

# Hard Core Effects in Mean Field Theories

A. M. Sonnet

`andre.sonnet@strath.ac.uk`

Department of Mathematics and Statistics, University of Strathclyde

# Steps Towards Mean Field

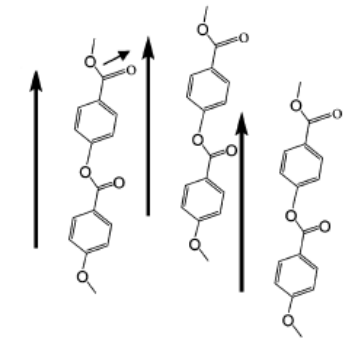
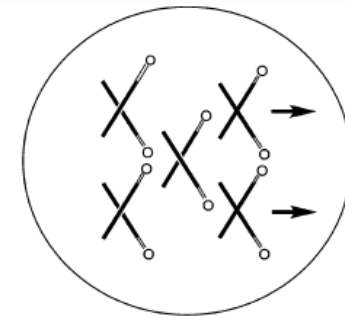
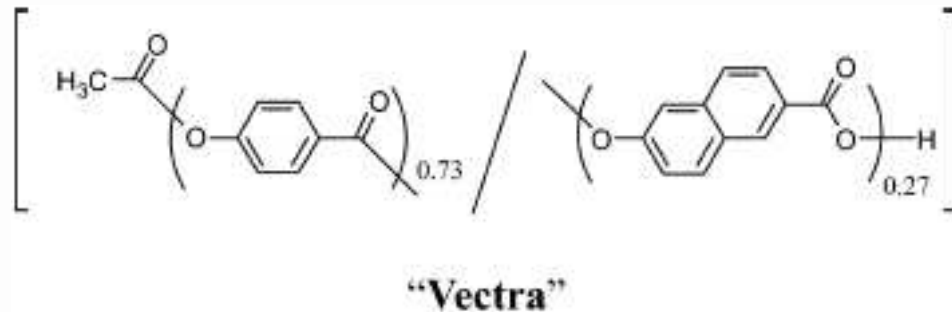
1. Find a two-particle Hamiltonian  $U$  that depends on the relative orientation and position of two molecules
2. Average over space to obtain a two-particle Hamiltonian  $H$  that depends on relative orientation only
3. By taking an ensemble average, obtain a one-particle Hamiltonian: a single molecule interacts with the mean field, the average orientation of all molecules

# Polar Electric Interactions

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KOIKE & AL. (2007)  
WATANABE (2008)

# Dipolar Interaction

$$\begin{aligned} U_{\text{dip}} &= \frac{1}{4\pi\epsilon_0 r^3} \{ \mathbf{p} \cdot \mathbf{p}' - 3(\mathbf{p} \cdot \mathbf{e})(\mathbf{p}' \cdot \mathbf{e}) \} \\ &= \frac{1}{4\pi\epsilon_0 r^3} \mathbf{p} \cdot (\mathbf{I} - 3\mathbf{e} \otimes \mathbf{e}) \mathbf{p}' \end{aligned}$$

# Dipolar Interaction

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$$= \frac{1}{4\pi\epsilon_0 r^3} \mathbf{p} \cdot (\mathbf{I} - 3\mathbf{e} \otimes \mathbf{e}) \mathbf{p}'$$

- $\mathbf{p}, \mathbf{p}'$  molecular electric dipoles
- $\epsilon_0$  dielectric constant in vacuum
- $r$  intermolecular distance
- $\mathbf{e}$  intermolecular unit vector

# Interaction Hamiltonian

$H_{\text{dip}}$  is the average energy  $U_{\text{dip}}$  exchanged between molecules with the same relative orientation.

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$$H_{\text{dip}} := \frac{1}{4\pi\epsilon_0} \mathbf{p} \cdot \left( \int_{\Omega} \frac{1}{r^3} (\mathbf{I} - 3\mathbf{e}_r \otimes \mathbf{e}_r) dv \right) \mathbf{p}',$$

where  $f_{\Omega} dv := \frac{1}{v(\Omega)} \int_{\Omega} dv$  denotes the average over a set  $\Omega$  in the three-dimensional Euclidean space  $\mathcal{E}$  and  $v$  is the volume measure.



# Isotropic Distribution, Spherical Domain

$$\begin{aligned}\int_{\Omega} \frac{1}{r^3} (\mathbf{I} - 3\mathbf{e}_r \otimes \mathbf{e}_r) dv &= \int_{2R}^{R_c} \int_{\mathbb{S}^2} \frac{1}{r} (\mathbf{I} - 3\mathbf{e}_r \otimes \mathbf{e}_r) da dr \\ &= 4\pi \ln(R_c/2R) \langle \mathbf{I} - 3\mathbf{e}_r \otimes \mathbf{e}_r \rangle_{\mathbb{S}^2}\end{aligned}$$

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But

$$\langle \mathbf{I} - 3\mathbf{e}_r \otimes \mathbf{e}_r \rangle_{\mathbb{S}^2} = \mathbf{0},$$

so  $H_{\text{dip}} = 0$ .

# What next

- Renounce spherical symmetry of integration domain or
- Consider more elaborate interaction?

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- Consider more elaborate interaction?
- Both!

W. MAIER UND A. SAUPE

## Eine einfache molekular-statistische Theorie der nematischen kristallinflüssigen Phase. Teil II. Z. Naturforschg. 15a 287–292 [1960]

Die sterisch bedingte Nahordnung läßt sich – allerdings in sehr stark vereinfachender Form – in unser Modell einbauen. Wir bezeichnen die Vorzugsrichtung der Längsachsen in einer sterisch bedingten Nahordnungsgruppe als Gruppenachse und nehmen an, daß innerhalb einer Gruppe aller Molekülachsen exakt parallel zur Gruppenachse orientiert seien. Die Drehung eines Moleküls ist damit von nun an mit der Drehung einer ganzen sterischen Nahordnungsgruppe verknüpft und so ist als Einheit bei der statistischen Behandlung nicht das einzelne Molekül, sondern die Gruppe anzusehen. Die mittlere Anzahl  $m$  von Molekülen pro Gruppe wird als temperaturunabhängige, substanzcharakteristische Konstante behandelt, die als zweiter anpaßbarer Parameter neben  $A$  in die Theorie eingeht. Zur Abschätzung ihrer Größe ist es plausibel, sich die sterische Nahordnungsgruppe als die kleinste Gruppe parallel liegender Moleküle vorzustellen, die angenähert Kugelform aufweist und sich demgemäß ohne wesentliche sterische Behinderung beliebig drehen kann. Im Falle des Azoxyanisols wird man z.B. etwa  $m = 4$  erwarten.

Für die die nematische Fernordnung bestimmende Wechselwirkung zwischen den Nahordnungsgruppen übernehmen wir Gl. (1) mit entsprechender Umdeutung des Faktors  $A/V^2$ . Die Rechtfertigung dieses plausible erscheinenden Schrittes muß der experimentellen Nachprüfung überlassen bleiben. Es sei noch betont, daß die Gültigkeit der in Teil 1 durchgeführten Überlegungen durch die Einführung des Nahordnungsparameters natürlich nicht berührt wird.

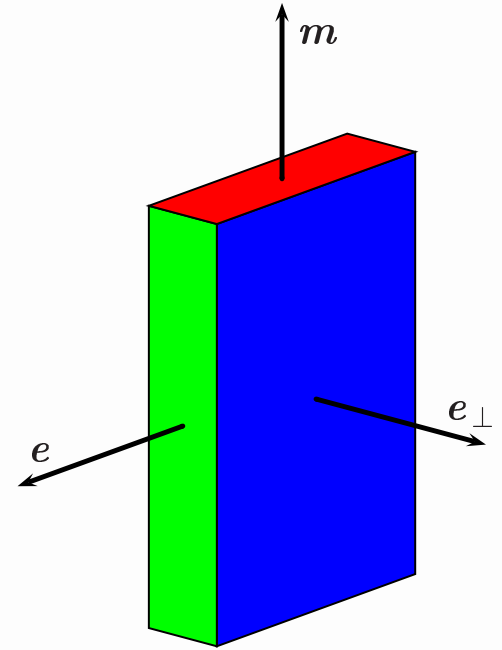
# Molecular Tensors

$$\mathbf{q} := m \otimes m - \frac{1}{3}\mathbf{I}$$

$$\mathbf{b} := e \otimes e - e_{\perp} \otimes e_{\perp}$$

$m$  long molecular axis

$m, e, e_{\perp}$  axes of any molecular polarisability tensor



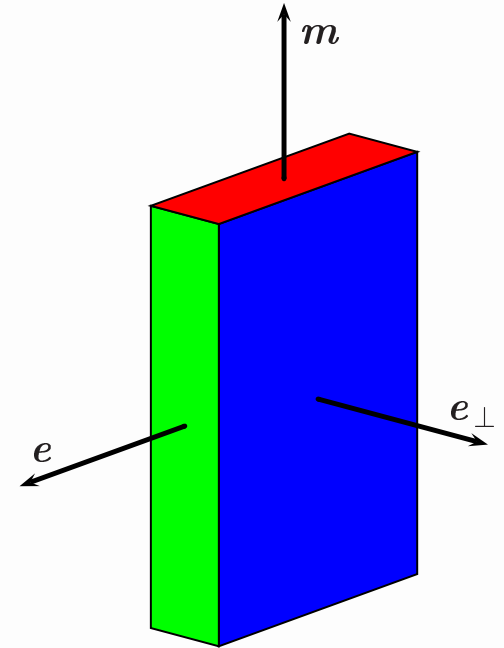
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$\mathbf{m}, \mathbf{e}, \mathbf{e}_\perp$  axes of any molecular polarisability tensor



For effectively uniaxial particles,  $\mathbf{b}$  is meaningless and ignored.

# Dispersion Interactions

The quadrupolar approximation to the dispersion interactions of  $D_{2h}$ -symmetric molecules is represented by the Hamiltonian

$$H(\mathbf{q}, \mathbf{b}; \mathbf{q}', \mathbf{b}') = -U_0 \{ \xi \mathbf{q} \cdot \mathbf{q}' + \gamma (\mathbf{q} \cdot \mathbf{b}' + \mathbf{b} \cdot \mathbf{q}') + \lambda \mathbf{b} \cdot \mathbf{b}' \}$$



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$U_0 > 0$  interaction strength  
 $\xi = \pm 1, \lambda, \gamma$  dimensionless parameters

STRALEY (1974)

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$$\mathbf{q}' = \mathbf{R}\mathbf{q}\mathbf{R}^\top \quad \mathbf{b}' = \mathbf{R}\mathbf{b}\mathbf{R}^\top \quad \mathbf{R} \in \text{O}(3)$$

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$H$  results from an *average* of the interaction potential  $U$  over the *intermolecular* vector.

# Uniaxial Molecules

If we set  $\xi = 1$ ,  $\lambda = \gamma = 0$ , we obtain the MAIER-SAUPE quadrupolar approximation to the dispersion interactions of  $D_{\infty h}$ -symmetric molecules,

$$H(\mathbf{q}; \mathbf{q}') = -U_0 \mathbf{q} \cdot \mathbf{q}'.$$

## *Alternative Representation*

$$H = -U_0 \left\{ (\xi - \lambda)(\mathbf{m} \cdot \mathbf{m}')^2 + 2(\lambda + \gamma)(\mathbf{e}_\perp \cdot \mathbf{e}'_\perp)^2 + 2(\lambda - \gamma)(\mathbf{e} \cdot \mathbf{e}')^2 - \left( \lambda + \frac{1}{3}\xi \right) \right\}$$

ROMANO, LONGA (2005)

# Hamiltonian Decomposition

The interaction Hamiltonian  $H$  can uniquely be written as superposition of two orthogonal quadratics

$$H = -U_0 \{a^+ \mathbf{q}^+ \cdot \mathbf{q}^{+'} + a^- \mathbf{q}^- \cdot \mathbf{q}^{-'}\}$$

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$$\mathbf{q}^+ \cdot \mathbf{q}^- = 0$$

$$\mathbf{q}^+ = \mathbf{q} + \gamma^+ \mathbf{b} \quad \mathbf{q}^- = \mathbf{q} + \gamma^- \mathbf{b}$$

$$\gamma^\pm = \frac{3\lambda - 1 \pm \sqrt{(3\lambda - 1)^2 + 12\gamma^2}}{6\gamma}$$

$$a^+ = \frac{\gamma - \gamma^-}{\gamma^+ - \gamma^-} \quad a^- = \frac{\gamma^+ - \gamma}{\gamma^+ - \gamma^-}$$

# Types of Interaction

## *fully attractive Hamiltonian*

Both  $a^+$  and  $a^-$  are *positive* whenever  $\lambda > \gamma^2$ . All potentials represented by points within the dispersion parabola are *fully attractive*, as they are superpositions of attractive, symmetric potentials.



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## *partly repulsive Hamiltonian*

Either  $a^+$  or  $a^-$  is **negative** whenever  $\lambda < \gamma^2$  within the stability region. The potentials represented by these points are **partly repulsive**. When  $a^- < 0$ , then  $\mathbf{q}^-$  is the **repulsive** molecular tensor.

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## *simply attractive Hamiltonian*

For  $\lambda = \gamma^2$  the interaction Hamiltonian  $H$  can be given the form

$$H = -U_0(\mathbf{q} + \gamma\mathbf{b}) \cdot (\mathbf{q}' + \gamma\mathbf{b}')$$

and it is called **simply attractive**.

# Mean-field Approximation

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$$\mathbf{Q} := \langle \mathbf{q} \rangle_{\rho_0} \quad \mathbf{B} := \langle \mathbf{b} \rangle_{\rho_0}$$
$$\rho_0 := \frac{1}{Z_0(T, \mathbf{Q}, \mathbf{B})} e^{-H_0(\mathbf{q}, \mathbf{b}; \mathbf{Q}, \mathbf{B}) / k_B T}$$

$$Z_0(T, \mathbf{Q}, \mathbf{B}) := \int_{\Omega} e^{-H_0(\mathbf{q}(\omega), \mathbf{b}(\omega); \mathbf{Q}, \mathbf{B}) / k_B T} d\omega$$

$\rho_0$  one-particle Boltzmann distribution function

$Z_0$  one-particle partition function

$\Omega$  orientational manifold

$k_B$  Boltzmann constant       $T$  absolute temperature

# Mean Field Hamiltonian

$$H_0(\mathbf{q}, \mathbf{b}; \mathbf{Q}, \mathbf{B}) := z \left( \langle H(\mathbf{q}, \mathbf{b}; \cdot, \cdot) \rangle_{\rho_0} - \frac{1}{2} \langle H(\cdot, \cdot; \cdot, \cdot) \rangle_{\rho_0^2} \right)$$

PALFFY-MUHORAY (2002) GARTLAND & VIRGA (2008)

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For an ensemble of  $N$  particles,  $z$  is chosen such that

$$\langle \mathcal{H} \rangle_{\rho_0^N} = \langle \mathcal{H}_0 \rangle_{\rho_0^N}$$

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$\mathcal{H}_0$  one-particle ensemble Hamiltonian

$z = \frac{2n}{N} \in [1, N - 1]$ ,  $n$  number of interacting pairs

# Mean-Field Free Energy

$$F_0(\beta, \mathbf{Q}, \mathbf{B}) := -\frac{1}{\beta} \ln \int_{\Omega} e^{-\beta H_0(\mathbf{q}(\omega), \mathbf{b}(\omega); \mathbf{Q}, \mathbf{B})} d\omega$$

$F_0$  free energy per particle scaled to  $zU_0$

$$\beta := \frac{zU_0}{k_B T}$$

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*scalar order parameters*

$$\mathbf{Q} = S \left( \mathbf{e}_z \otimes \mathbf{e}_z - \frac{1}{3} \mathbf{I} \right) + \frac{1}{3} P \left( \mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y \right)$$

$$\mathbf{B} = D \left( \mathbf{e}_z \otimes \mathbf{e}_z - \frac{1}{3} \mathbf{I} \right) + \frac{1}{3} C \left( \mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y \right)$$

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*dispersion forces*

In UNSÖLD's approximation, we write the induced *dipole–dipole* dispersion interaction energy between two molecules as

$$U_{\text{disp}} = -\frac{U_1 U_2}{4(U_1 + U_2)} \frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \mathbf{U}(\mathbf{e}_r) \boxtimes \mathbf{U}(\mathbf{e}_r) [\mathbf{A}_1] \cdot \mathbf{A}_2$$

BUCKINGHAM (1967)

# Interaction Potential

$$U_{\text{disp}} = -\frac{U_1 U_2}{4(U_1 + U_2)} \frac{1}{(4\pi \varepsilon_0)^2} \frac{1}{r^6} \mathbf{U}(\mathbf{e}_r) \boxtimes \mathbf{U}(\mathbf{e}_r) [\mathbf{A}_1] \cdot \mathbf{A}_2$$

$U_1, U_2$  average excitation energies

$\varepsilon_0$  dielectric constant in vacuum

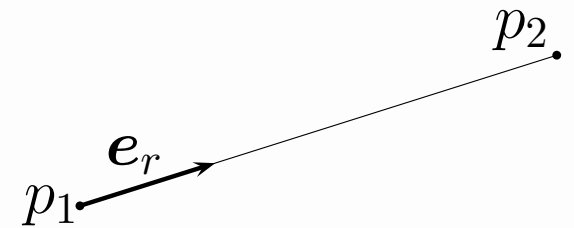
$\mathbf{A}_1, \mathbf{A}_2$  polarisability tensors

$p_1, p_2$  molecular charge centers

$r := |p_2 - p_1|$  intermolecular distance

$\mathbf{e}_r := \frac{1}{r}(p_2 - p_1)$  intermolecular unit vector

$\mathbf{U}(\mathbf{e}_r) := \mathbf{e}_r \otimes \mathbf{e}_r - \frac{1}{3}\mathbf{I}$  uniaxial tensor along  $\mathbf{e}_r$



# Square Tensor Product

The square tensor product  $\mathbf{A} \boxtimes \mathbf{B}$  between two second-rank tensors  $\mathbf{A}$  and  $\mathbf{B}$  is the fourth-rank tensor defined by

$$\mathbf{A} \boxtimes \mathbf{B}[\mathbf{C}] := \mathbf{A}\mathbf{C}\mathbf{B}^T$$

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In particular,

$$\mathbf{U} \boxtimes \mathbf{U}[\mathbf{A}_1] \cdot \mathbf{A}_2 = \mathbf{A}_2 \cdot \mathbf{U}\mathbf{A}_1\mathbf{U} = \mathbf{A}_1 \cdot \mathbf{U}\mathbf{A}_2\mathbf{U}$$



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Inner product:

$$\mathbf{A} \cdot \mathbf{B} = \text{tr } \mathbf{A}\mathbf{B}^\top = A_{ij} B_{ij}$$

# van der Waals Regions

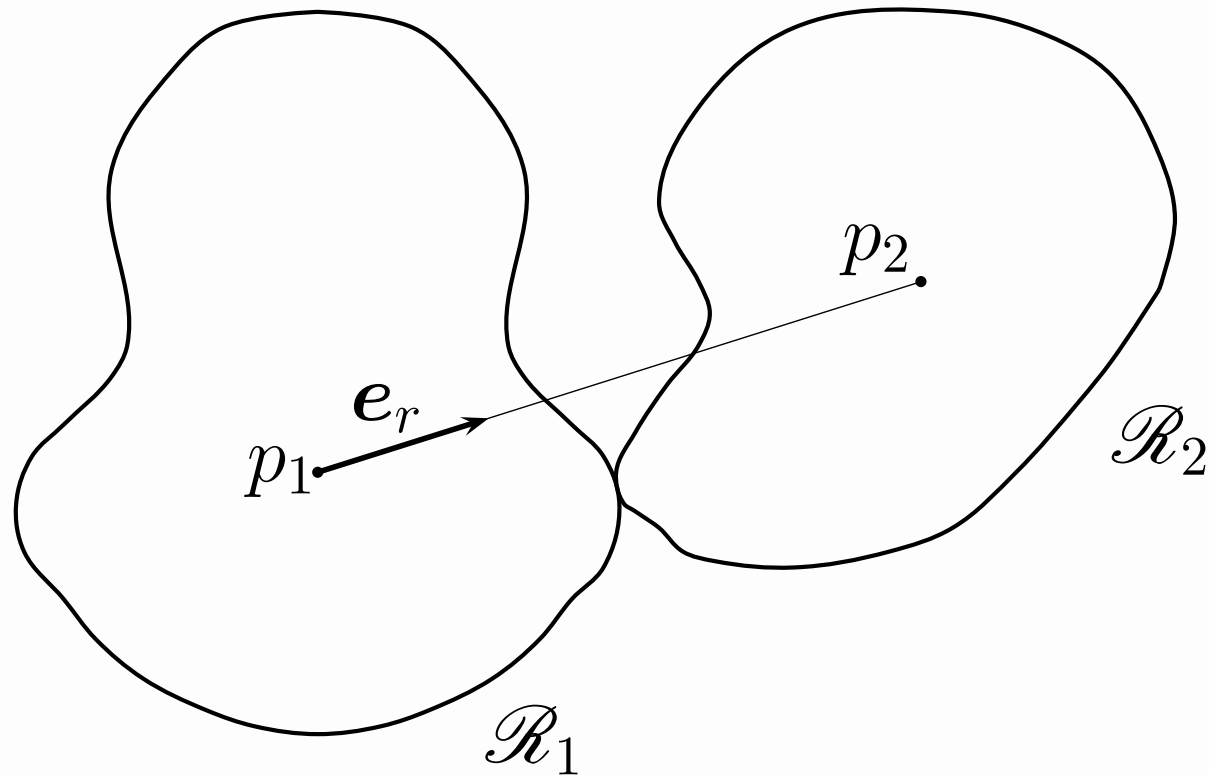
$U_{\text{disp}}$  is the potential of *soft forces*. For neutral, non-polar molecules, it is the first term in a multipolar expansion, valid only if  $p_1$  and  $p_2$  are sufficiently *far apart*.

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We imagine that each charge center is surrounded by an impenetrable hard region that represents the *range* of the repulsive *hard forces*.

# Molecules in Contact



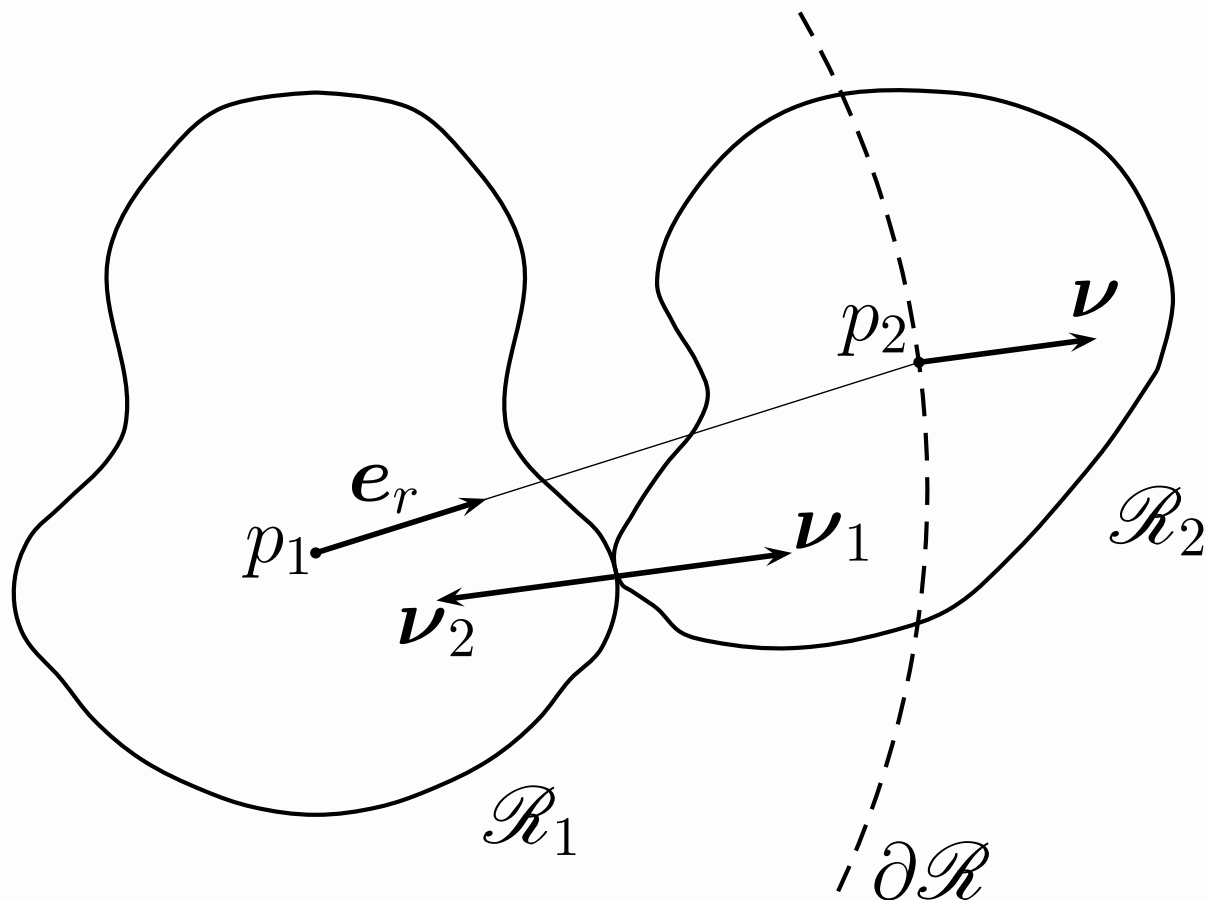
$\mathcal{R}_1, \mathcal{R}_2$  van der Waals regions  
 $p_1, p_2$  charge centers

# Relative Excluded Region

It is equivalently the region  $\mathcal{R}$  that  $p_2$  cannot access by the hindrance of  $\mathcal{R}_1$  and the region that  $p_1$  cannot access by the hindrance of  $\mathcal{R}_2$ .

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# Interaction Hamiltonian

$$H := -C \int_{\mathcal{E} \setminus \mathcal{R}} \frac{1}{r^6} \mathbf{A}_1 \cdot \mathbf{U}(\mathbf{e}_r) \mathbf{A}_2 \mathbf{U}(\mathbf{e}_r) dv$$

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$\mathcal{E}$  whole three-dimensional space

$v$  volume measure

$\mathcal{R}$  relative excluded region



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$H$ : energy that a probe molecule exchanges with all others with the same relative excluded region, assuming that the intermolecular vector  $\mathbf{r} := r \mathbf{e}_r$  is *isotropically* distributed in space.

# Steric Tensor

The relative excluded region  $\mathcal{R}$  is assumed to be *star-shaped*,

$$\mathcal{R} = \{p \in \mathcal{E} \mid p - p_1 = r e_r \mid r < u^*(e_r)\},$$

where  $u^*$  is a *shape function* that maps the unit sphere  $S^2$  around  $p_1$  into  $\mathcal{R}$ .

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where  $u^*$  is a *shape function* that maps the unit sphere  $\mathbb{S}^2$  around  $p_1$  into  $\mathcal{R}$ .

The radial part of the volume integration can then be performed explicitly.

$$H = -C \mathbb{I}_{\mathcal{R}} [\mathbf{A}_1] \cdot \mathbf{A}_2$$

$$\mathbb{I}_{\mathcal{R}} := \frac{1}{3} \int_{\mathbb{S}^2} \frac{1}{u^{*3}(\mathbf{e}_r)} \mathbf{U}(\mathbf{e}_r) \boxtimes \mathbf{U}(\mathbf{e}_r) d\alpha$$

# Spheroids

Assume that  $\mathcal{R}_1$  is *star-shaped* and represent  $\partial\mathcal{R}_1$  in spherical coordinates.

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$$p - p_1 = u(\mathbf{e}_r)\mathbf{e}_r$$

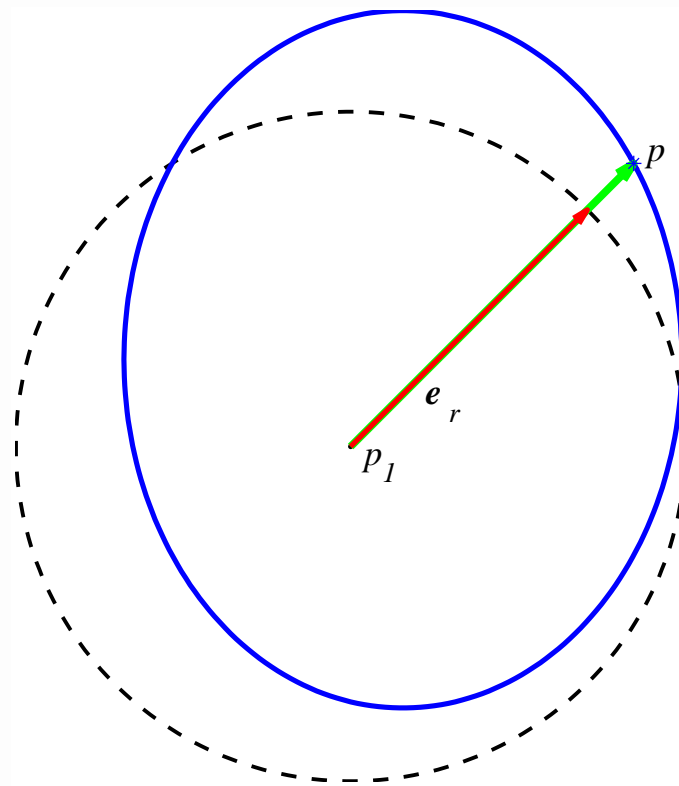
$$u(\mathbf{e}_r) = R [1 + \varepsilon v(\mathbf{e}_r)]$$

$$\langle v(\mathbf{e}_r) \rangle_{S^2} = 0$$

$R$  average radius

$\langle \cdot \rangle_{S^2}$  average on  $S^2$

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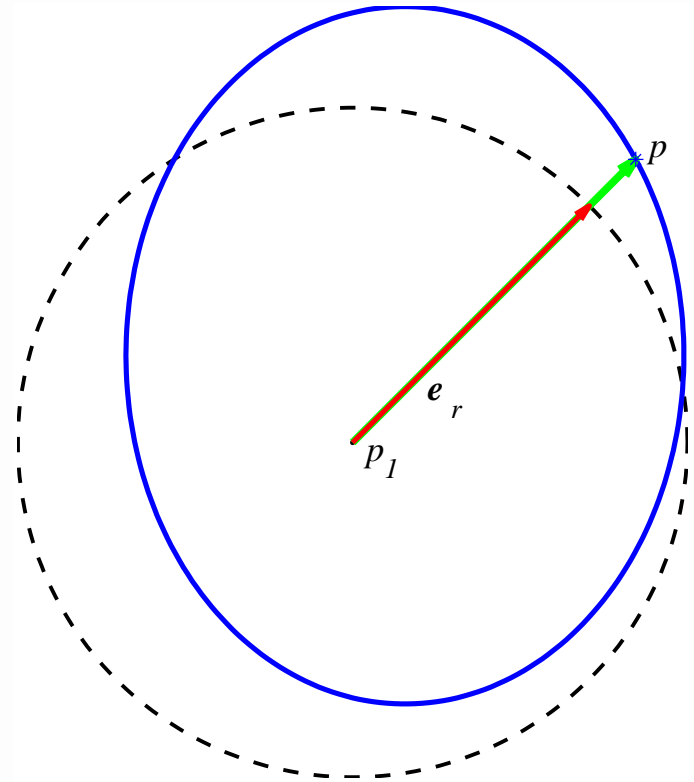
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A shape in this family is convex if  $\varepsilon$  is sufficiently small.

# Shape Multipole Expansion

$$v(\mathbf{e}_r) = \mathbf{E} \cdot \mathbf{e}_r + \mathbf{E} \cdot \overline{\mathbf{e}_r \otimes \mathbf{e}_r} + \mathbf{E}^{(3)} \cdot \overline{\mathbf{e}_r \otimes \mathbf{e}_r \otimes \mathbf{e}_r} + \dots$$

$\overline{\dots}$  symmetric irreducible part of a tensor

$\mathbf{E}$ : *shape dipole*

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$$\mathbf{E} = \frac{15}{2} \langle v \overline{\mathbf{e}_r \otimes \mathbf{e}_r} \rangle_{S^2} = \frac{15}{2} \langle v(\mathbf{e}_r \otimes \mathbf{e}_r - \frac{1}{3} \mathbf{I}) \rangle_{S^2}.$$

# Quadrupolar Shape Tensor

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$$\begin{aligned} R^* &= 2R \\ \mathbf{A} &= \mathbf{A}_0 + \frac{1}{3}(\text{tr } \mathbf{A})\mathbf{I} \\ \mathbf{E}' &= \mathbf{R}\mathbf{E}\mathbf{R}^\top \\ \mathbf{A}' &= \mathbf{R}\mathbf{A}\mathbf{R}^\top \end{aligned}$$

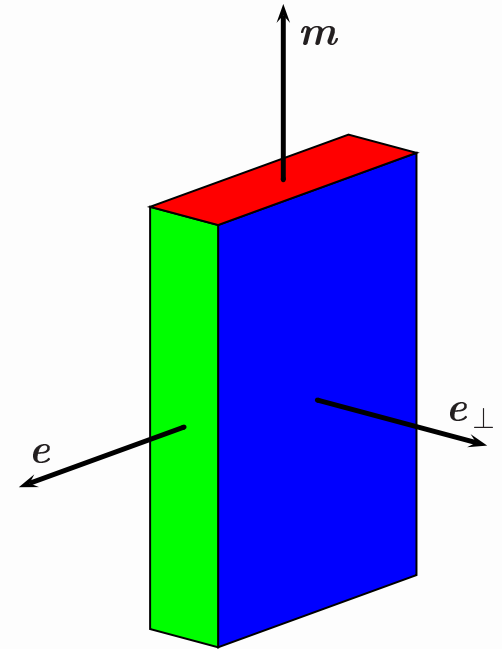
# Molecular Tensors

$$\mathbf{q} := m \otimes m - \frac{1}{3}\mathbf{I}$$

$$\mathbf{b} := e \otimes e - e_{\perp} \otimes e_{\perp}$$

$m$  long molecular axis

$m, e, e_{\perp}$  axes of any molecular polarisability tensor



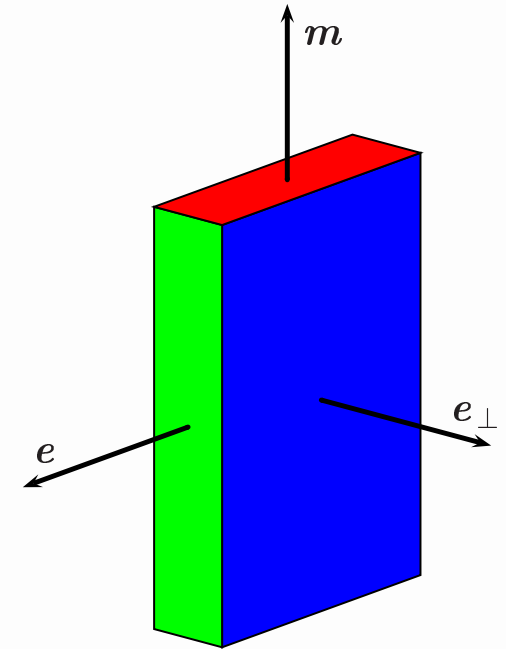
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As a special case, we assume that the shape quadrupole tensor  $\mathbf{E}$  has the same eigenframe as the polarisability tensor  $\mathbf{A}$ . Then

$$\varepsilon\mathbf{E} = \rho\mathbf{q} + \beta\mathbf{b}$$

with scalar parameters  $\rho$  and  $\beta$ .

# General Biaxial Molecules

$$\mathbf{A} = \alpha \mathbf{I} + \Delta\alpha \mathbf{q} + \Delta\alpha_{\perp} \mathbf{b} \quad \text{and} \quad \mathbf{A}' = \alpha \mathbf{I} + \Delta\alpha \mathbf{q}' + \Delta\alpha_{\perp} \mathbf{b}'$$

$$\alpha = \frac{1}{3} \text{tr} \mathbf{A} = \frac{1}{3} (\alpha_{11} + \alpha_{22} + \alpha_{33})$$

$$\Delta\alpha = \alpha_{33} - \frac{1}{2} (\alpha_{11} + \alpha_{22}) \quad \Delta\alpha_{\perp} = \alpha_{11} - \alpha_{22}$$

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$$H = -\frac{\pi C}{945 R^{*3}} \{a \mathbf{q} \cdot \mathbf{q}' + b (\mathbf{q} \cdot \mathbf{b}' + \mathbf{b} \cdot \mathbf{q}') + c \mathbf{b} \cdot \mathbf{b}'\}$$

$$a : = \Delta\alpha [28\Delta\alpha + 8\rho(2\Delta\alpha - 21\alpha) - 24\beta\Delta\alpha_{\perp}],$$

$$b : = 14\Delta\alpha\Delta\alpha_{\perp} - 2\beta(4\Delta\alpha^2 + 3\Delta\alpha_{\perp}^2) - 42\alpha(2\beta\Delta\alpha + \rho\Delta\alpha_{\perp}),$$

$$c : = \Delta\alpha_{\perp} [7\Delta\alpha_{\perp} - 4\beta(2\Delta\alpha + 21\alpha) - 4\rho\Delta\alpha_{\perp}].$$



# Maier-Saupe Interaction

Here  $\Delta\alpha_{\perp} = 0$ , and so

$$a = \Delta\alpha[28\Delta\alpha + 8\rho(2\Delta\alpha - 21\alpha)],$$

$$b = -8\beta\Delta\alpha^2 - 84\alpha\beta\Delta\alpha,$$

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***Spherical shape***,  $\rho = \beta = 0$ :

$$a = 28\Delta\alpha^2, \quad b = c = 0.$$

# Biaxial Interaction

If the shape is spherical and so  $\rho = \beta = 0$ , then

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Then  $b^2 - ac = 0$  and the interaction is simply attractive.

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Steric hindrance can transform a simply attractive Hamiltonian into a partly repulsive Hamiltonian:

$$b^2 - ac = 4 \left[ \rho\Delta\alpha_{\perp} (4\Delta\alpha - 21\bar{\alpha}) + \beta (42\bar{\alpha}\Delta\alpha + 4\Delta\alpha^2 - 3\Delta\alpha_{\perp}^2) \right]^2 \geq 0.$$

# Dipolar Interaction

$$U_{\text{dip}} = \frac{1}{4\pi\epsilon_0 r^3} \{ \mathbf{p} \cdot \mathbf{p}' - 3(\mathbf{p} \cdot \mathbf{e})(\mathbf{p}' \cdot \mathbf{e}) \}$$
$$= \frac{1}{4\pi\epsilon_0 r^3} \mathbf{p} \cdot (\mathbf{I} - 3\mathbf{e} \otimes \mathbf{e}) \mathbf{p}'$$

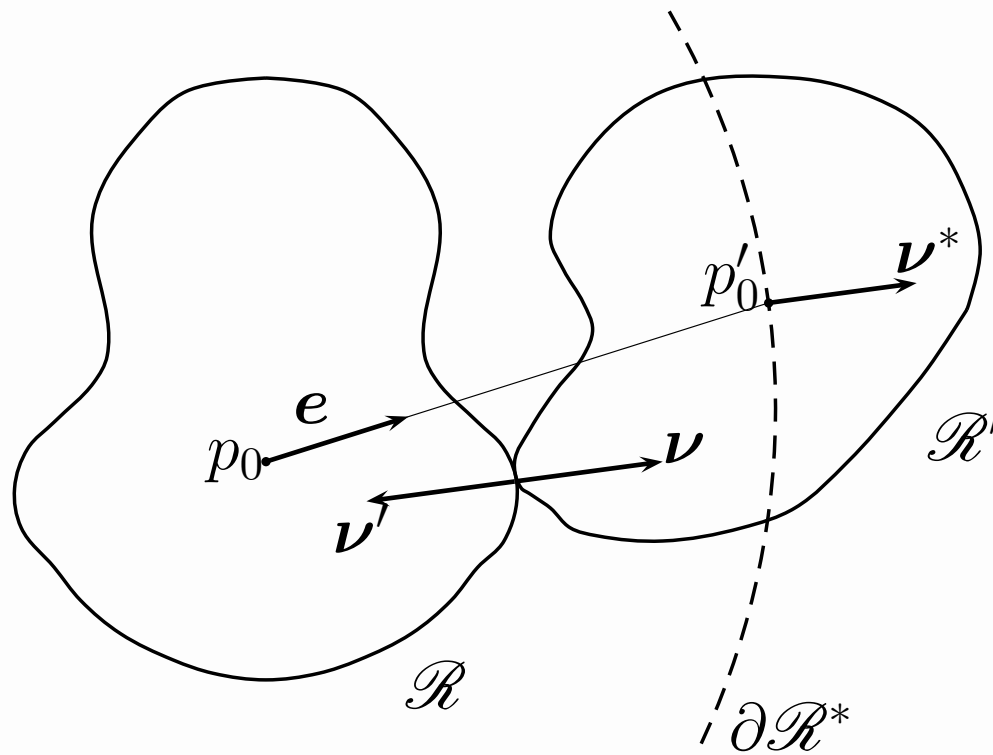
- $\mathbf{p}, \mathbf{p}'$  molecular electric dipoles
- $\epsilon_0$  dielectric constant in vacuum
- $r$  intermolecular distance
- $\mathbf{e}$  intermolecular unit vector

# Interaction Hamiltonian

$H$  is the average energy  $U_{\text{dip}}$  exchanged between molecules with the same excluded region  $\mathcal{R}^*$ .

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$\mathcal{R}, \mathcal{R}'$  van der Waals regions  
 $\mathcal{R}^*$  excluded region



# Isotropic Distribution

$$H = \frac{1}{\epsilon_0} \mathbf{p} \cdot \mathbf{I}_{\mathcal{R}^*}[\mathbf{p}']$$

$$\mathbf{I}_{\mathcal{R}^*} := \left\langle \ln \left( \frac{1}{u^*(\mathbf{e})} \right) (\mathbf{I} - 3\mathbf{e} \otimes \mathbf{e}) \right\rangle_{\mathbb{S}^2}$$

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$\mathbf{I}_{\mathcal{R}^*}$  steric tensor  
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*spherical shape*

$$\mathbf{I}_{\mathcal{R}^*} = \ln \left( \frac{1}{2R} \right) \langle \mathbf{I} - 3\mathbf{e} \otimes \mathbf{e} \rangle_{\mathbb{S}^2} = \mathbf{0}$$

$$H \equiv 0$$

# Spheroidal Shape

$$u(\mathbf{e}) = R(1 + \varepsilon u_r(\mathbf{e})) \quad \langle u_r \rangle_{S^2} = 0$$

$$u_r = \mathbf{e} \cdot \mathbf{E} \mathbf{e}$$

$R$  average molecular radius

$\mathbf{E}$  shape tensor

$$\mathbf{E} = \mathbf{E}^T \quad \text{tr } \mathbf{E} = 0$$

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$$\mathbf{E} = \mathbf{E}^\top \quad \text{tr } \mathbf{E} = 0$$

$$\mathbf{I}_{\mathcal{R}^*} = \frac{\varepsilon}{5}(\mathbf{E} + \mathbf{E}') + o(\varepsilon) \quad \mathbf{E}' = \mathbf{R} \mathbf{E} \mathbf{R}^\top$$

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$$H = U_0 (\mathbf{E} \boldsymbol{\ell} \cdot \boldsymbol{\ell}' + \mathbf{E}' \boldsymbol{\ell}' \cdot \boldsymbol{\ell})$$

$\boldsymbol{\ell} \in S^2$  molecular electric polarity  $\mathbf{p} = p \boldsymbol{\ell}$   
 $\boldsymbol{\ell}' = \mathbf{R} \boldsymbol{\ell}$

# Credits

## Co-workers

FULVIO BISI  
EPIFANIO G. VIRGA

## Discussions

EUGENE C. GARTLAND, JR.  
GEORGE E. DURAND  
RICCARDO ROSSO

## Funding

INDAM (Italian National Institute of Higher Mathematics)