

Diffusion aux
petits angles

Diffusion aux petits angles

Doru Constantin
doru.constantin@u-psud.fr

Introduction

Doru Constantin
doru.constantin@u-psud.fr

Laboratoire de Physique des Solides
Orsay, France

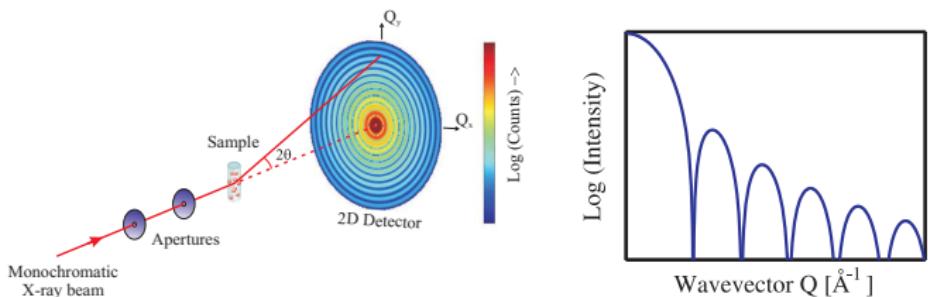
19 octobre 2018



<https://www.equipes.lps.u-psud.fr/constantin/>

Introduction

- ▶ [Guinier and Fournet(1955)]
Classique, complet, daté.
- ▶ [Als-Nielsen and McMorrow(2011)]
Introductif, pédagogique.
- ▶ [Roe(2000)]
Applications à la matière molle.
- ▶ [Glatter(2018)]
Pédagogique. Discute les techniques de transformation des données.



[Als-Nielsen and McMorrow(2011)]

- ▶ Angle de diffusion : $2\theta = (\vec{k}', \vec{k})$
- ▶ Vecteur de diffusion : $\vec{q} = \vec{k}' - \vec{k}; q = |\vec{q}| = 2k \sin \theta = \frac{4\pi}{\lambda} \sin \theta$
- ▶ Intensité diffusée $I(\vec{q})$
- ▶ Intensité intégrée $I(q) = \langle I(\vec{q}) \rangle_\phi$

Diffusion du rayonnement par une distribution continue I

Système mono-atomique ou mono-moléculaire :

$$I(\vec{q}) = (fr_0)^2 \left| \sum_n e^{i\vec{q} \cdot \vec{r}_n} \right|^2 = (fr_0)^2 |\widetilde{\Phi}(\vec{q})|^2, \quad (1)$$

avec $\widetilde{\Phi}(\vec{q})$ la transformée de Fourier de la densité de particules $\Phi(\vec{r}) = \sum_n \delta(\vec{r} - \vec{r}_n)$.

Prenons la moyenne de $\Phi(\vec{r})$ sur un petit volume v autour de la position \vec{r} :

$$\rho_{\text{at}}(\vec{r}) = \frac{1}{v} \int_v dv \Phi(\vec{r}') = \frac{k}{v} \quad (2)$$

si le volume v contient en moyenne k particules.

Diffusion du rayonnement par une distribution continue II

L'intensité diffusée peut s'écrire :

$$I(\vec{q}) = \left| \int_V \rho_{\text{sl}} e^{i\vec{q} \cdot \vec{r}} dV \right|^2, \quad (3)$$

où (en rayons X) $\rho_{\text{sl}} = fr_0\rho_{\text{at}}$ est la **densité de longueur de diffusion**
(*sl* pour « scattering length »).

L'intensité diffusée aux petits angles est la transformée de Fourier de la densité de longueur de diffusion.

Contraste

Introduction

Particules homogènes de densité (de longueur de diffusion) ρ_p dans un solvant de densité ρ_s . Dans l'équation (3) il suffit de remplacer ρ_{sl} par le contraste $\Delta\rho = \rho_p - \rho_s$.

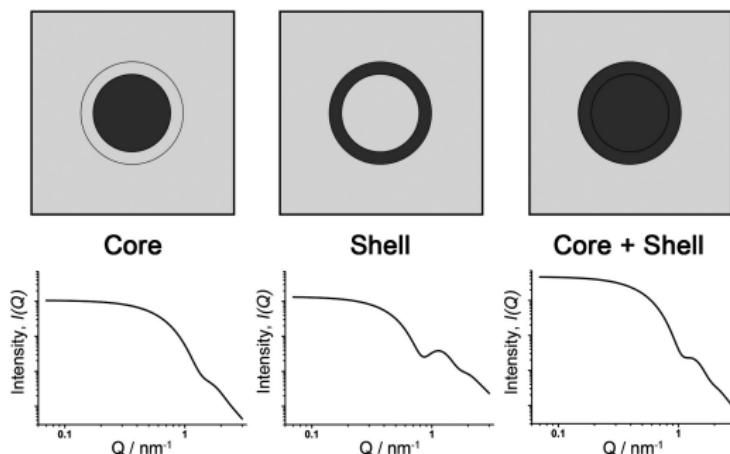
Le contraste est essentiel : il régit la « visibilité » de la structure.

Comment le moduler ?

- ▶ Varier l'énergie du rayonnement : ASAXS
[Ballauff and Jusufi(2006)]
- ▶ Varier la composition de la particule et/ou du solvent!

Adaptation du contraste I

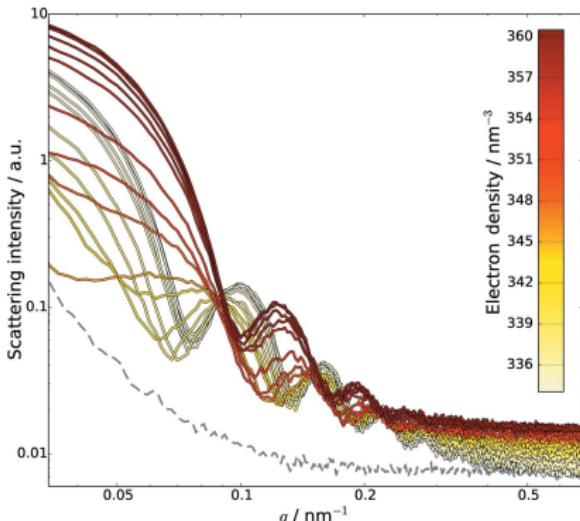
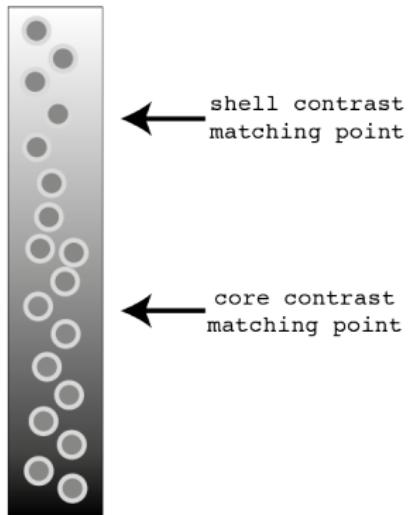
- ▶ **Neutrons** : la longueur de diffusion varie beaucoup en fonction du nombre de masse, en particulier entre H et D! On peut utiliser des produits deutérés.



M. J. Hollamby, *Phys. Chem. Chem. Phys.* **15**, 10566-10579 (2013).

Adaptation du contraste II

- ▶ **Rayons X** : la longueur de diffusion est proportionnelle à la densité électronique (plus difficile à changer). Gamme de variation très faible.



[Garcia-Diez et al.(2015) Garcia-Diez, Gollwitzer, and Krumrey]

Facteurs de forme et de structure

Collection d'objets identiques et de même orientation :

$$I(\vec{q}) = |F(\vec{q})|^2 S(\vec{q}) \quad (4)$$

- ▶ **Facteur de forme** $|F(\vec{q})|^2$: décrit la morphologie de la particule.
- ▶ **Facteur de structure** $S(\vec{q})$: décrit l'arrangement dans l'espace de l'ensemble de particules.
- ▶ \vec{q} défini dans le référentiel du laboratoire !
- ▶ Comment prendre en compte la rotation des objets ?

$$\langle I(\vec{q}) \rangle = \left\langle |F(\vec{q})|^2 \right\rangle \langle S(\vec{q}) \rangle$$

Diffusion aux
petits angles

Doru Constantin
doru.constantin@u-
psud.fr

Facteur de forme

Paramètres
indépendants du
modèle

Modélisation

Facteur de forme

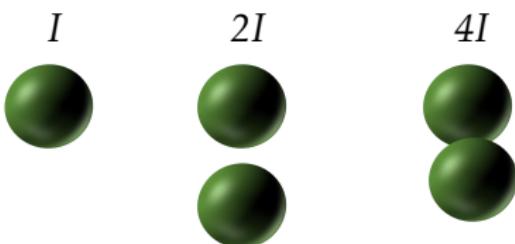
« Pouvoir diffusant » de l'objet

Particules séparées et homogènes :

On prend la limite $q \rightarrow 0$ dans l'équation (3)

$$I(q \rightarrow 0) = n\Delta\rho^2 V_{\text{part}}^2 \quad (5)$$

- ▶ Il faut déterminer l'intensité en unités absolues ($[L^{-1}]$). Problème de l'**étalonnage**.
- ▶ Le résultat combine les trois paramètres n , $\Delta\rho$ et V_{part} .
- ▶ Très sensible au volume : $I(q \rightarrow 0) \propto V_{\text{part}}^2$!



Extension de l'objet

Dans l'équation (3) on développe le facteur de phase :

$$e^{i\vec{q} \cdot \vec{r}} = 1 + i\vec{q} \cdot \vec{r} - \frac{(\vec{q} \cdot \vec{r})^2}{2}$$

$$I(q \rightarrow 0) \simeq n\Delta\rho^2 V_{\text{part}}^2 \exp\left(\frac{-q^2 R_G^2}{3}\right) \quad (6)$$

Rayon de giration

$$R_G^2 = \frac{1}{V_{\text{part}}} \int_{V_{\text{part}}} r^2 dV \quad (\text{objet homogène}) \quad (7)$$

Mesure de l'extension spatiale de l'objet.

Facteur de forme

Paramètres
indépendants du
modèle

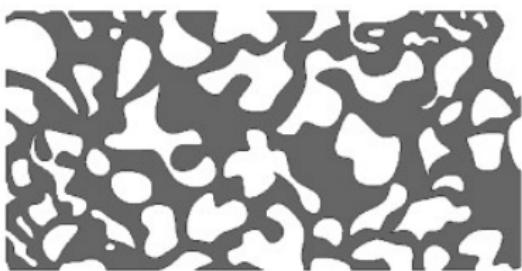
Modélisation

- ▶ Objets fractals
- ▶ Objets très anisotropes (bâtonnets, plaquettes)

Voir l'appendice et [Roe(2000)].

Régime de Porod

q grand : $L = 2\pi/q \ll d_{\text{syst}}$ (tailles typiques du système)



$$I(q \rightarrow \infty) \simeq \frac{2\pi\Delta\rho^2 S_V}{q^4} \quad (8)$$

S_V : surface spécifique (aire d'interface par unité de volume).

Invariant et fraction volumique

Intensité totale (diffusée dans tout l'espace réciproque)

$$Q = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} I(\vec{q}) dV_q = \frac{1}{2\pi^2} \int_0^\infty q^2 I(q) dq \quad (9)$$

Système bi-phasic (fraction vol. Φ) à frontière nette :

$$Q = \Delta\rho^2\Phi(1 - \Phi) \quad (10)$$

Liens avec la fonction de corrélation et le principe de Babinet : [Roe(2000), Glatter and Kratky(1982)]

Volume de l'objet

Particules séparées, homogènes et identiques (même volume) :

$$V_{\text{part}} = \frac{I(q=0)}{Q} \frac{1 - \Phi}{S(q=0)} \quad (11)$$

Il n'y a besoin ni de l'intensité en unités absolues, ni de la densité électronique !

O. Spalla, Chapitre 2 dans [Goudeau and Guinebretière(2012)]

Vue d'ensemble

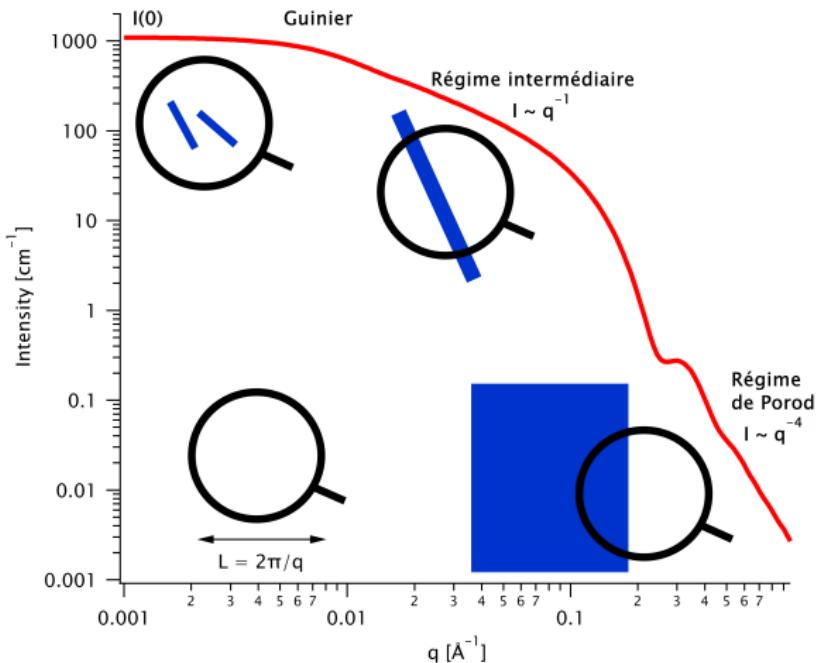
Particules cylindriques

Doru Constantin
doru.constantin@u-
psud.fr

Facteur de forme

Paramètres
indépendants du
modèle

Modélisation



Transformation des données

Pour des objets identiques, isolés et sans interaction :

- ▶ La fonction de corrélation $\gamma(r)$ est reliée à l'intensité moyennée par :

$$I(q) = 4\pi \int_0^\infty r^2 \gamma(r) \frac{\sin(qr)}{qr} dr \quad (12)$$

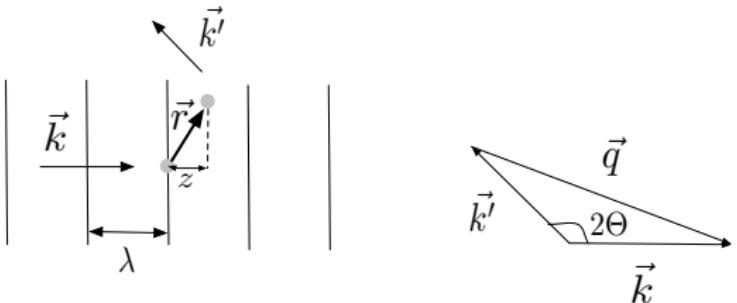
$$\gamma(r) = \frac{r^2}{2\pi^2} \int_0^\infty q^2 I(q) \frac{\sin(qr)}{qr} dq \quad (13)$$

- ▶ En utilisant (13) on calcule la fonction de distribution des distances $p(r) = r^2 \gamma(r)$.
- ▶ On extrait de $p(r)$ des informations sur la forme des objets.

[Glatter and Kratky(1982), Glatter(2018)]

Formule de Debye

Deux particules à une distance fixe r :



Facteur de forme

Paramètres
indépendants du
modèle

Modélisation

$$A(\vec{q}) \sim f_1 + f_2 e^{i\vec{q} \cdot \vec{r}} \Rightarrow I(\vec{q}) = f_1^2 + f_2^2 + 2f_1 f_2 \cos(\vec{q} \cdot \vec{r}) \quad (14)$$

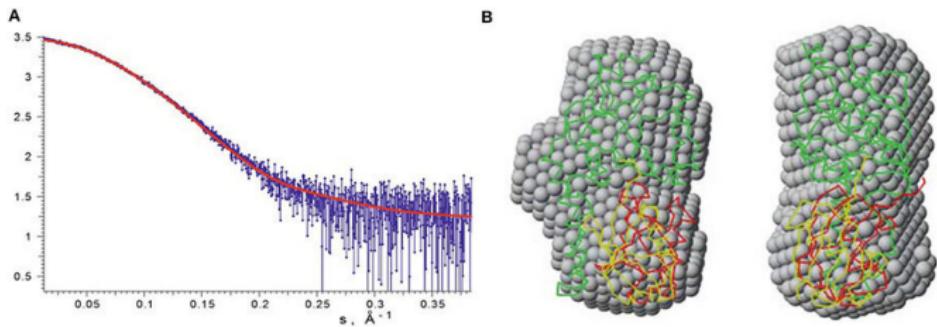
Le vecteur de position $\vec{r} = (r, \alpha, \beta)$; moyenne sur
l'orientation $\Omega = (\alpha, \beta)$ (à \vec{q} fixé !)

$$\langle I(\vec{q}) \rangle_{\Omega} = f_1^2 + f_2^2 + 2f_1 f_2 \frac{\sin(qr)}{qr} \quad (15)$$

La moyenne sur l'orientation a une expression très simple !

Discrétisation

- ▶ « Découper » l'objet N en petits morceaux.
- ▶ Appliquer la formule de Debye (15) à chaque paire de tels morceaux.
- ▶ $\langle I(\vec{q}) \rangle_{\Omega}$ est la somme de ces N^2 termes.



S. Faggiano et al., *Front. Mol. Biosci.* **2**, 2 (2015).

[Svergun and Koch(2003)]

Modèles analytiques

- ▶ Décrire l'objet par une fonction analytique $\rho(\vec{r})$.
- ▶ Calculer sa TF $\tilde{\rho}(\vec{q})$ et l'intensité $I(\vec{q})$
- ▶ Prendre la moyenne sur l'orientation.

- ▶ SasView
- ▶ SASFIT
- ▶ Macros du NCNR(NIST), en IgorPro
- ▶ SCATTER
- ▶ ...

Facteur de forme

Paramètres
indépendants du
modèle

Modélisation

Diffusion aux
petits angles

Doru Constantin
doru.constantin@u-
psud.fr

Facteur de
structure

Integral Equations

Bibliographie

Facteur de structure

- ▶ [Chandler(1987)] Excellente introduction.
- ▶ [Gould and Tobochnik(2006)] Plus développe.
- ▶ [Hansen and McDonald(2006)] Complet et rigoureux (référence).

Definitions

System of N identical particles in the volume V , at a temperature T ; the pressure is P .

- ▶ $\rho = \frac{N}{V}$ *number density!*
- ▶ $u_{ij} = u(\mathbf{r}_i - \mathbf{r}_j) = u(r)$ *isotropic interaction potential*
- ▶ $e(r) = e^{-\beta u(r)}$ with $\beta = \frac{1}{k_B T}$
- ▶ $f(r) = e(r) - 1 = e^{-\beta u(r)} - 1$ Mayer f -function
- ▶ $\frac{P}{\rho k_B T} = 1 + \rho B_2(T) + \rho^2 B_3(T) + \dots$

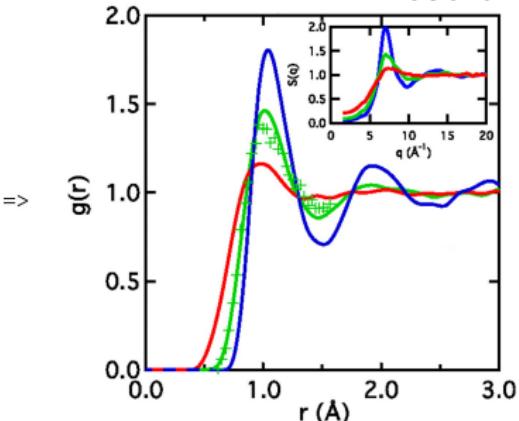
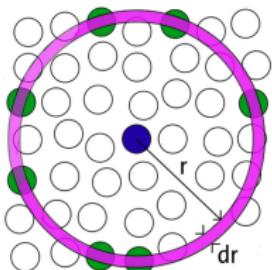
Equation Of State (EOS)

Facteur de
structure

Integral Equations

Bibliographie

Radial Distribution Function $g(r)$



- It contains the **structure** of the system :

$$S(q) - 1 = \rho \int d^D r [g(r) - 1] e^{i\mathbf{r}\mathbf{q}}$$

- It contains the **thermodynamics** of the system :

$$\frac{P}{\rho k_B T} = 1 - \frac{\rho}{6k_B T} \int_V r \frac{du(r)}{dr} g(r) d^D r.$$

- The fundamental problem of liquid theory : knowing $u(r)$ and ρ , find $g(r)$!.

Relation between $g(r)$ and $S(q)$

$$dn(\mathbf{r}) = \langle \sum_{i \neq 0} \delta [\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_0)] \rangle d^D \mathbf{r} \quad \text{yields :}$$

$$g(\mathbf{r}) = \frac{1}{\rho} \left\langle \sum_{i \neq 0} \delta [\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_0)] \right\rangle = V \frac{N-1}{N} \langle \delta [\mathbf{r} - (\mathbf{r}_1 - \mathbf{r}_0)] \rangle$$

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{N} \left\langle \sum_{ij} e^{-i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle = 1 + \frac{1}{N} \left\langle \sum_{i \neq j} e^{-i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle \\ &= 1 + \frac{1}{N} \left\langle \int_V d^D \mathbf{r} e^{-i\mathbf{q}\mathbf{r}} \sum_{i \neq j} \delta [\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle \\ &= 1 + \frac{N(N-1)}{N} \int_V d^D \mathbf{r} e^{-i\mathbf{q}\mathbf{r}} \langle \delta [\mathbf{r} - (\mathbf{r}_1 - \mathbf{r}_0)] \rangle \\ &= 1 + \rho \int d^D \mathbf{r} e^{-i\mathbf{r}\mathbf{q}} g(\mathbf{r}) \end{aligned}$$

“Taming” the distribution

Problem : $\lim_{r \rightarrow \infty} g(r) = 1$ yields a Dirac peak at $S(\mathbf{q} = 0)$

$$S'(\mathbf{q}) = S(\mathbf{q}) - \rho\delta(\mathbf{q}) = 1 + \rho \int d^D \mathbf{r} [g(\mathbf{r}) - 1] e^{-i\mathbf{r}\mathbf{q}}$$

Drop the prime, bring back the isotropy :

$$S(q) - 1 = \rho \int d^D \mathbf{r} [g(r) - 1] e^{i\mathbf{r}\mathbf{q}} = \rho h(q)$$

$h(r) = g(r) - 1$: **total correlation function.**

Remarks :

- ▶ Definition of the ensemble average $\langle \cdot \rangle$,
[Hansen and McDonald(2006)].
- ▶ Alternative derivation : general formalism of
response functions.

- ▶ To lowest order : $g(r) = e(r) = e^{-\beta u(r)}$
- ▶ Following terms :

$$g(r) = e(r)y(r) = e(r) \left[1 + \sum_{n=1}^{\infty} \rho^n y_n(r) \right]$$

- ▶ $y_1(r) = \int f(\mathbf{r})f(\mathbf{r} - \mathbf{r}') d^3\mathbf{r}'$

The method is accurate for low densities. The results are exact to a given order in ρ and thermodynamically consistent!

Liquids are not crystals

Crystals with disorder : defined with respect to the underlying lattice.

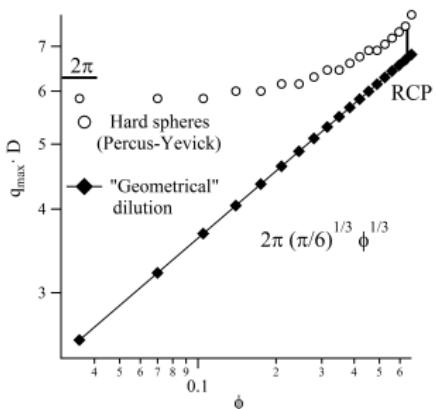
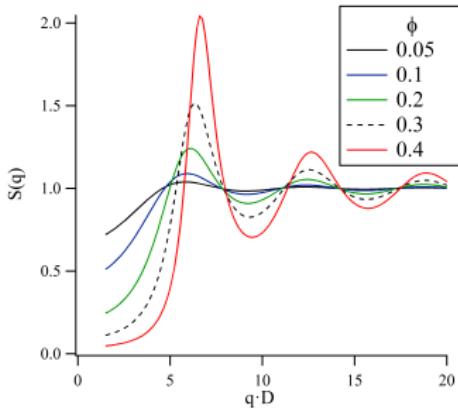
In liquids, there is no such lattice.

Low-dimensionality systems are particular cases : there is a **local** reference lattice, but not a **global** one.

Hard sphere liquid

- ▶ Ideal gas : $u(r) = 0$, $g(r) = 1$ and $S(q) = 1$.
- ▶ Hard sphere liquid : $u(r) = \infty$ for $r < 2R$ and 0 elsewhere.

$$\phi = \rho V_{\text{part}}, \text{ where } V_{\text{part}} = (4\pi/3)R^3$$



The hard sphere liquid **does not obey the dilution law!**

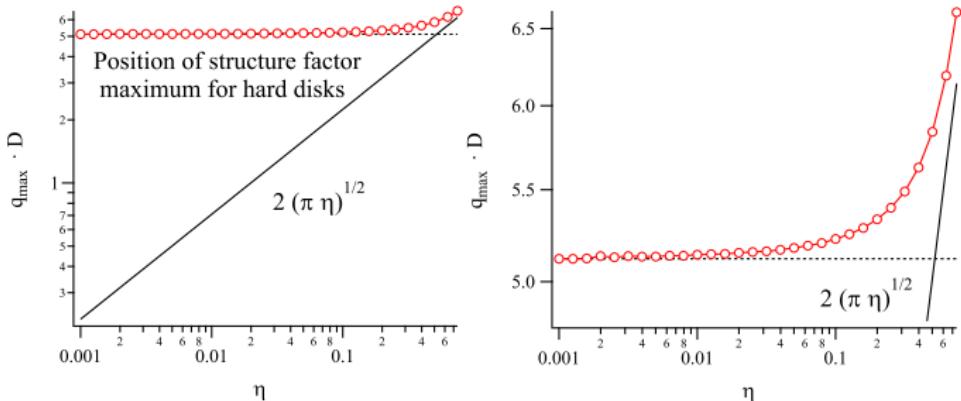
Hard disk liquid

Doru Constantin
doru.constantin@u-
psud.fr

Facteur de
structure

Integral Equations

Bibliographie



The hard disk liquid **does not obey the dilution law either!**

$$c(r) = c_{\text{ref}}(r) - e^{-\beta u(r)} \quad r > 2R$$

$$\frac{1}{S(q)} = \frac{1}{S(q)_{\text{ref}}} + \beta \rho \tilde{u}(q)$$

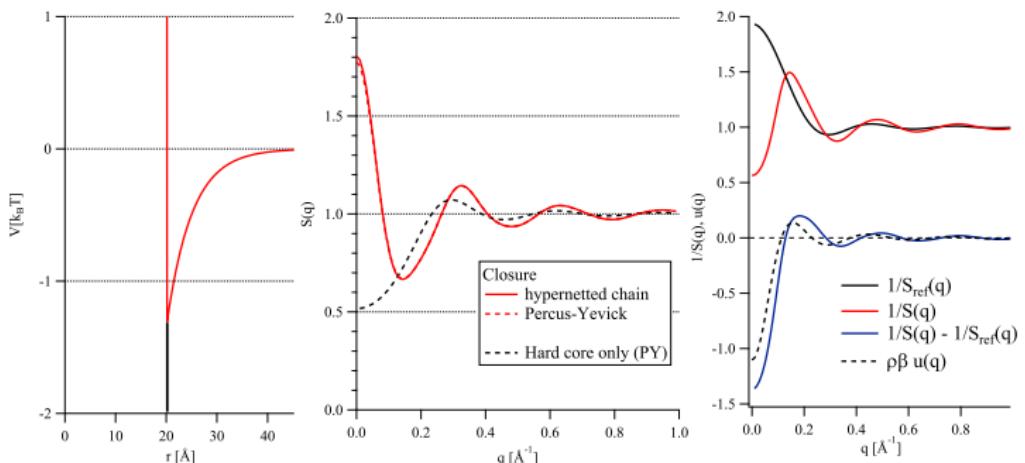
Combining two potentials

Doru Constantin
 doru.constantin@u-
 psud.fr

Facteur de
 structure

Integral Equations

Bibliographie



- ▶ When one of the potentials is infinite, the definition is ambiguous!
- ▶ The RPA does not yield the fine details of the total potential!

Diffusion aux
petits angles

Doru Constantin
doru.constantin@u-
psud.fr

Facteur de
structure

Integral Equations

Bibliographie

Integral Equations

$$h(r) = g(r) - 1$$

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(\mathbf{r}') d^3 \mathbf{r}'$$

Fourier transforming yields :

$$h(q) = c(q) + \rho c(q) h(q) \Rightarrow h(q) = \frac{c(q)}{1 - \rho c(q)} \quad c(q) = \frac{h(q)}{1 + \rho h(q)}$$

We need an additional relation between $c(r)$ and $g(r)$ (closure) to solve the problem !

Reminder : $S(q) = 1 + \rho h(q)$

Percus–Yevick (1958)

$$c(r) = f(r)y(r) = [1 - e^{\beta u(r)}]g(r) \quad \text{short range}$$

Hard spheres :

$$\begin{cases} h(r) &= -1 & r < 2R \\ c(r) &= 0 & r > 2R \end{cases}$$

Works better for short-range potentials

Mean Spherical Approximation (1966)

Mainly applied for potentials with a hard core (e.g. hard spheres with Yukawa tails)

$$\begin{cases} h(r) = -1 & r < 2R \\ c(r) = e^{-\beta u(r)} & r > 2R \end{cases}$$

Analytically solvable in many cases ; does not yield the correct density expansion (not even to first order !)

Hypernetted chain

Diffusion aux
petits angles

Doru Constantin
doru.constantin@u-
psud.fr

Facteur de
structure

Integral Equations

Bibliographie

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r)$$

Works better for long-range potentials

Sum rule for impenetrable core systems

Impenetrable core of size R_c : $g(r < 2R_c) = 0$

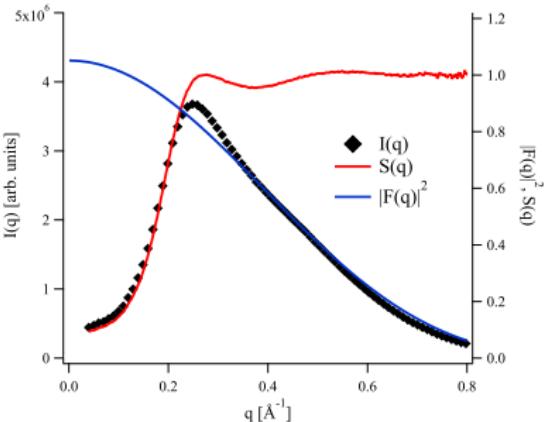
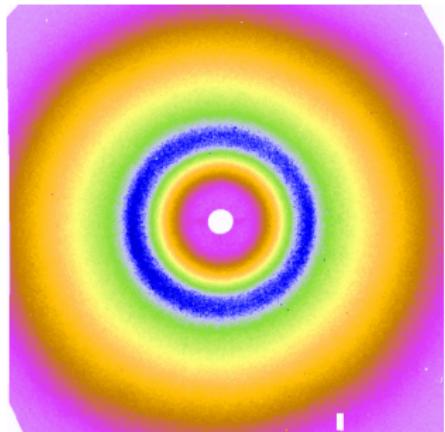
$$g(r) - 1 = \frac{1}{\rho} \frac{1}{(2\pi)^3} \int d^3q [S(q) - 1] e^{-iqr}$$

Setting $g(0) = 0$ yields the sum rule :

$$\frac{1}{(2\pi)^3} \int d^3q [S(q) - 1] = \frac{1}{2\pi^2} \int_0^\infty dq q^2 [S(q) - 1] = -\rho$$

- ▶ Valid for almost all colloidal particles.
- ▶ Useful for extracting $S(q)$ from the experimental $I(q)$.
- ▶ Relation between height and width of peak in $S(q)$.

Bhatia and March, *Phys. Chem. Liq.*, **13**, 313-316 (1984).

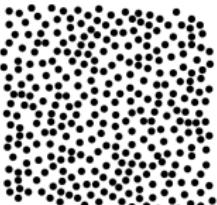


- ▶ SAXS image $\rightarrow I(q)$
- ▶ $I(q) = |F(q)|^2 \times S(q)$
- ▶ $|F(q)|^2$: form factor
- ▶ $S(q)$: structure factor

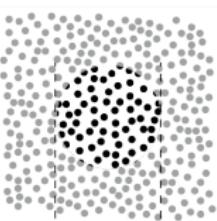
A peak in $I(q)$ does not necessarily imply a peak in $S(q)$!

Finite-sized systems

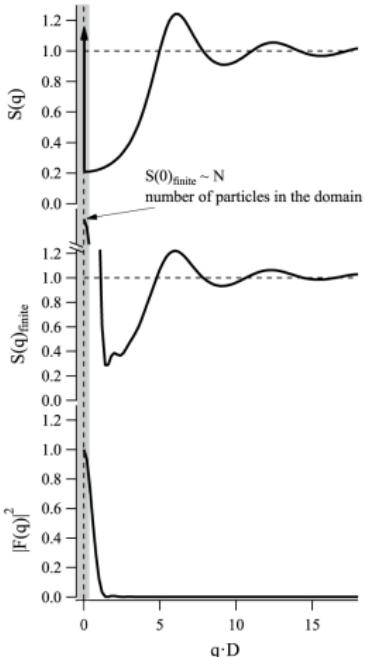
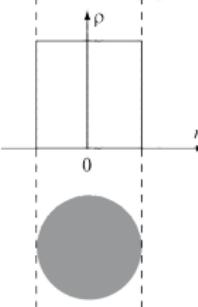
- Infinite system :
 $S(q) = S'(q) + \delta(0)$



- Finite size :
 $S_{\text{finite}}(q) = S(q) * |F|^2(q)$



- Separation between SAXS and WAXS



Bibliographie I

-  Als-Nielsen, J., and D. McMorrow. 2011.
Elements of modern X-ray physics. Wiley, Hoboken.
Chapitre 4. Introductif, pédagogique.
-  Attwood, D. 2007.
Soft X-Rays and Extreme Ultraviolet Radiation : Principles and Applications. Cambridge University Press.
Très lisible. Aspect techniques (synchrotrons, cohérence) moins discutés ailleurs.
-  Ballauff, M., and A. Jusufi. 2006.
Anomalous small-angle X-ray scattering : analyzing correlations and fluctuations in polyelectrolytes.
Colloid and Polymer Science. 284 :1303–1311.
Diffusion anomale des rayons X (ASAXS) en matière molle.

Bibliographie II

-  Barker, J. A., and D. Henderson. 1976.
What is “liquid”? Understanding the states of matter.
Rev. Mod. Phys. 48 :587–671.
Vue d’ensemble des différentes approches en théorie des liquides.
-  Chandler, D. 1987.
Introduction to modern statistical mechanics. Oxford University Press.
Excellente introduction.
-  Fischer, H. E., A. C. Barnes, and P. S. Salmon. 2006.
Neutron and x-ray diffraction studies of liquids and glasses.
Reports on Progress in Physics. 69 :233–299.
Discussion détaillée des facteurs de structure.

Bibliographie III

-  Garcia-Diez, R., C. Gollwitzer, and M. Krumrey. 2015. Nanoparticle characterization by continuous contrast variation in small-angle X-ray scattering with a solvent density gradient. *Journal of Applied Crystallography*. 48 :20–28. Adaptation du contraste en SAXS.
-  Glatter, O. 2018. Scattering Methods and their Application in Colloid and Interface Science. Elsevier. Pédagogique, complet.

Bibliographie IV



Glatter, O., and O. Kratky, editors. 1982.

Small angle x-ray scattering. Academic Press, London;
New York.

Classique, lisible. Discute les techniques de transformation
des données.



Goudeau, P., and R. Guinebretière, editors. 2012.

X-rays and materials. ISTE, London.

Chapitre 2. Caractérisation de nanoparticules.



Gould, H., and J. Tobochnik. 2006.

Thermal and Statistical Physics. Princeton University
Press.

Assez détaillé et très lisible.

Bibliographie V

-  Guinier, A., and G. Fournet. 1955.
Small-angle scattering of X-rays. Wiley.
Classique, complet, daté.
-  Hansen, J. P., and I. R. McDonald. 2006.
Theory of simple liquids. Academic Press.
Complet et rigoureux (référence, pas introduction).
-  Pedersen, J. S. 1997.
Analysis of small-angle scattering data from colloids and
polymer solutions : modeling and least-squares fitting.
Advances in Colloid and Interface Science. 70 :171–210.
Modèles analytiques.

Bibliographie VI



Roe, R.-J. 2000.

Methods of X-ray and Neutron Scattering in Polymer Science. Topics in Polymer Science, Oxford University Press, Oxford, New York.

Applications à la matière molle.



Svergun, D. I., and M. H. Koch. 2003.

Small-angle scattering studies of biological macromolecules in solution.

Reports on Progress in Physics. 66 :1735.

BioSAXS et modèles associés.

1 Power laws in the scattering spectra of particles

The small-angle X-ray scattering (SAXS) spectrum of particles with a well-defined shape (such as rods or platelets) is often characterized by a power-law dependence: $I(q) \sim q^{-\alpha}$, where the exponent α is directly related to the particle geometry. For "compact" particles, the large- q intensity scales as q^{-4} (Porod regime). Below, I'll give the most concise and yet –hopefully– understandable derivation I can think of for these power laws.

To simplify the derivation, we'll consider these objects as infinitely thin and infinitely large, meaning that we'll be looking at them on length scales much larger than their thickness and much smaller than their lateral extension. The approximation is legitimate, since it is in this range of length (or, conversely, scattering vector) that the power-law regimes are encountered.

1.1 Platelets: $\alpha = 2$

For a platelet, this simplification yields the following electron density profile:

$$\rho(\mathbf{r}) = \text{Cst}(x)\text{Cst}(y)\delta(z)$$

where "Cst" (constant) means that the density does not vary as a function of x and y . Of course, a constant does not need an argument, but we will specify it in order to keep track of the space dimensions.

We now need the Fourier transform of $\rho(\mathbf{r})$, $\tilde{\rho}(\mathbf{q})$. Since the Fourier transform of a constant is a Dirac delta and viceversa, we simply have:

$$\tilde{\rho}(\mathbf{q}) = \delta(q_x)\delta(q_y)\text{Cst}(q_z)$$

The intensity scattered at a given wave vector $I(\mathbf{q}) = |\tilde{\rho}(\mathbf{q})|^2$, and we'll admit that the latter function has the same form as $\tilde{\rho}(\mathbf{q})$. This is plausible: if a distribution is perfectly localized, we expect its square to share this property. Rigorously speaking, however, the square of a Dirac delta makes no sense (within classical distribution theory) so a proper derivation involves considering a finite size for the object, taking the modulus square of its Fourier transform and only letting the size go to infinity in the last step¹. Finally, the intensity scattered by a platelet perpendicular to the z axis is a thin rod parallel to q_z , as shown in the Figure below.

In solution, colloidal particles assume all possible orientations, so that this intensity is spread evenly over the sphere of constant q . Consider two

¹Another strategy consists in using the correlation function $\gamma(\mathbf{r})$.

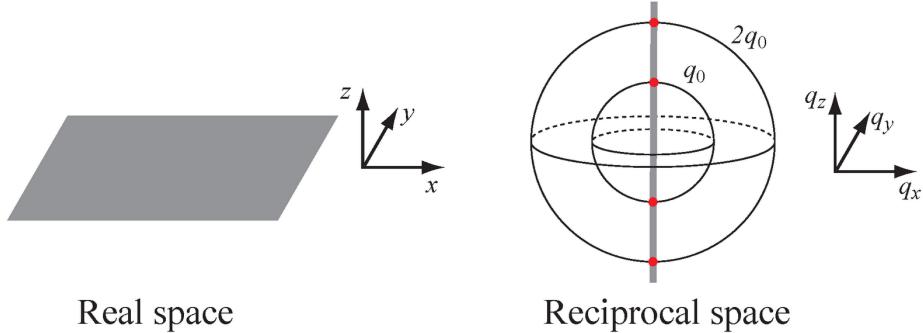


Figure 1: Fourier transform of a platelet.

such spheres, with radii q_0 and $2q_0$. The rod contributes to each sphere the same amount, namely twice its (constant) intensity $2I_0$, shown as red dots at the poles. This signal must however be divided by the surface area of the sphere, an area that increases as the square of the radius:

$$I(q_0) = \frac{2I_0}{4\pi q_0^2} \quad \text{and} \quad I(2q_0) = \frac{2I_0}{4\pi(2q_0)^2}$$

so that $I(2q_0) = I(q_0)/4$ and, finally, $\alpha = 2$.

1.2 Rods: $\alpha = 1$

Above, I showed that the SAXS intensity scattered by a platelet system goes like $I(q) \sim q^{-2}$, at least in some intermediate (but as yet unspecified) q range. Here I will show that for thin rods this dependence becomes q^{-1} . I will then derive the terminal (Porod) behavior q^{-4} and briefly consider the transition between these two regimes.

For a rod, the electron density profile:

$$\rho(\mathbf{r}) = \delta(x)\delta(y)\text{Cst}(z)$$

with the same notations as in Section 1.1. Its Fourier transform $\tilde{\rho}(\mathbf{q}) = \text{Cst}(q_x)\text{Cst}(q_y)\delta(q_z)$ and, as in part I, I will assume the same form for the intensity $I(\mathbf{q})$. The "dual" object of a rod under Fourier transform is a platelet, see Figure 2:

When spreading this intensity over reciprocal space we must keep in mind that the intersection of the plane with a sphere of constant q is a great circle (shown in red in the Figure above). Thus, the total contribution $2\pi q I_0$ increases with q , but it must also be divided by the surface area of the sphere,

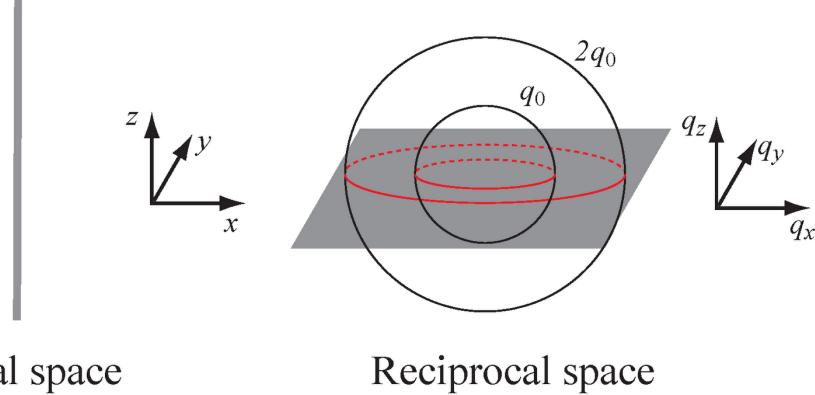


Figure 2: Fourier transform of a rod.

yielding for the two spheres:

$$I(q_0) = \frac{2\pi q_0 I_0}{4\pi q_0^2} = \frac{I_0}{2q_0} \quad \text{and} \quad I(2q_0) = \frac{4\pi q_0 I_0}{4\pi(2q_0)^2} = \frac{I_0}{4q_0}$$

so that $I(2q_0) = I(q_0)/2$ and $\alpha = 1$.

1.3 Interfaces: $\alpha = 4$ (Porod)

The density profile of an interface is invariant under x and y translations and is a Heaviside (step) function along z :

$$\rho(\mathbf{r}) = \text{Cst}(x)\text{Cst}(y)H(z)$$

The Fourier transform of $H(z)$ is $1/q_z$, as one can see either by direct evaluation or by noting that the derivative of $H(z)$ is the Dirac delta etc. Finally,

$$|\tilde{\rho}(\mathbf{q})|^2 = \delta(q_x)\delta(q_y)q_z^{-2}$$

As for the platelet in Section 1.1, the scattering is confined along a rod perpendicular to the interface, but its intensity, instead of being constant, decreases along its length. Further spreading this signal over the sphere adds an additional q^{-2} factor, for a final q^{-4} dependence.

1.4 Crossover

Although both are infinitely extended in the plane, a single interface (Porod) and two interfaces very close together (thin plate) exhibit very different scattering laws. However, at high enough scattering vector, all objects reach the

Porod regime. We will discuss this crossover for the case of a plate with finite thickness. The Fourier transform of this object along its normal is easily shown to be a cardinal sine, so that: $|\tilde{\rho}(q_z)|^2 = \left[\frac{\sin(q_z a)}{q_z a} \right]^2$. Close to the origin, ie. for $q_z a \ll 1$, this function is flat, hence the approximation $\sim \text{Cst}(q_z)$ we used for the platelet in Section 1.1. At high q , on the other hand, it behaves as q^{-2} , yielding the Porod law. To put it differently, when the typical scale $L = 2\pi/q$ over which we observe the object is much larger than its thickness, we are in the "platelet" regime and do not resolve the two interfaces. When $L \ll 2a$, on the other hand, we only observe "one interface at a time", justifying the treatment above and thus the q^{-4} law. This regime is "terminal" insofar there is no smaller typical length scale in the system, until that of the composing atoms or molecules.