

Técnicas não-microscópicas de determinação de tamanho e forma

- Úteis quando se trabalha em meios inacessíveis às técnicas microscópicas usuais.
- Úteis quando se trata de objetos pequenos, muito moles e/ou com pouco contraste.

Tamanho de partículas

- Espalhamento de luz
 - estático (LA)LLS ou dinâmico (PCS)
- Espalhamento de raios-X (SAXS)
- Espalhamento de nêutrons (SANS)
- Sedimentação
 - Gradientes de densidade
- Membranas
- Cromatografia em géis
- Espectrometria de massa

Forma de partículas

- Esfera, elipsóide, bastão?
- Orientação de partículas
 - Em campo elétrico
 - Em campo hidrodinâmico
- Contacto entre partículas
 - Entrelaçamento

Associação entre partículas

- Formação de redes
 - Reologia
 - Viscosidade
 - Propriedades elétricas
 - Percolação
 - Propriedades óticas
 - Espalhamento

Propriedades ópticas

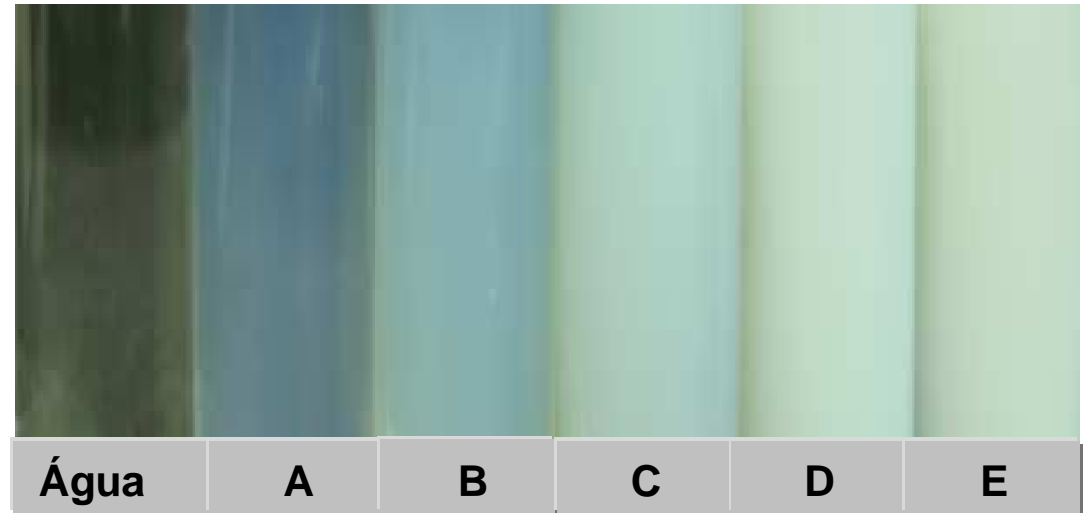
- Dispersões coloidais são freqüentemente *turvas*, soluções são transparentes.
- Importância prática em colóides usados como *pigmentos*.
- *Absorção e espalhamento da luz.*
- Propriedades óticas associadas às *dimensões* das partículas (como o *confinamento quântico*)
- Efeitos da *organização*, como a *difração*, *opalescência*, *iridescência* e as *cores de interferência*.

O espalhamento da luz

- Em um meio material contínuo, a luz interage com as cargas e os dipolos induzidos e permanentes de íons, moléculas e seus agregados, sofrendo desvios e redução da sua velocidade de propagação, mesmo sem *absorção*, isto é, não há aumento da energia do meio.
- Uma medida da intensidade da interação entre o campo elétrico da onda luminosa e as cargas e dipolos da matéria é o *índice de refração* da substância. O índice de refração tem uma relação simples com a constante dielétrica, $n^2 = \epsilon$.

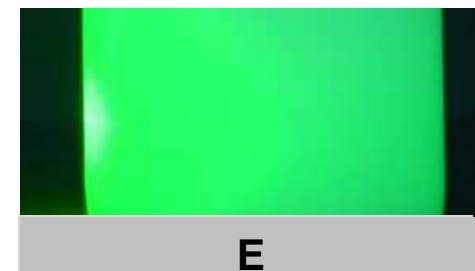
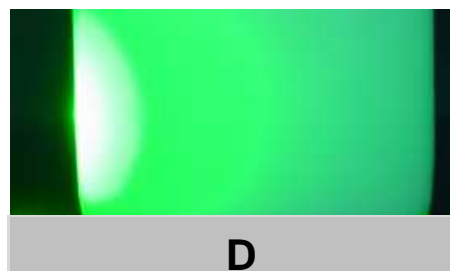
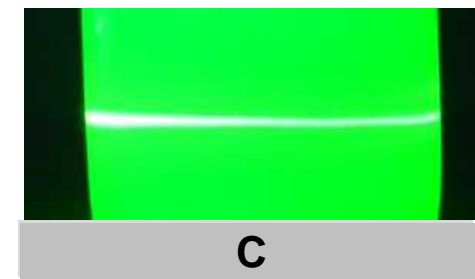
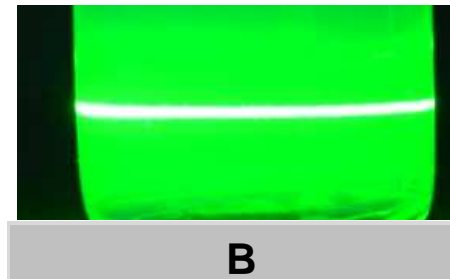
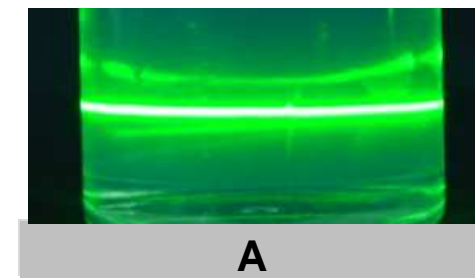
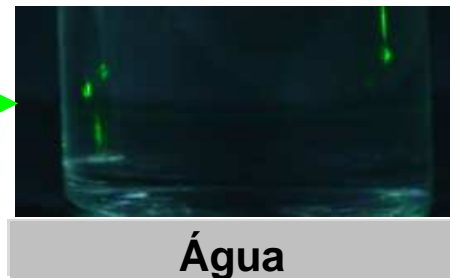
Dispersões de sílica em etanol

- incidência indireta de luz branca



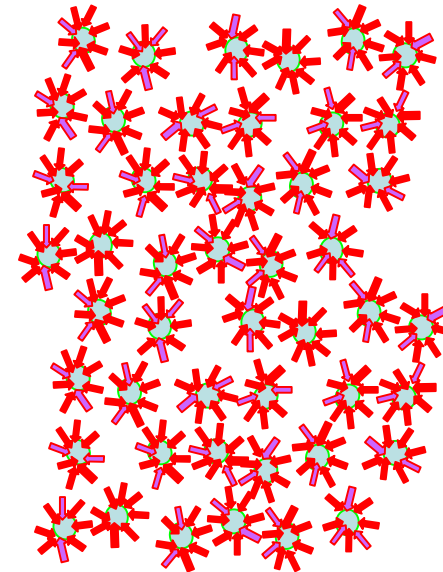
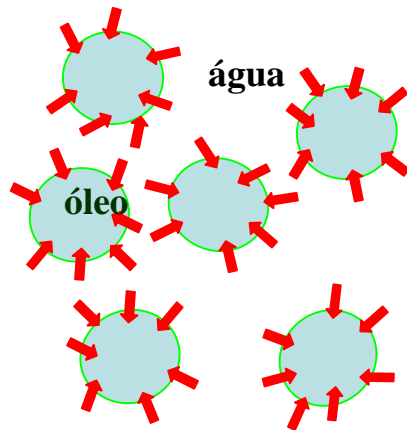
laser →

- incidência de um feixe de laser (5 mW e 532nm)



Opacidade de emulsões

- Emulsões O/A
 - Opacas, leitosas
 - Termodinamicamente estáveis
- Termodinamicamente estáveis
 - Transparentes ou translúcidas



Índice de refração e polarização elétrica

- O índice de refração e a constante dielétrica de um meio variam com a frequência da luz, ou do campo elétrico alternado aplicado ao meio.
- Informam a respeito das propriedades do sistema molecular. Em frequências baixas do campo elétrico, cargas elétricas são deslocadas, moléculas podem girar, dipolos são induzidos e podem orientar-se.
- Moléculas e partículas se *polarizam*; a sua polarização é tanto maior quanto maiores forem a sua constante dielétrica (e o seu índice de refração).

Efeito da frequência sobre a polarização

- Se a frequência do campo (ou da radiação) aumenta: as **moléculas podem passar a serem incapazes de acompanhar** as rápidas mudanças de módulo e sentido do campo.
- A **polarização diminui**, dependendo da relação entre a frequência da luz e o tempo característico de cada tipo de polarização.
- Os **dipolos permanentes deixam de contribuir em frequências de ordem de MHz**, porque nessa região as variações de frequência já são muito rápidas para serem acompanhadas pelas moléculas

Número de Deborah

- Relação entre o tempo de perturbação e o tempo de resposta de um sistema
- $De = t_p/t_r$
- Quando $De = 1$, a taxa de dissipação de energia é máxima
- Quando De difere muito de 1, a taxa de dissipação de energia tende a zero.

Espalhamento de Rayleigh

- $R_{\theta} = I_{\theta} r^2 / I_{0,u} = (K/\lambda^4) a^3 \varphi (1 + \cos \theta)$

(vale quando $a < 1/20 \lambda$) onde

I é a intensidade da luz incidente ou espalhada (ângulo θ),

r é a distância entre detector e observador,

K é uma constante ótica que depende da diferença entre os índices de refração das partículas e do meio ($=0$, quando os índices são iguais),

a é o raio das partículas

φ é o volume de partículas por unidade de volume (fração de volume)

Porque o céu (sem nuvens) é azul?)

Teoria de Mie

- Teoria muito geral, que permite calcular espalhamento da luz mesmo em sistemas muito complexos, soluções concentradas, sólidos polifásicos e contendo partículas de qualquer tamanho, que sejam também absorvedoras da luz.
- Tem sido aplicada a vários tipos de problemas que envolvam a cobertura ótica de superfícies, ou a penetração da luz em um meio complexo.
- Não é resumida em poucas equações, resolvidas analiticamente.

Podemos fazer um pigmento branco de fosfato de alumínio?

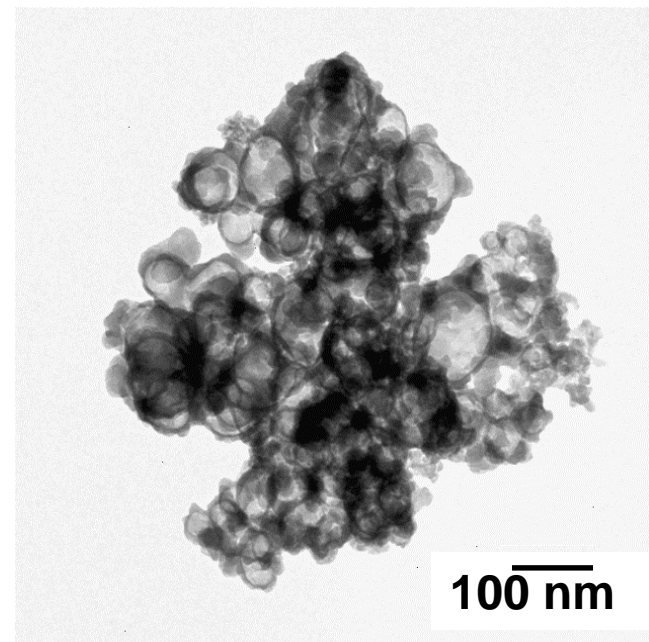
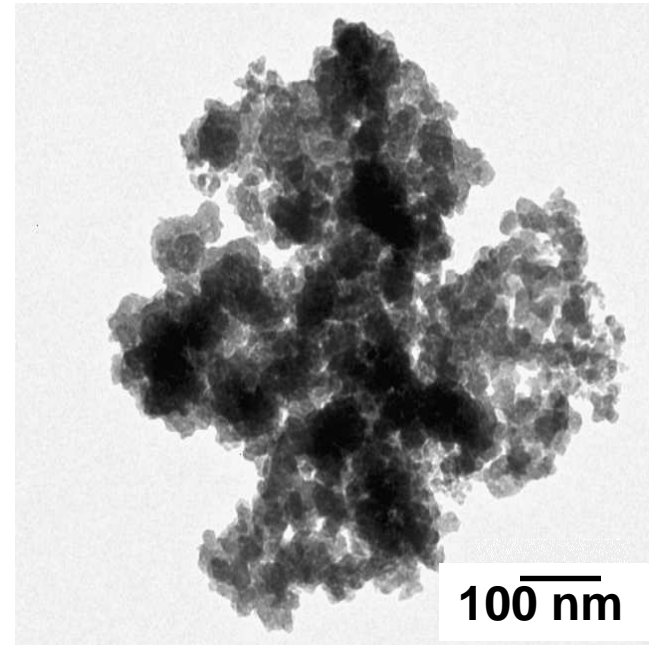
- **Sim, pigmento branco baseado na formação de partículas com vazios (ocas).**
- **Os vazios podem ser:**
 - preformados
 - formados durante a secagem da tinta
 - uma propriedade **emergente**
 - o resultado de um raro processo de formação de nano-estruturas auto-organizadas.

Pigmento branco de fosfato de alumínio

- **Partículas brancas, com poros fechados**
 - Biphor, um novo pigmento branco
 - Criado, **patenteado** e publicado na Unicamp, nos anos 90
 - poster premiado na ICSCS em Compiègne, 1991
 - contrato com a Serrana de Mineração, em 1995
 - Lançado pela Bunge Fertilizantes no Congresso da Abrafati em 9/2005, www.biphorpigments.com
 - Apresentação na International Coatings Expo (New Orleans) em 11/2006
 - Apresentação em Nuremberg, 2007

Nanoestrutura de caroço-casca

- Partículas sob o feixe de elétrons perdem material do seu interior sem sofrer mudanças significativas no volume.
- Interior plástico, paredes rígidas.



[http://www.absoluteastronomy.com/encyclopedia/
m/mi/mie_theory.htm](http://www.absoluteastronomy.com/encyclopedia/m/mi/mie_theory.htm)

In contrast to Rayleigh scattering or dipole scattering, the Mie theory embraces all possible ratios of diameter to wavelength. It assumes an homogeneous, isotropic and optically linear material irradiated by an infinitely extending plane wave.

A profound description and a basic FORTRAN program of the Mie theory can be found in the book by Bohren and Huffman.

More recent implementations of Mie theory in FORTRAN, [C++](#), [PASCAL](#), [Maple](#), [Mathematica](#) and [Mathcad](#) can be found at the web site www.T-Matrix.de.

Método de Zimm

A intensidade da luz espalhada por partículas **com dimensões comparáveis à de λ** (o comprimento de onda da luz) é dada pela equação:

$$Kc/R_{\theta} = 1/(M.P(\theta)) + 2 A_2c$$

onde $K = 2\pi^2 n^2 (dn/dc)^2 / (\lambda^4 N_A)$; $R_{\theta} = (I r^2 / I_o)_{\theta}$;

$$1/P(\theta) = 1 - (16\pi^2/3\lambda^2) .S^2 \sin^2 \theta/2$$

e o significado dos símbolos é: **n**: índice de refração; **c**: concentração; λ : comprimento de onda da luz; **N_A**: número de Avogadro; **I**: intensidade detectada à distância **r**; **I_o**: intensidade incidente; θ : ângulo entre feixe incidente e feixe espalhado; **S**: raio de giração.

Static laser light scattering (SLLS) investigations of the scattering parameters of a synthetic polymer

R. Ghazy_, B. El-Baradie, A. El-Shaer and F. El-Mekawey

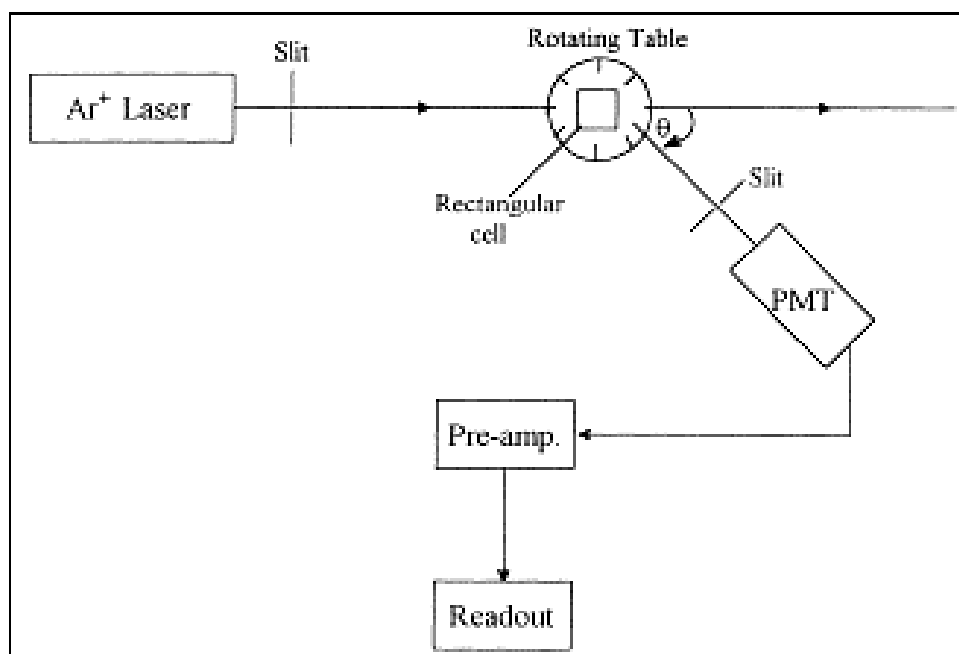


Fig. 1. Schematic diagram of experimental set-up of static laser light scattering (SLLS) measurements.

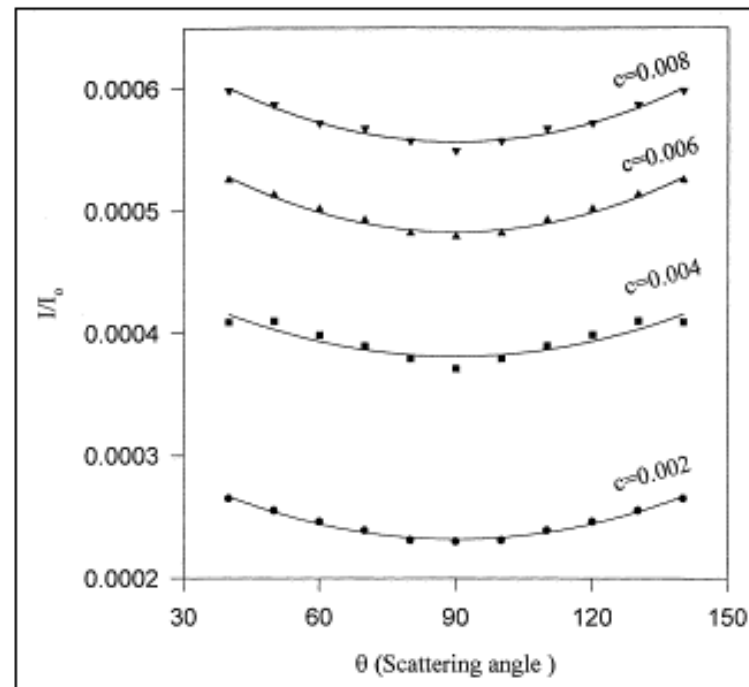


Fig. 2. The angular distribution of static laser light scattering intensities for PMMA solved in acetone.

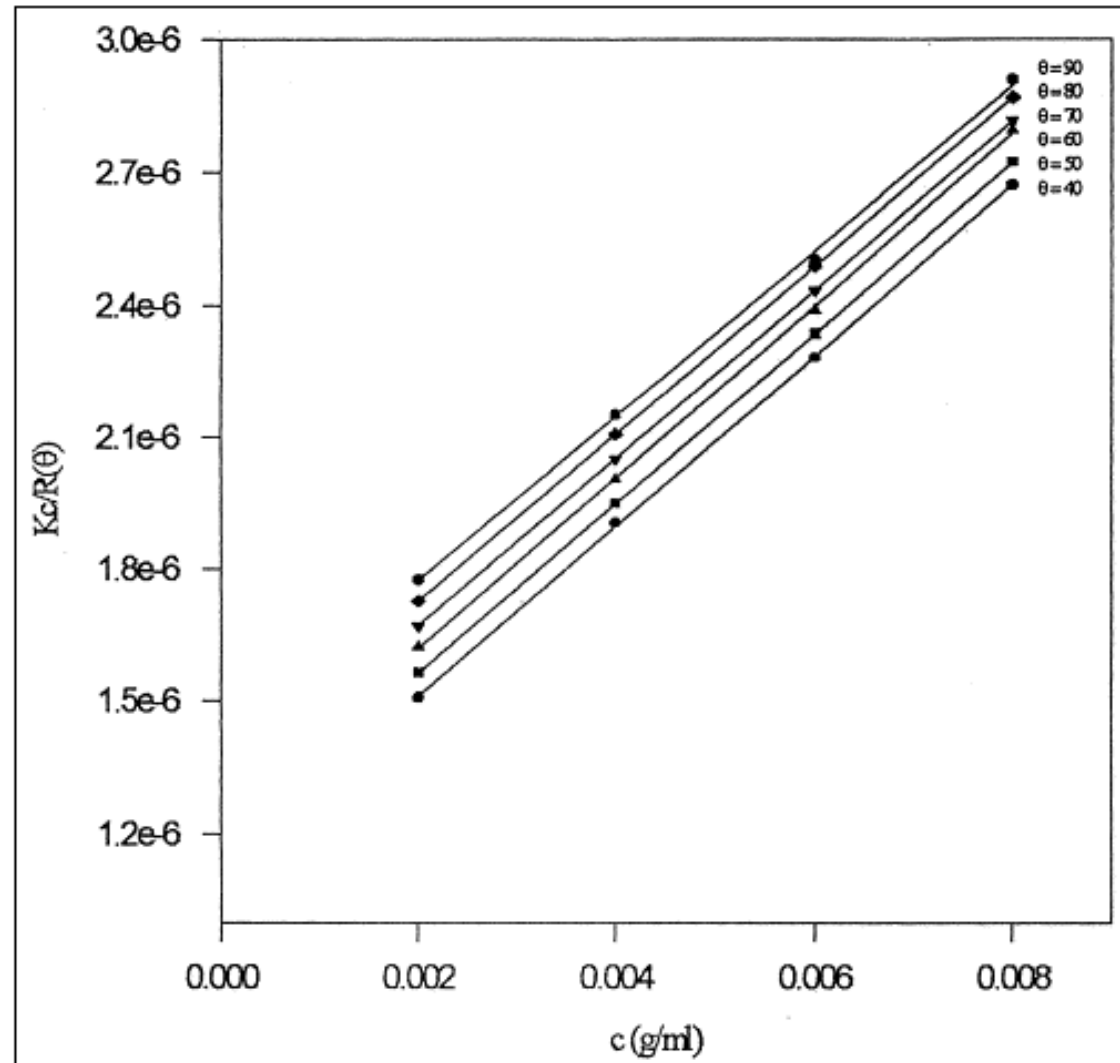


Fig. 3. $Kc/R(\theta)$ for polymethyl-methacrylate as a function of the concentrations, c , at constant observation angles, θ .

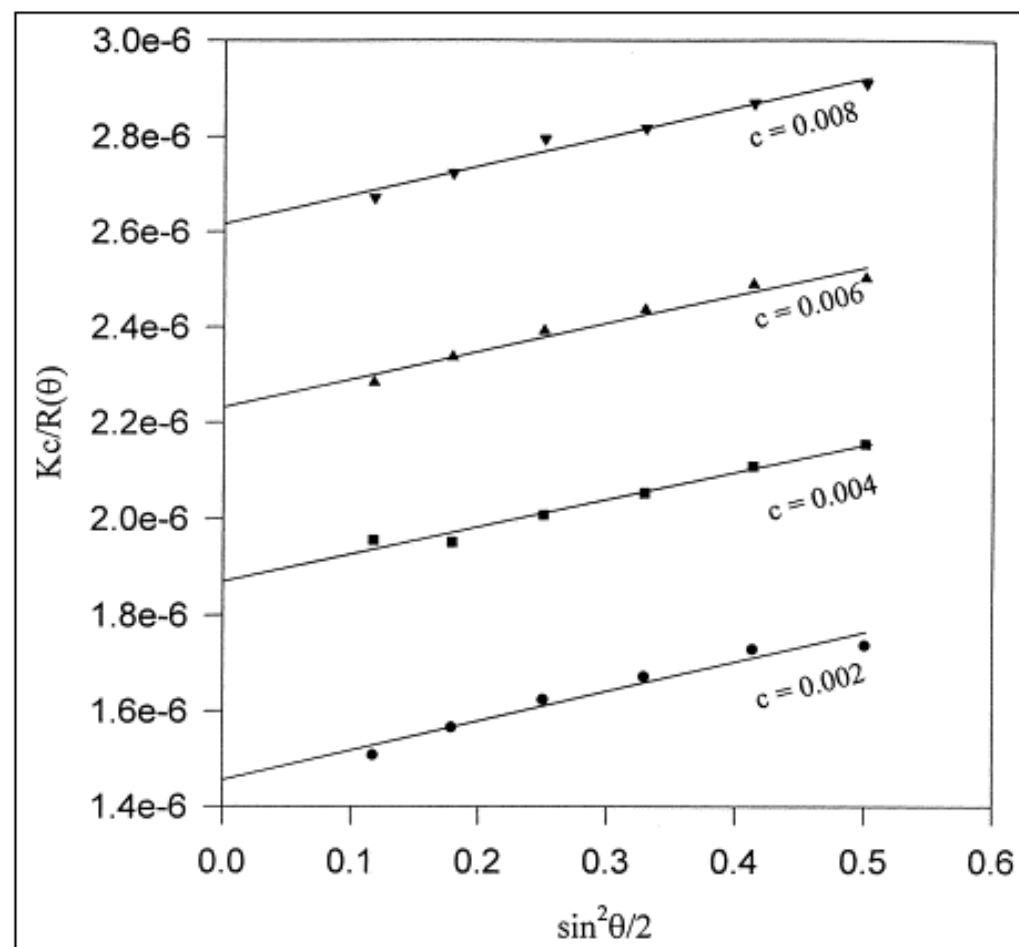


Fig. 4. $Kc/R(\theta)$ for polymethyl-methacrylate as a function of the observation angles, θ at constant concentrations, c .

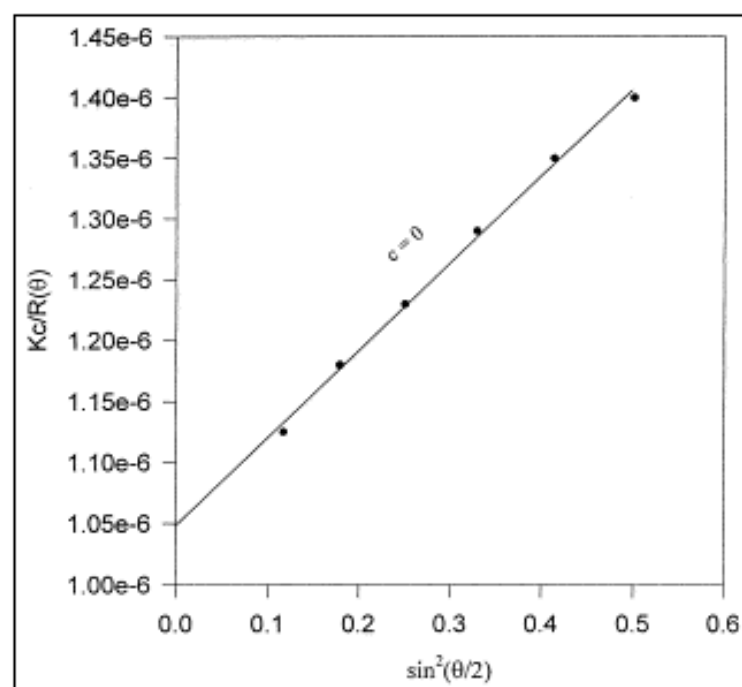


Fig. 5. Extrapolation of the limiting values $Kc/R(\theta)$ at $c=0$ for PMMA vs $\sin^2(\theta/2)$.

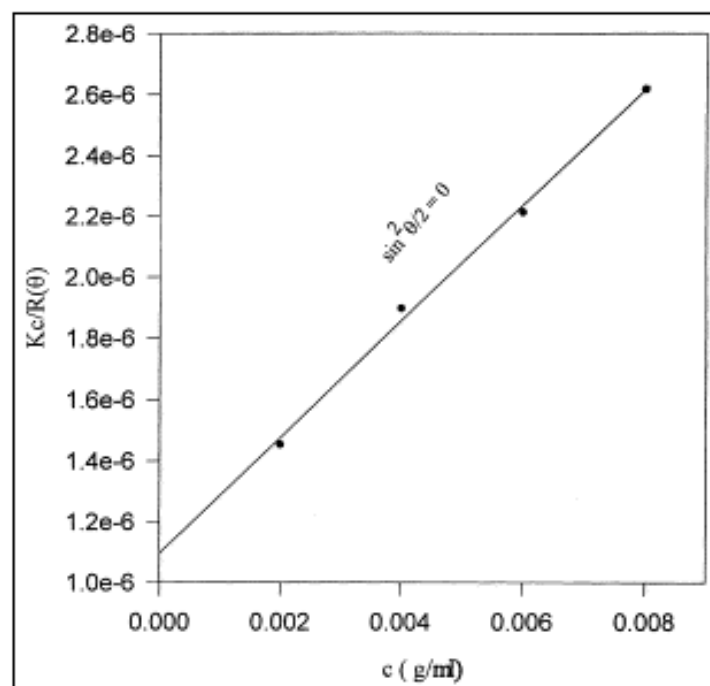


Fig. 6. Extrapolation of the limiting values $Kc/R(\theta)$ at $\sin^2(\theta/2)=0$ for PMMA vs c .

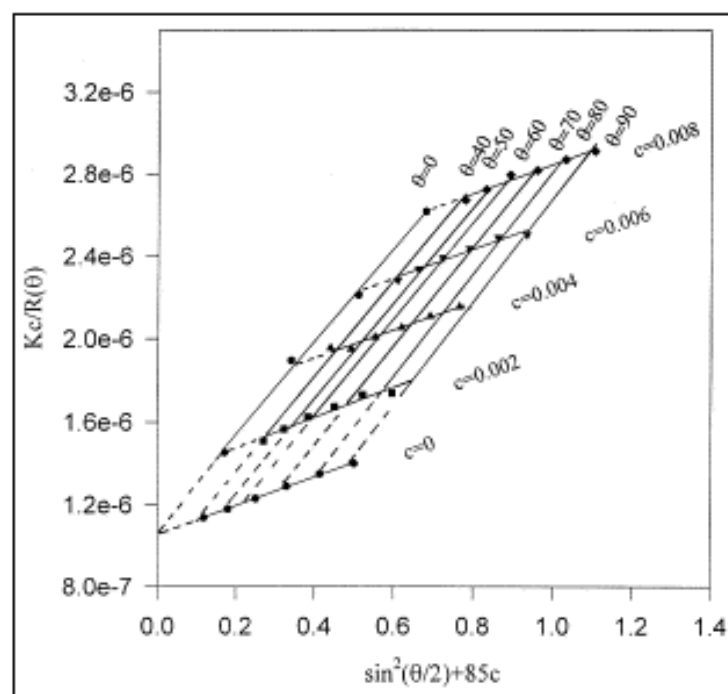


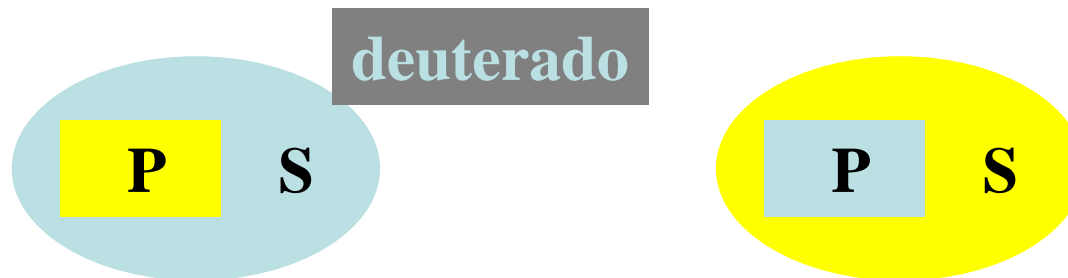
Fig. 7. Zimm plot for PMMA solved in acetone at room temperature (24°C).

Raios-X, LALS, SAXS

- $Kc/R_\theta = f(\sin^2 \theta/2 + kc)$ fornece o **raio de giração** S , a **massa molar** das partículas e o **coeficiente virial** de interação entre as partículas. Usando-se a massa molar e o raio de giração é possível saber se as partículas estão mais ou menos intumescidas com solvente.
- No caso do espalhamento de luz em pequeno ângulo (LALS) ocorre uma importante simplificação no tratamento dos resultados, devido à possibilidade de se fazer $P(\theta)=1$.
- Quando se quer obter o raio de giração de partículas pequenas, é preferível usar raios-X (SAXS) do que usar luz visível, para que o termo S/λ seja significativo.

Espalhamento de nêutrons

- A seção de choque de nêutrons com compostos deuterados é muito maior do que com compostos com hidrogênio.
- Fornece contraste quando se quer examinar as partículas formadas pela agregação de moléculas orgânicas de natureza diferente, como por exemplo um complexo entre polímero (H ou D) e detergente (D ou H), em solução.



- Okamoto T, Haraguchi M, Fukui M
[Light intensity enhancement and optical nonlinear response due to localized surface plasmons in nanosize Ag sphere](#)
 JAPANESE JOURNAL OF APPLIED PHYSICS PART 1-REGULAR PAPERS SHORT NOTES & REVIEW PAPERS 43 (9A): 6507-6512 SEP 2004 2. Lyamani H, Olmo FJ, Alados-Arboledas L
[Long-term changes in aerosol radiative properties at Armilla \(Spain\)](#)
 ATMOSPHERIC ENVIRONMENT 38 (35): 5935-5943 NOV 2004 3. Liu GS
[Approximation of single scattering properties of ice and snow particles for high microwave frequencies](#)
 JOURNAL OF THE ATMOSPHERIC SCIENCES 61 (20): 2441-2456 OCT 2004 4. Reinholdt A, Pecenka R, Pinchuk A, et al.
[Structural, compositional, optical and colorimetric characterization of TiN-nanoparticles](#)
 EUROPEAN PHYSICAL JOURNAL D 31 (1): 69-76 OCT 2004 5. Yang Y, Zhang ZX, Yang XH, et al.
[Blood cell counting and classification by nonflowing laser light scattering method](#)
 JOURNAL OF BIOMEDICAL OPTICS 9 (5): 995-1001 SEP-OCT 2004
- Ponyavina A, Kachan S, Sil'vanovich N
[Statistical theory of multiple scattering of waves applied to three-dimensional layered photonic crystals](#)
 JOURNAL OF THE OPTICAL SOCIETY OF AMERICA B-OPTICAL PHYSICS 21 (10): 1866-1875 OCT 2004 7. Iranipour GT, Garcia-Rubio LH, Harmon JP
[Modeling and simulation of aggregation processes in colloidal systems](#)
 JOURNAL OF DISPERSION SCIENCE AND TECHNOLOGY 25 (4): 555-565 JUL 2004 8. McFarquhar GM, Cober SG
[Single-scattering properties of mixed-phase Arctic clouds at solar wavelengths: Impacts on radiative transfer](#)
 JOURNAL OF CLIMATE 17 (19): 3799-3813 OCT 2004 9. Asllanaj F, Jeandel G, Roche JR, et al.
[Transient combined radiation and conduction heat transfer in fibrous media with temperature and flux boundary conditions](#)
 INTERNATIONAL JOURNAL OF THERMAL SCIENCES 43 (10): 939-950 OCT 2004 10. Laven P
[Simulation of rainbows, coronas and glories using Mie theory and the Debye series](#)
 JOURNAL OF QUANTITATIVE SPECTROSCOPY & RADIATIVE TRANSFER 89 (1-4): 257-269 NOV-DEC 2004

Alguns resultados

- **o cálculo do poder de cobertura conferido a filmes de tintas, pela presença de pequenas bolhas;**
 - Biphor
- **a verificação de que a densidade ótica de uma dispersão coloidal de nanopartículas metálicas depende quase exclusivamente da absorção da luz pelas partículas, e não do espalhamento da luz;**
 - Tese de doutorado de I. Joeques
- **o cálculo da dependência angular da intensidade da luz espalhada, que permite prever e realizar "janelas" que são transparentes em alguns ângulos de visada, mas opacas em outros.**
 - Telas à prova de curiosos para laptops

Turbidez $(\tau = 16\pi R_{90} / 3)$

- Definida de maneira idêntica à absorbância, pode ser determinada em qualquer espectrofotômetro ou colorímetro.
- Na turbidez a transmitância é reduzida pelo **espalhamento** da luz.
- Na absorbância, é reduzida pela **absorção** da luz.
- Quando ocorrem absorção e espalhamento simultaneamente, não medimos absorbância nem turbidez, e sim a **densidade ótica**.
- É uma grandeza fácil de medir e extremamente poderosa no estudo de dispersões coloidais complexas.

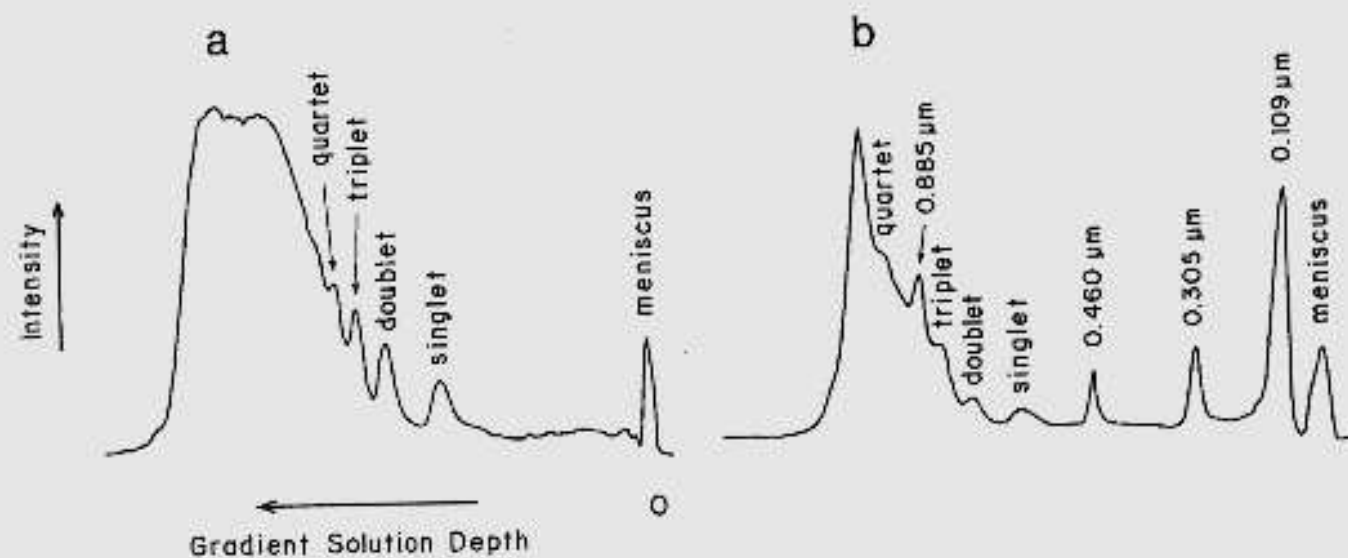
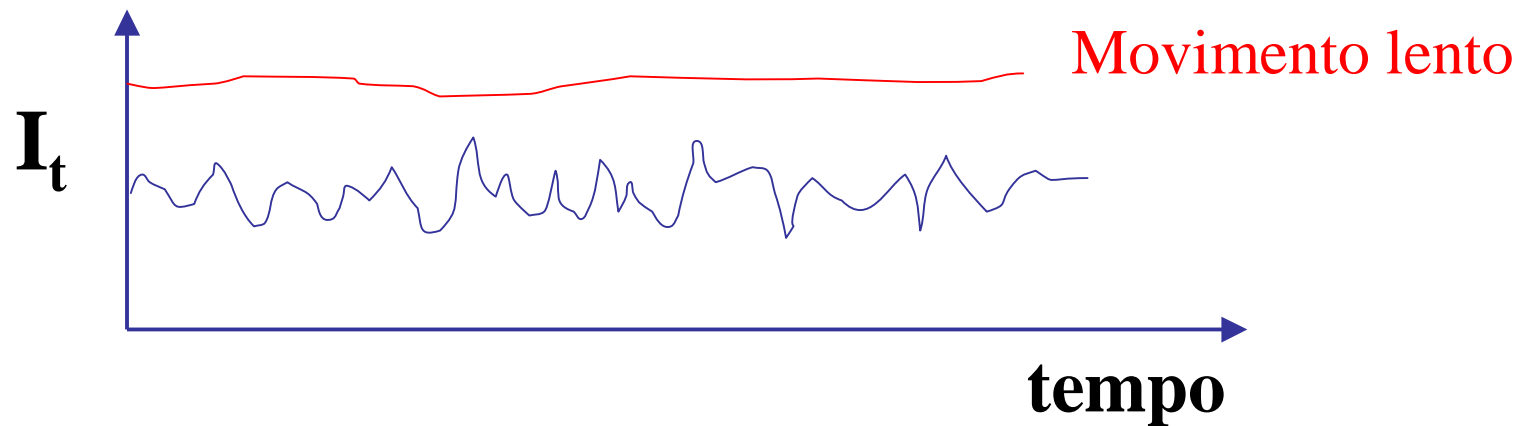


FIG. 1. Scattered light scan of centrifugation tubes containing (a) a latex sample coagulated in 0.50 mol/L NaCl after centrifugation in a density gradient and (b) the same gradient tube used in (a) but after layering a mixture of calibration latexes on top of the solution column and further centrifugation, in the same conditions.

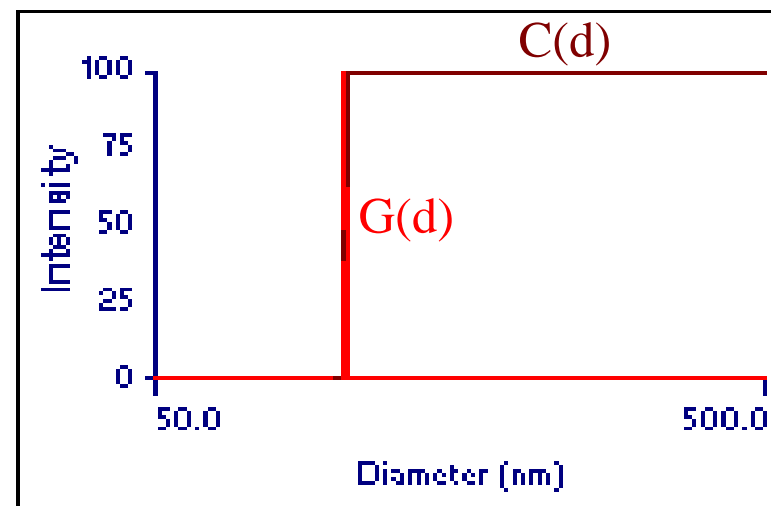
Espalhamento de luz dinâmico.



$$G_{\phi}(\tau) = \left\langle e^{-iqr(t)} e^{iqr(t+\tau)} \right\rangle$$
$$= \exp(-Dq^2t)$$

Determinação dos tamanhos das partículas da amostra D por PCS: diâmetros uniformes

Effective Diameter: **102.7 nm**
Polydispersity: **0.004**
Avg. Count Rate: **399.7 kcps**
Sample Quality: **9.9**



| d(nm) | G(d) | C(d) | d(nm) | G(d) | C(d) | d(nm) | G(d) | C(d) |
|-------|------|------|-------|------|------|-------|------|------|
| 99.7 | 0 | 0 | 101.8 | 5 | 1 | 103.8 | 0 | 100 |
| 99.9 | 0 | 0 | 102.0 | 14 | 4 | 104.2 | 0 | 100 |
| 100.1 | 0 | 0 | 102.2 | 34 | 10 | 104.4 | 0 | 100 |
| 100.2 | 0 | 0 | 102.3 | 62 | 23 | 104.6 | 0 | 100 |
| 100.4 | 0 | 0 | 102.5 | 89 | 40 | 104.8 | 0 | 100 |
| 100.6 | 0 | 0 | 102.7 | 100 | 60 | 105.0 | 0 | 100 |
| 100.8 | 0 | 0 | 102.9 | 89 | 77 | 105.2 | 0 | 100 |
| 101.0 | 0 | 0 | 103.1 | 62 | 90 | 105.4 | 0 | 100 |

Concordância entre técnicas diâmetros médios em diferentes meios

| Amostra | | A | B | C | D | E |
|---|-----------|-------|------|------|-------|--------|
| água, 25°C | PCS (nm) | 54±5 | 66±6 | 77±2 | 103±1 | 136±1 |
| etanol, 25°C | PCS (nm) | 72±2 | 74±2 | 67±6 | 99±1 | 131±1 |
| ar, 55% UR, 25°C | AFM (nm) | 33±2 | 45±4 | 57±5 | 81±8 | 125±11 |
| 10 ⁻⁶ mbar | FESEM(nm) | 22±2 | 39±3 | 51±4 | 79±7 | 118±10 |
| 10 ⁻⁶ mbar | TEM (nm) | 15±2 | 33±3 | 47±4 | 76±7 | 115±10 |
| Coeficiente de intumescimento em água (% em volume) | | 4500 | 700 | 340 | 149 | 65 |
| Coeficiente de intumescimento em etanol (% em volume) | | 10900 | 1028 | 190 | 121 | 48 |
| Conteúdo de sólidos (% em massa) | | 2.7 | 2.7 | 2.6 | 2.5 | 2.5 |
| Potencial Zeta (em KCl 10 ⁻³ M) (mV) | | -27 | -38 | -36 | -46 | -49 |

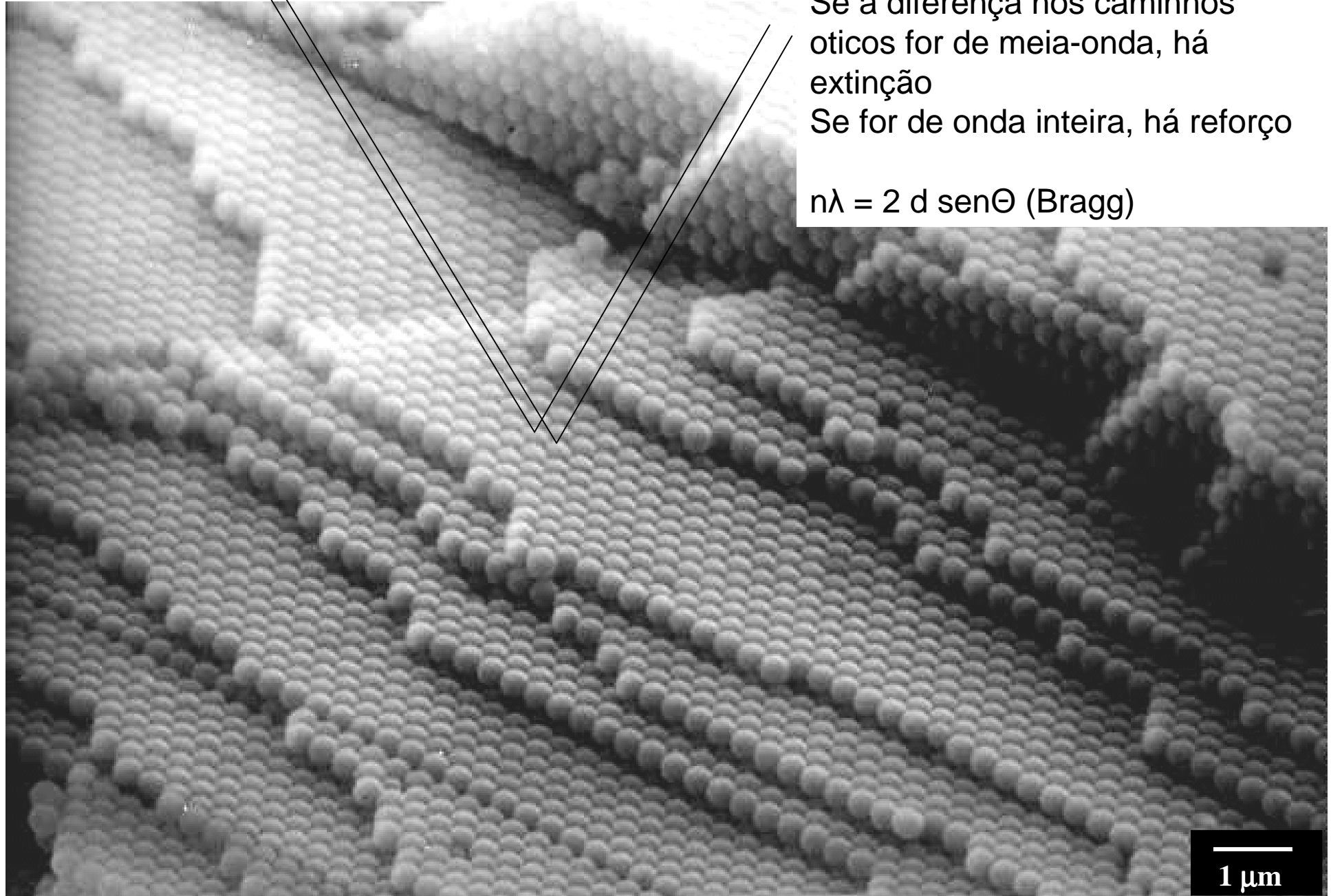
- As partículas apresentam grandes variações de volume em função do meio, especialmente as partículas menores

Difração da luz

- Evidencia a existência de estruturas com dimensões de ordem de grandeza do comprimento de onda da luz.

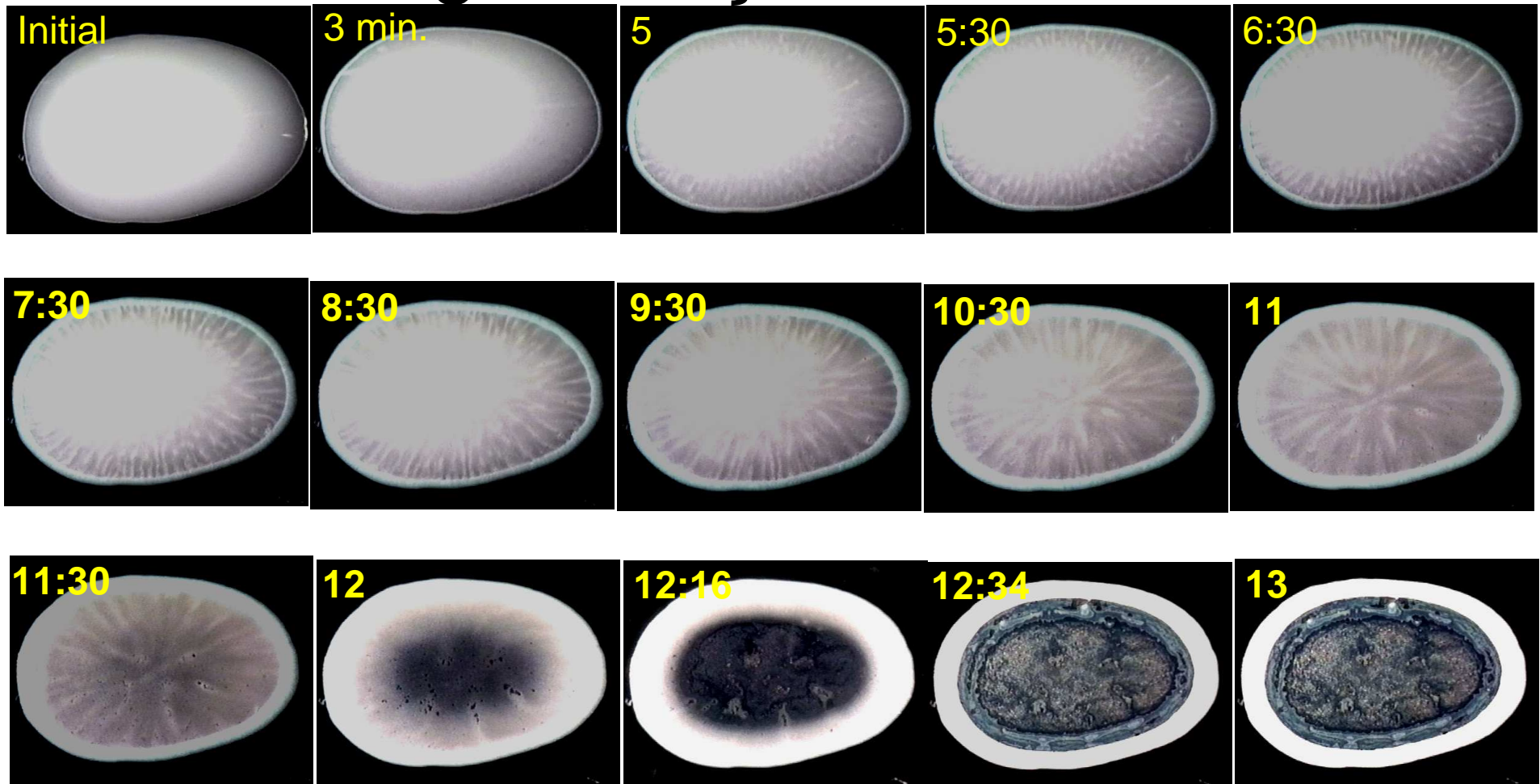
Se a diferença nos caminhos
óticos for de meia-onda, há
extinção
Se for de onda inteira, há reforço

$$n\lambda = 2 d \sin\Theta \text{ (Bragg)}$$



1 μm

Geração de defeitos na formação do macrocristal: separação de fases e segmentação de domínios



Opalescent Appearance of an IgG1 Antibody at High Concentrations and Its Relationship to Noncovalent Association

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Jessica L. Combs,¹ and Allen H. Pekar¹

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Purpose. Therapeutic antibodies are often formulated at a high concentration where they may have an opalescent appearance. The aim of this study is to understand the origin of this opalescence, especially its relationship to noncovalent association and physical stability.

Methods. The turbidity and the association state of an IgG1 antibody were investigated as a function of concentration and temperature using static and dynamic light scattering, nephelometric turbidity, and analytical ultracentrifugation.

Results. The antibody had increasingly opalescent appearance in the concentration range 5–50 mg/ml. The opalescence was greater at refrigerated temperature but was readily reversible upon warming to room temperature. Turbidity measured at 25°C was linear with concentration, as expected for Rayleigh scatter in the absence of association. In the concentration range 1–50 mg/ml, the weight average molecular weights were close to that expected for a monomer. Zimm plot analysis of the data yielded a negative second virial coefficient, indicative of attractive solute-solute interactions. The hydrodynamic diameter was independent of concentration and remained unchanged as a function of aging at room temperature.

Conclusions. The results indicate that opalescent appearance is not due to self-association but is a simple consequence of Rayleigh scatter. Opalescent appearance did not result in physical instability.

KEY WORDS: light scattering; protein aggregation; protein formulation; reversible association; turbidity.

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MATERIALS AND METHODS

Materials

IgG1 antibody, IgG4 antibody, trisodium citrate dihydrate, and sodium chloride were obtained from Eli Lilly and Company (Indianapolis, IN, USA). Dulbecco's phosphate-buffered saline (without calcium chloride and magnesium chloride) was obtained from Gibco (Carlsbad, CA, USA). Deionized water was used in making all solutions. Solutions were made by serial dilution of the IgG1 antibody at a concentration of 20 or 50 mg/ml into the corresponding buffer (10 mM citric acid, 100 mM NaCl, pH 5.5).

Turbidity Measurements

Turbidity of antibody solutions as a function of concentration was measured in 13-mm glass culture tubes at room temperature using a HACH 2100N turbidimeter (Hach Company, Loveland, CO, USA). The temperature dependence of turbidity was measured by following Rayleigh scatter on a Fluorolog-3 Fluorometer (JY Horiba, Edison, NJ, USA) that allowed temperature control. Rayleigh scatter was measured at 510 nm, and the apparent turbidity was calculated by reference to a standard curve generated using suspensions of known turbidity.

Static Light Scattering

The weight average molecular weights of antibody solutions as a function of concentration were measured at 25°C using static light scattering at multiple angles (30–130°) on a Brookhaven Instruments Corporation (Holtsville, NY, USA) laser light scattering instrument. Samples were filtered through 0.22- μ m, 13-mm Millel GV durapore membrane filters (Millipore, Billerica, MA, USA). The scatter data at 90° were used to derive WAMW. The complete data set at multiple angles was also used to create Zimm plots to derive molecular weight and second virial coefficient (8). For an ideal solution,

$$KC/R_9 = 1/M \quad (1)$$

where, M is molecular weight, K is a constant, R_9 is Rayleigh ratio that combines a number of experimental parameters, and C is concentration.

The effects of solution nonideality can be incorporated in to an equation of the form,

$$KC/R_9 = 1/M + 2BC + \dots \quad (2)$$

where B is the second virial coefficient. To obtain M , it is necessary to extrapolate KC/R_9 to zero angle and zero concentration. A Zimm plot has KC/R_9 on the ordinate and $\sin^2(\theta/2) + kC$ on the abscissa, where k is an arbitrary constant, and allows both extrapolations to be made on the same graph. M and B can be obtained from the intercept and slope, respectively, of the zero angle line. The sign and magnitude of second virial coefficient are related to excluded volume effects and intermolecular interactions. Both excluded volume

Dynamic Light Scattering

The hydrodynamic diameter of antibody solutions as a function of concentration was determined at 25°C or 5°C by measuring the autocorrelation function at 90° scattering angle on a Brookhaven Instruments Corporation laser light scattering instrument. Samples were filtered through 0.22- μ m, 13-mm Millel GV durapore membrane filters. The effective diameter and polydispersity was computed from the autocorrelation function using a quadratic fit. The intensity-based or volume-based distribution of diameter was determined using CONTIN analysis. Four separate measurements were made to derive average and standard deviation. The data were corrected for changes in viscosity of the antibody solutions as a function of concentration. The viscosity was measured at 5°C or 25°C using Viscolab4100 Laboratory Viscometer (Cambridge Applied Systems, Medford, MA, USA).

Equilibrium Sedimentation

Sedimentation equilibrium experiments were performed on a Beckman Model XLI ultracentrifuge (Fullerton, CA, USA). A 0.5 mg/ml solution of the antibody was loaded into a 2-sector, 0.297-cm path-length centerpiece cell with quartz windows and placed into an An-60 Ti 4-hole rotor. The cell was centrifuged at 8000 rpm, and radial scans at 280 nm were collected at 4-, 14-, 16-, and 18-h time points. The 16- and 18-h scans were superimposable, suggesting equilibrium had been achieved. The final data set is an average of five scans, and the error associated with absorbance measurements was in the range 0.001–0.005 AU. The 18-h radial scan was then fit to a single ideal species using the "self-association" model of the manufacturer-supplied version of Origin (XL10KLA Data Analysis Software v. 4.0). Values of $\rho = 1$ g/ml and $v\text{-bar} = 0.73$ ml/g were used in the calculation of molecular weight (14). In a sedimentation equilibrium experiment, a solution of the sample is centrifuged at a constant rotor velocity until equilibrium is reached. At equilibrium, a concentration gradient is established relative to the distance from the center of rotation that reflects the balance of sedimentation and diffusion. For a single solute component, the concentration gradient at equilibrium is related to molecular weight by

$$d \ln C/d(r^2) = \omega^2 M(1 - v\rho)/2RT \quad (3)$$

where C is the concentration at radius r (distance from the center of rotation), ω is the angular velocity, M is molecular weight, v is the partial specific volume, and ρ is the solution density. Reversible macromolecular associations can be characterized quantitatively by using analogous expressions (9,15).

RESULTS AND DISCUSSION

Analytical Ultracentrifugation: Equilibrium Sedimentation

Equilibrium sedimentation analysis was carried out at a loading concentration of 0.5 mg/ml in citrate buffer (10 mM

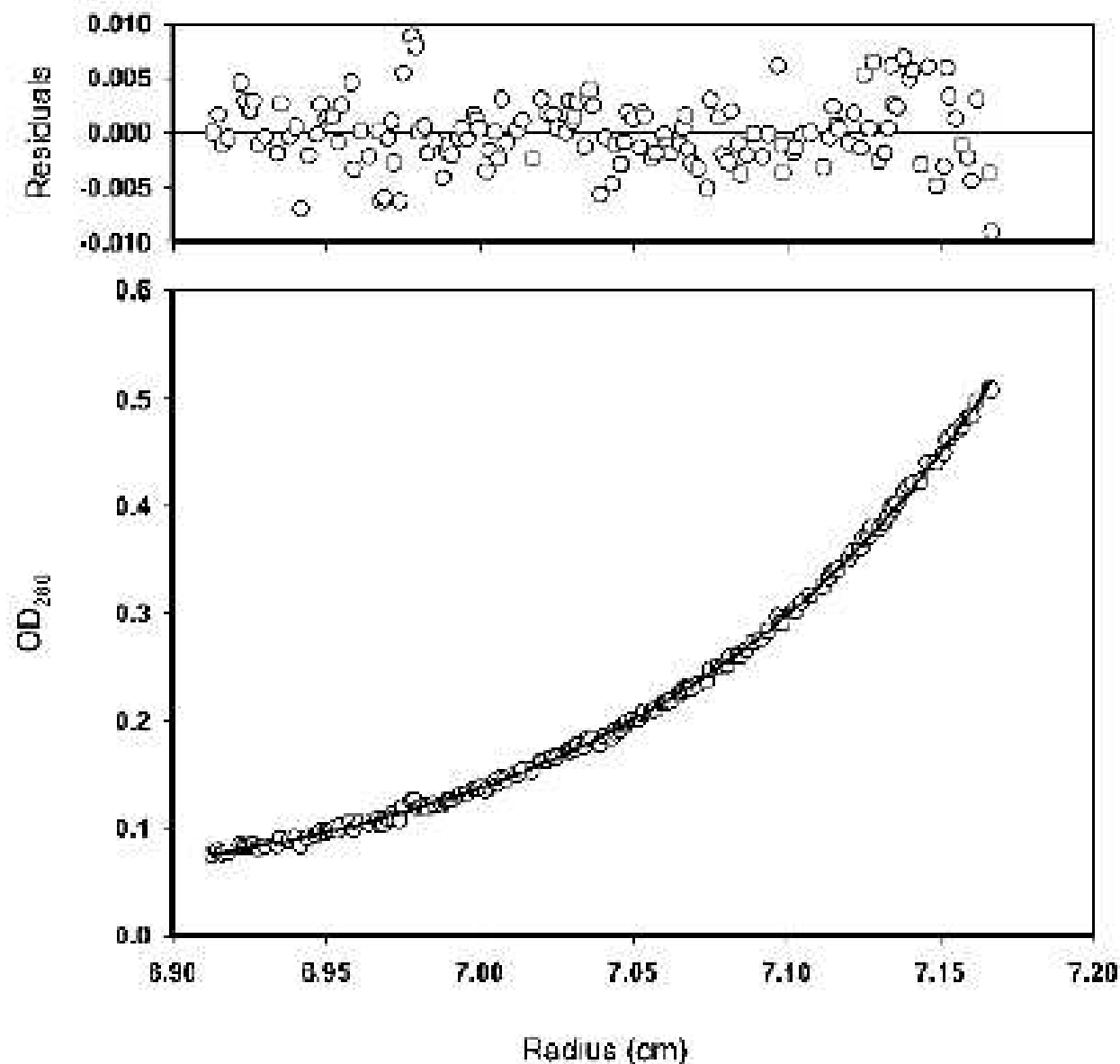


Fig. 1. Analytical ultracentrifugation equilibrium sedimentation analysis of IgG1 antibody at a loading concentration of 0.5 mg/ml. Radius plotted on abscissa is the distance from the center of rotation. Solid line indicates fit to a monomer. The residuals are plotted in the panel above the absorbance data.

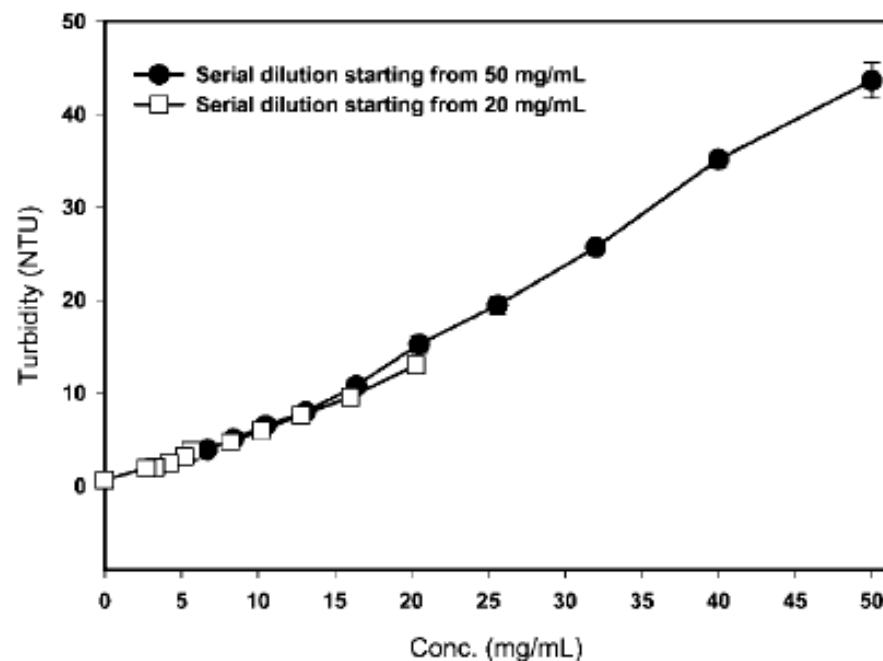


Fig. 2. Turbidity of antibody solutions measured as a function of concentration at ambient temperature using HACH turbidimeter. Filled circles correspond to serial dilution of a 50 mg/ml stock. Squares correspond to serial dilutions of a 20 mg/ml stock. Where error bars are not visible, they are smaller than the size of the symbol.

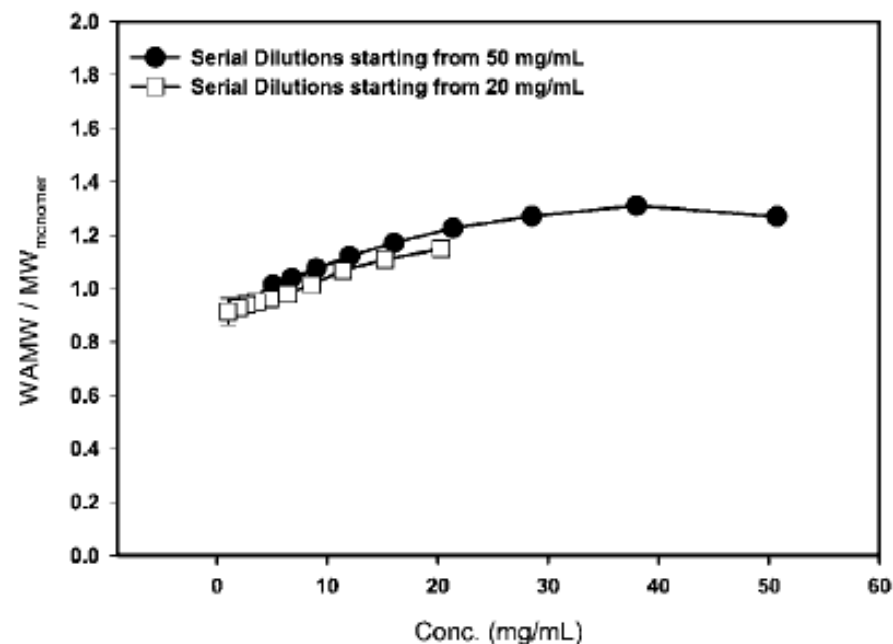


Fig. 3. Weight average molecular weight of antibody as a function of concentration, determined by static light scattering. Filled circles correspond to serial dilution of a 50 mg/ml stock. Squares correspond to serial dilutions of a 20 mg/ml stock. Where error bars are not visible, they are smaller than the size of the symbol.

Second virial coefficient measurements of dilute gold nanocrystal dispersions using small-angle X-ray scattering, Saunders AE, Korgel BA

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Abstract: Small-angle X-ray scattering (SAXS) was used to study the size-dependent two-body solvent-mediated **interparticle interactions** between **dodecanethiol-coated gold** nanocrystals (2-6 nm in diameter) in dilute toluene dispersions. Using a modified **Zimm** analysis of concentration-dependent X-ray scattering data, the **second virial coefficient B_2** was measured as a function of nanocrystal diameter and compared to theoretical predictions. **The measured values of B_2 are more negative than those expected for hard spheres, indicating that interparticle attractions are significant in this system, even though the particles are dispersed in good solvents for the ligands.** The data can be fit using a square well potential to model the pair interactions with nanocrystal size-dependent well depths ranging between **0.1 and 0.4 kT** and a **range of interaction of 30 Å**. The interaction potentials between particles in the larger size range (i.e., >5 nm diameter) are close to those expected from a simple steric stabilization model accounting for the core-core van der Waals attraction modified by an osmotic repulsion between adsorbed chains. Smaller particles, however, exhibited significantly stronger attraction than expected from this simple model, which could possibly be due to decreased ligand surface coverage at the smaller nanocrystal sizes.