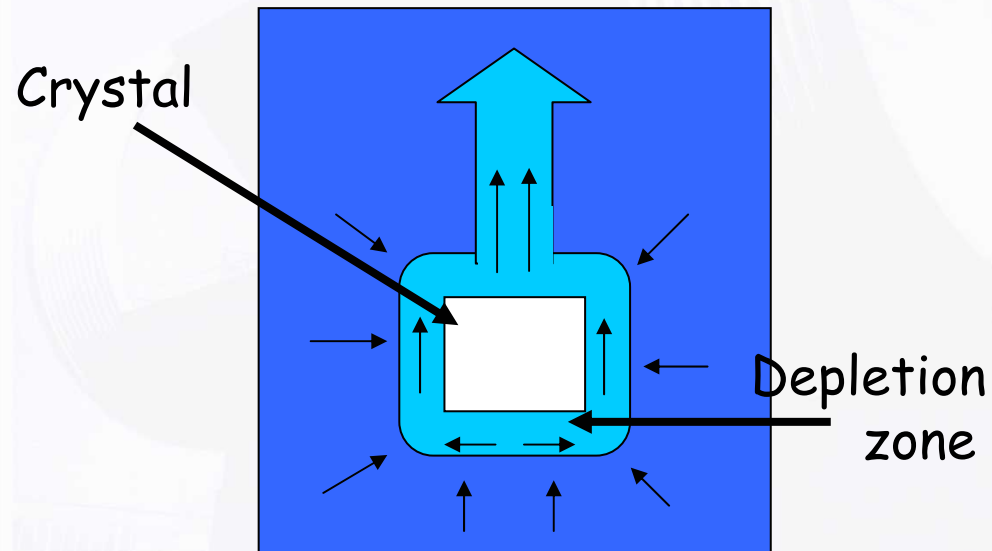


	ρ (kg/m ³)	χ (10 ⁻⁶)	ρ/χ (10 ⁸ kg/m ³)	$B\nabla B$ (T ² /m)
Water	1000	-8.8	1.14	-1401
Hemoglobin	1330	-3.38	3.93	-4850
Fibrinogen	1570	-6.12	2.56	-3162
Cholesterol	1020	-7.61	1.34	-1652
DNA	1280	-4.99	2.56	-3162

Hirota et al., *Physica B* **346**, 267 (2004)
 See also: Catherall et al, *Nature* **422**, 579 (2003)

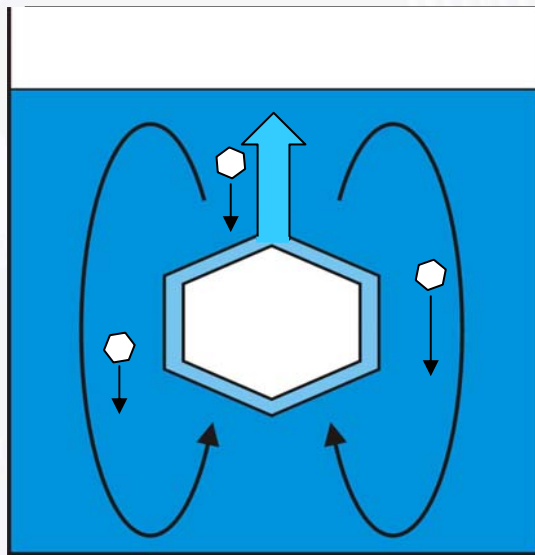
Microgravity application: crystal growth

- High supersaturation
- Mass transport & Fluid dynamics

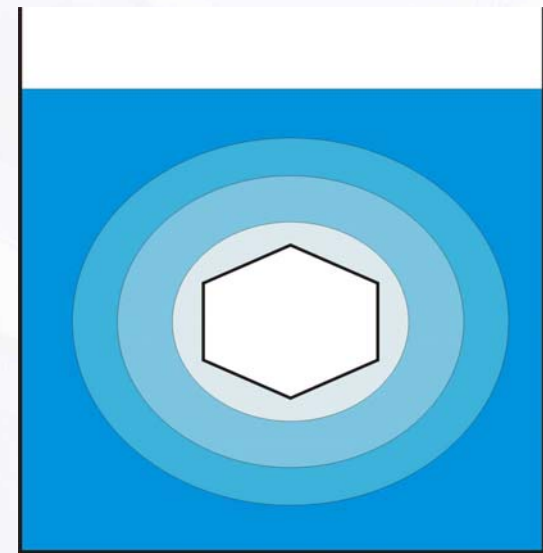


Microgravity application: crystal growth

- High supersaturation
- Mass transport & Fluid dynamics
- Sedimentation



Microgravity

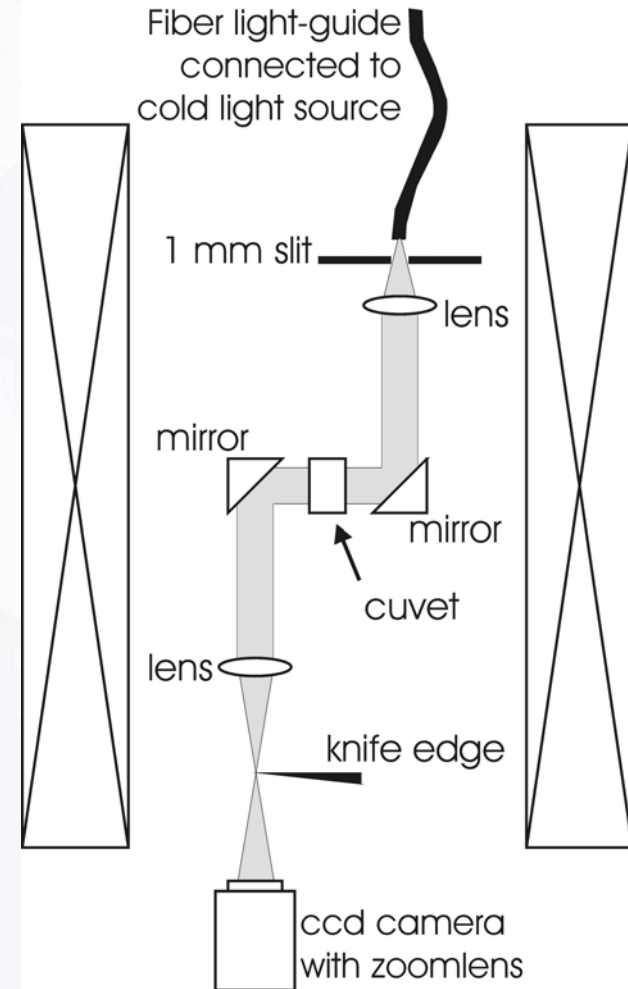


Magnetic field gradients ?

Schlieren microscope

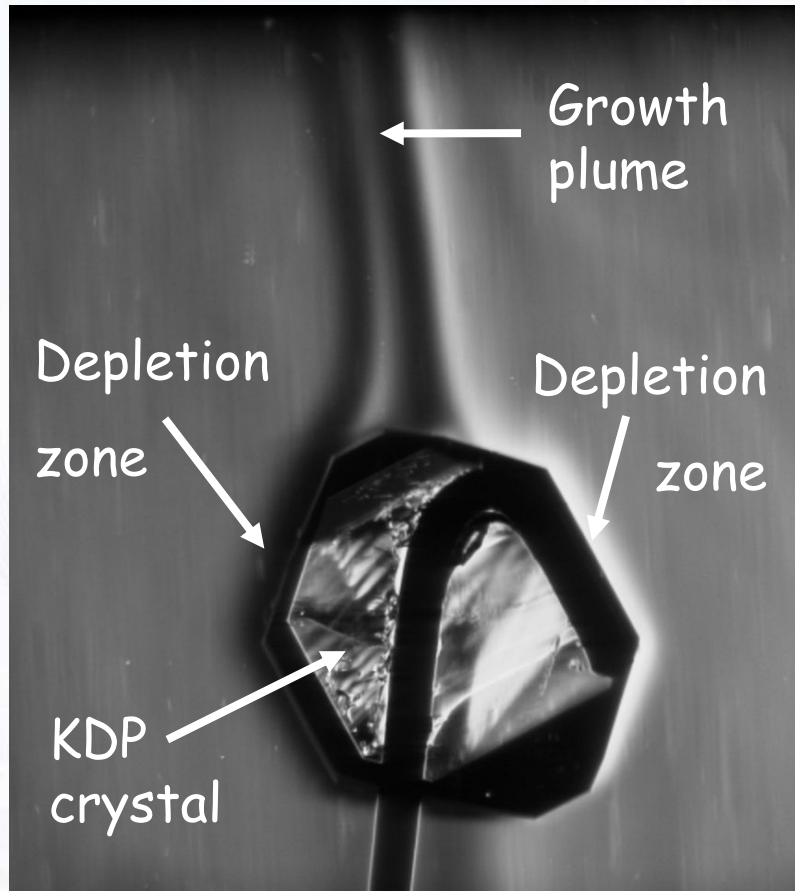
The Schlieren insert:

- 32 mm bore 20 T magnet
- $NA = 0.08$, Theoretical resolution of $6.5\mu\text{m}$
- Field of view $\sim 4.5\text{mm}$



Schlieren microscopy of growth plume

Example: Growing KDP (KH_2PO_4) crystal

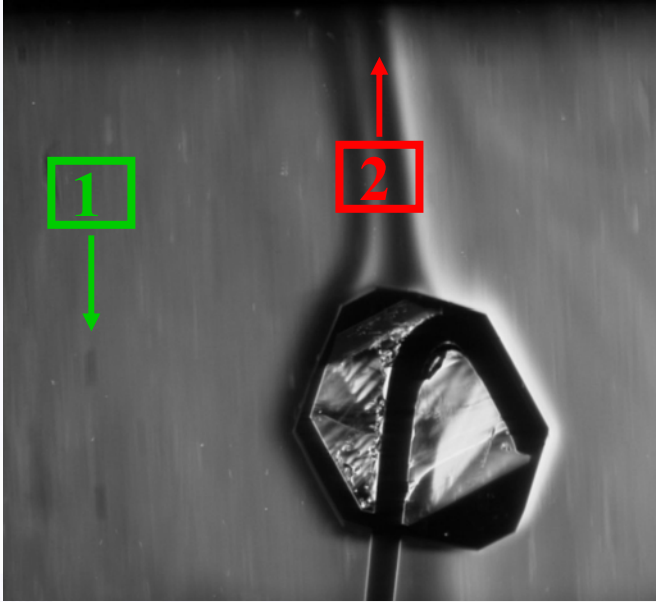


Local variations in:
concentration c
and thus in the
refractive index n

Schlieren microscopy

$$I \propto \frac{\partial n}{\partial x} \propto \frac{\partial c}{\partial x}$$

Damping convection



No convection if: $F_2(z) - F_1(z) = 0$

$$F_{mag}(z) = \frac{V\chi}{\mu_0} B(z)B'(z) \quad F_{gravity}(z) = -V\rho g$$

Balance of forces if

$$B(z)B'(z) = \frac{\Delta\rho}{\Delta\chi} \mu_0 g \quad \Delta\rho = \rho_2 - \rho_1$$

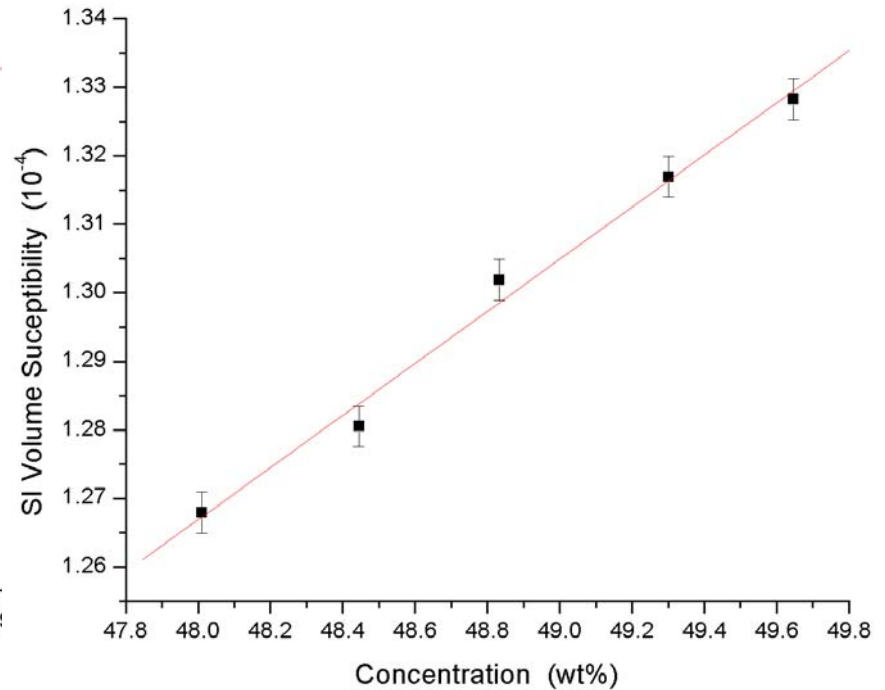
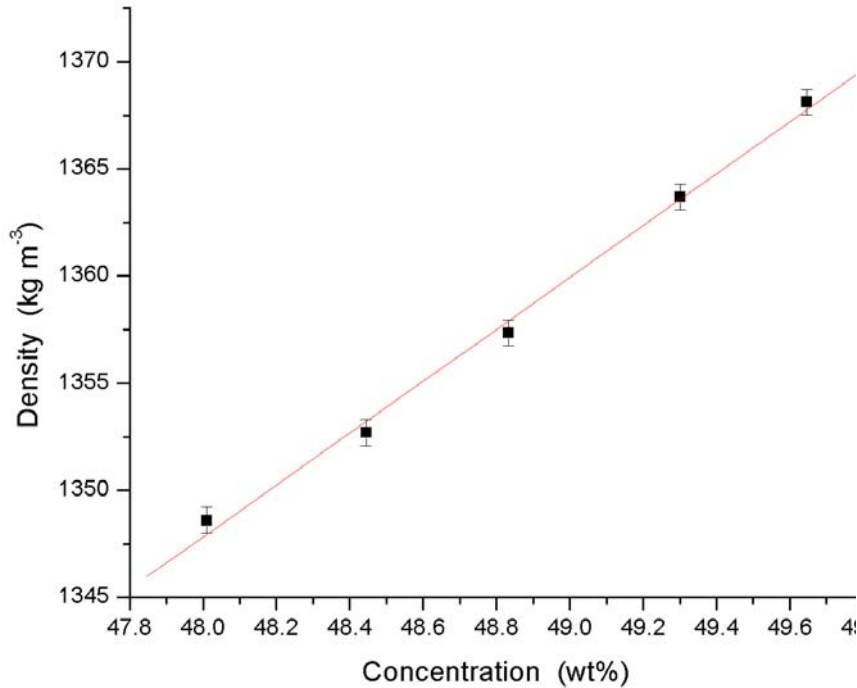
$$\Delta\chi = \chi_2 - \chi_1$$

For small variations in c : $\rho(c) = \rho_0 + \alpha c$; $\chi(c) = \chi_0 + \beta c$

$$\Rightarrow B(z)B'(z) = \frac{\alpha}{\beta} \mu_0 g$$

$$g_{eff} = g \left[1 - \frac{\beta}{\alpha\mu_0 g} B(z)B'(z) \right]$$

Paramagnetic NiSO₄ hexahydrate

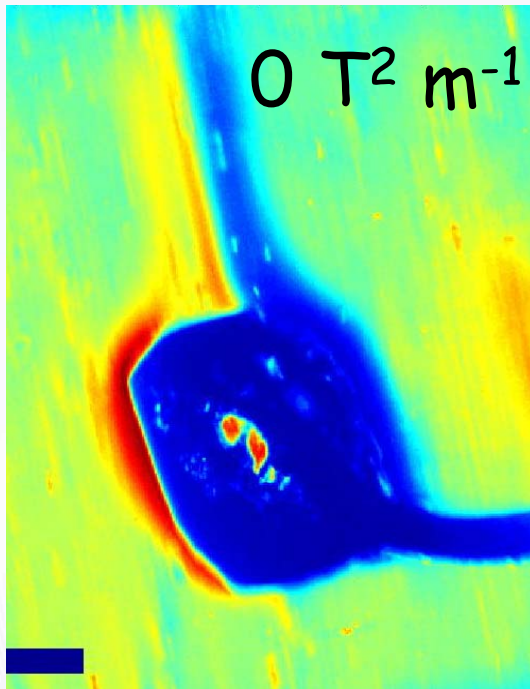


$$\alpha = 12.1 \pm 0.5 \text{ kg m}^{-3} \text{ wt}^{\circ\text{-}1}$$

$$\beta = (+3.8 \pm 0.2) \times 10^{-6} \text{ wt}^{\circ\text{-}1}$$

$$B(z)B'(z) = +39 \pm 3 \text{ T}^2 \text{ m}^{-1}$$

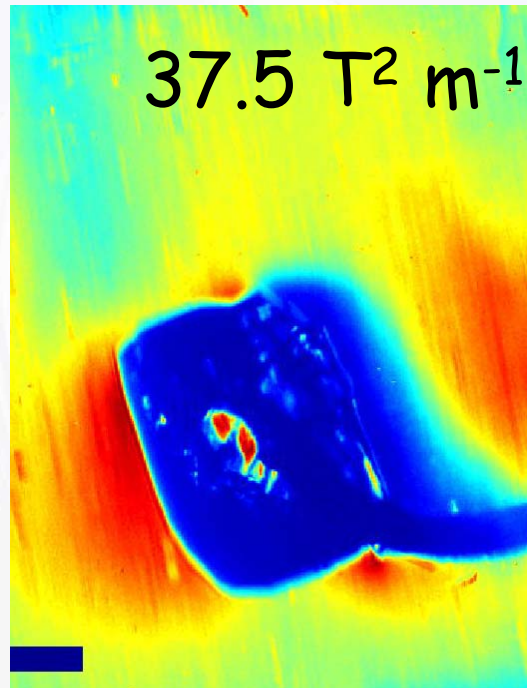
Tuning effective gravity



$$g_{\text{effective}} = 1 \text{ g}$$

Normal growth

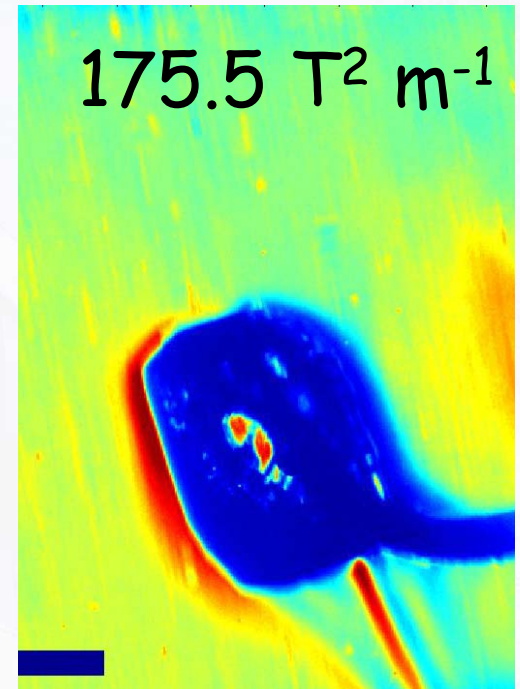
Plume upwards



$$g_{\text{effective}} = 0 \text{ g}$$

No Plume!

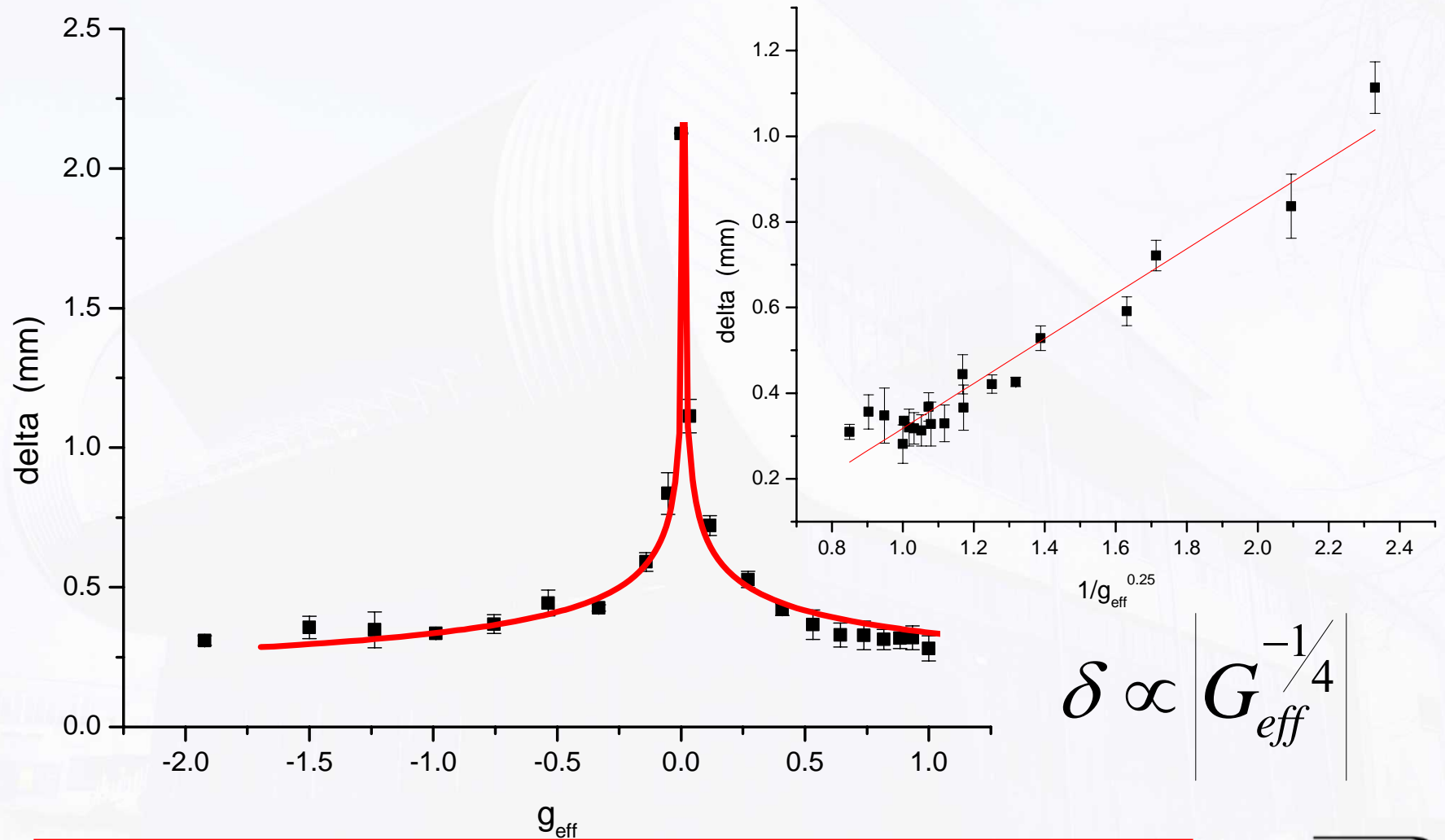
Large depletion zone!



$$g_{\text{effective}} = -3.5 \text{ g}$$

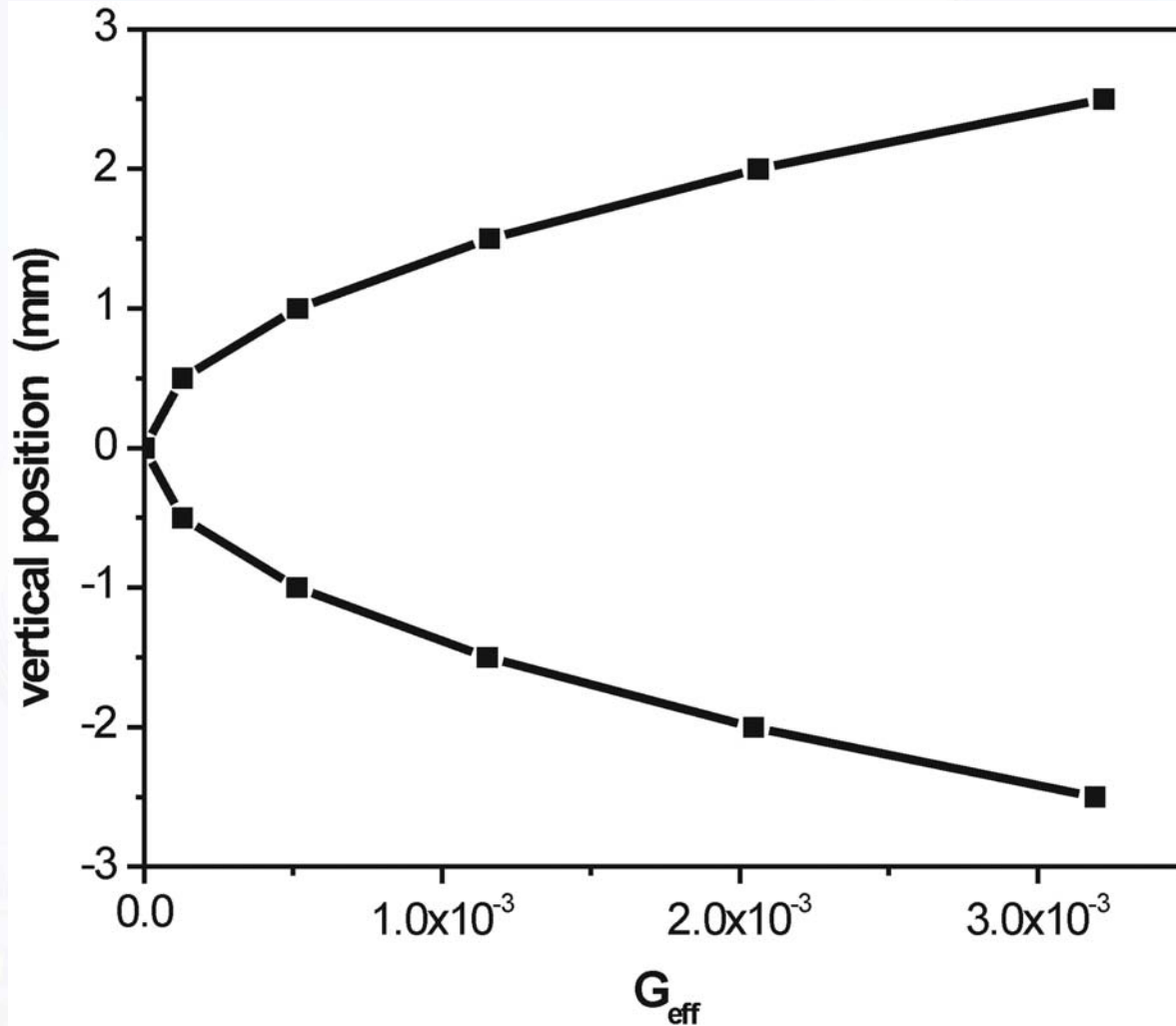
Plume downwards

Width of depletion zone



$$\delta \propto \left| G_{\text{eff}}^{-1/4} \right|$$

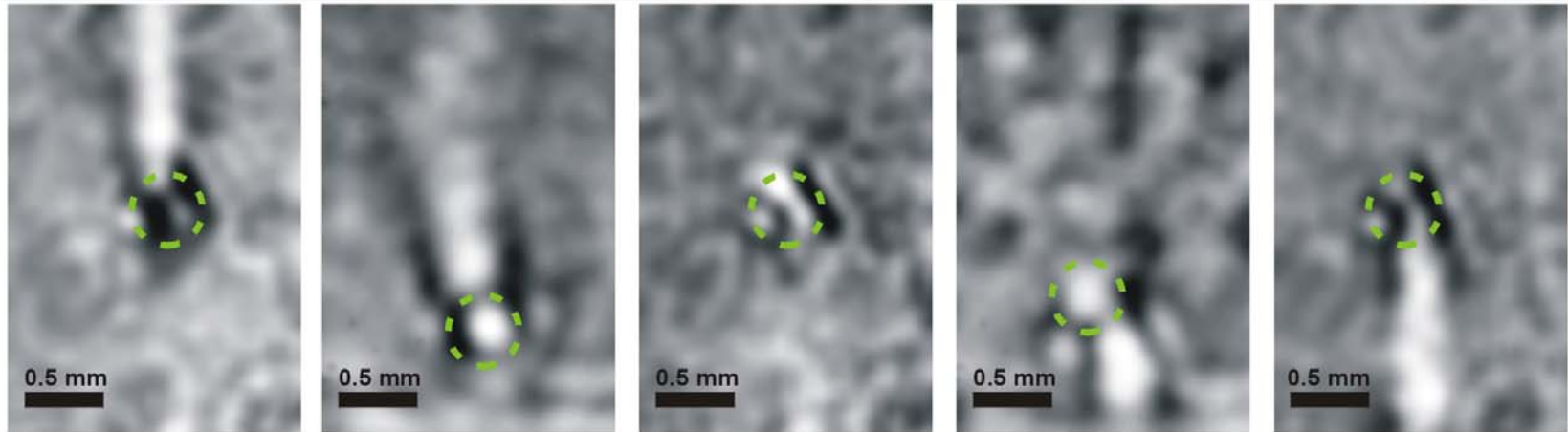
Microgravity ?



Milligravity

is sufficient to dampen convection

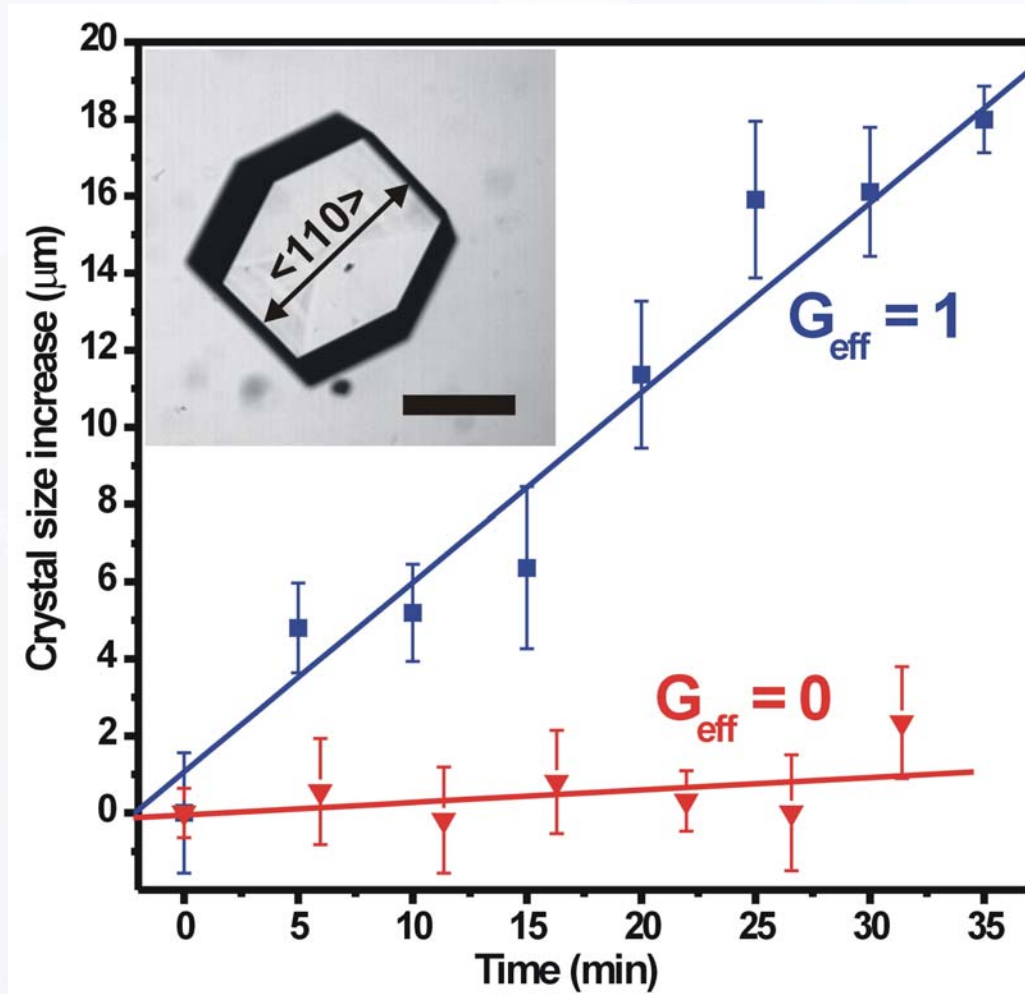
It also works for diamagnetic Lysozyme !



B_0	0	26.0	27.0	27.5	29.0 T
$B_Z B'_Z$	0	-4130	-4450	-4630	-5140 T ² /m
G_{eff}	1	0.07	0	-0.04	-0.15

growth of Lysozyme crystals in tunable gravity

Growth rate in reduced gravity



Conclusions Part I

- regular magnetic levitation

$$B(z) B'(z) = \frac{\rho}{\chi} \mu_0 g$$

- magneto-archimedes effect

$$B(z) B'(z) = \frac{\rho - \rho_{med}}{\chi - \chi_{med}} \mu_0 g$$

- suppression of convection

$$B(z) B'(z) = \frac{\alpha}{\beta} \mu_0 g$$

$$\rho(c) = \rho_0 + \alpha c; \chi(c) = \chi_0 + \beta c$$

Magnetic field is a powerful tool to tune effective gravity