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Particle sizing in highly turbid dispersions by Photon Density Wave spectroscopy

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ABSTRACT

Photon Density Wave (PDW) spectroscopy is presented as a fascinating technology for the independent determination of scattering (μ_s') and absorption (μ_a) properties of highly turbid liquid dispersions. The theory is reviewed introducing new expressions for the PDW coefficients k_I and k_Φ. Furthermore, two models for dependent scattering, namely the hard sphere model in the Percus–Yevick Approximation (HSPYA) and the Yukawa model in the Mean Spherical Approximation (YMSA), are experimentally examined. On the basis of the HSPYA particle sizing is feasible in dispersions of high ionic strength. It is furthermore shown that in dialyzed dispersions or in technical copolymers with high particle charge only the YMSA allows for correct dilution-free particle sizing.

1. Introduction

Particle size analysis is of fundamental importance for liquid dispersions. Thus, a large number of different measurement approaches, e.g., dynamic light scattering (DLS), transmission electron microscopy (TEM), diffusing wave spectroscopy (DWS), were realized [1]. The disadvantage of all these techniques is either the need for strong sample dilution or the disregard of particle interactions at high concentrations. Furthermore, most of these techniques require special calibration procedures. Yet, calibration-free particle sizing in highly concentrated dispersions is of utmost importance, both for academic research and applications in production processes [2]. PDW spectroscopy, based on radiation transport theory, incorporating multiple scattering, determines the optical absorption and scattering properties of such samples. If suitable models for particle interactions are considered, dilution-free particle sizing is then possible even at highest concentrations.

By now, PDW spectroscopy was applied by different groups [3–7], mostly on the basis of the Diffusion Approximation (DA) [8, p. 196 ff.] and partly with the aid of the HSPYA [9] and YMSA [10,11] for particle sizing in well-defined material. Here, a new theoretical formulation of the PDW coefficients is presented and data analysis is performed without DA, yielding higher accuracy. Furthermore, the applicability of PDW spectroscopy for dilution-free particle sizing at highest concentrations even in technical copolymer dispersions is evaluated on the basis of the HSPYA and YMSA.

2. Theory and experiment

2.1. Photon Density Wave spectroscopy

In the following, a weakly absorbing and strongly light scattering material is considered. Additionally, the expansion of the material is assumed being infinite, meaning no photons are lost due to boundaries. When

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monochromatic light propagates in the material, the intensity $\psi(\boldsymbol{r},t,\boldsymbol{\Omega})$ [m^{-3} sr^{-1}], i.e., the number of photons per volume at a point $\boldsymbol{r}$ [m], moving at time t [s], in the direction $\boldsymbol{\Omega}$ [sr], changes due to the light source $S(\boldsymbol{r},t,\boldsymbol{\Omega})$ [m^{-3} s^{-1}] and due to interaction with the material. Possible interactions considered here are absorption and scattering, expressed by the absorption and scattering coefficients μ_a [m^{-1}] and μ_s [m^{-1}], respectively. $\psi(\boldsymbol{r},t,\boldsymbol{\Omega})$ is then decreased at $\boldsymbol{r}$ either by scattering of photons from $\boldsymbol{\Omega}$ in $\boldsymbol{\Omega}'$ or by absorption. In contrast, $\psi(\boldsymbol{r},t,\boldsymbol{\Omega})$ increases due to scattering of photons at $\boldsymbol{r}$ from $\boldsymbol{\Omega}'$ in $\boldsymbol{\Omega}$. Combining these contributions yield the time-dependent Boltzmann transport equation [12, p. 662], with c [m s^{-1}] being speed of light in the material

$$\left[\boldsymbol{\Omega}\cdot\boldsymbol{\nabla}+\frac{\partial}{c\partial t}+[\mu_a+\mu_s]\right]\psi(\boldsymbol{r},t,\boldsymbol{\Omega}) = c^{-1}S(\boldsymbol{r},t,\boldsymbol{\Omega})+\mu_s\int\psi(\boldsymbol{r},t,\boldsymbol{\Omega}')f(\boldsymbol{\Omega}',\boldsymbol{\Omega})\,d\boldsymbol{\Omega}'. \quad (1)$$

Here, $f(\boldsymbol{\Omega}',\boldsymbol{\Omega})$ is the normalized scattering phase function [13, p. 76] and denotes the probability for scattering of a photon from $\boldsymbol{\Omega}'$ into $\boldsymbol{\Omega}$. Eq. (1) is solved by applying the well-known P1–approximation [8, p. 196 ff.]. The intensity is expanded in spherical harmonics and truncated after the second term [12, p. 664][1]

$$\psi(\boldsymbol{r},t,\boldsymbol{\Omega})\approx[4\pi c]^{-1}[c\rho(\boldsymbol{r},t)+3\boldsymbol{J}(\boldsymbol{r},t)\cdot\boldsymbol{\Omega}], \quad (2)$$

with the photon density [m^{-3}]

$$\rho(\boldsymbol{r},t)=\int\psi(\boldsymbol{r},t,\boldsymbol{\Omega})\,d\boldsymbol{\Omega} \quad (3)$$

and the photon flux density [m^{-2} s^{-1}]

$$\boldsymbol{J}(\boldsymbol{r},t)=c\int\boldsymbol{\Omega}\psi(\boldsymbol{r},t,\boldsymbol{\Omega})\,d\boldsymbol{\Omega}. \quad (4)$$

The same approximation is applied for the light source. For an isotropic source the second term is zero, giving [14, p. 18]

$$S(\boldsymbol{r},t,\boldsymbol{\Omega})=[4\pi]^{-1}s_0(\boldsymbol{r},t), \quad (5)$$

with $s_0(\boldsymbol{r},t)$ [m^{-3} s^{-1}] denoting the source density. If polarization and interference are neglected, $f(\boldsymbol{\Omega}',\boldsymbol{\Omega})$ only depends on the cosine of the scattering angle θ [rad] between $\boldsymbol{\Omega}'$ and $\boldsymbol{\Omega}$. Then, the Boltzmann transport equation in the P1–approximation reads (cf. Appendix A)

$$\left[\boldsymbol{\Omega}\cdot\boldsymbol{\nabla}+\frac{\partial}{c\partial t}+\mu_a\right]c\rho(\boldsymbol{r},t) +3\left[\boldsymbol{\Omega}\cdot\boldsymbol{\nabla}+\frac{\partial}{c\partial t}+\mu_a+\mu_s'\right]\boldsymbol{\Omega}\cdot\boldsymbol{J}(\boldsymbol{r},t)=s_0(\boldsymbol{r},t), \quad (6)$$

where

$$\mu_s'=\mu_s[1-g] \quad (7)$$

is the reduced scattering coefficient [5] [m^{-1}], accounting for multiple scattering.

$$g=\langle\cos(\theta)\rangle=\int\boldsymbol{\Omega}'\cdot\boldsymbol{\Omega}\,f(\boldsymbol{\Omega}',\boldsymbol{\Omega})\,d\boldsymbol{\Omega}' \quad (8)$$

is the average of the cosine of θ, often called anisotropy factor [13, p. 93]. To substitute $\boldsymbol{J}(\boldsymbol{r},t)$ in Eq. (6) by an expression for the photon density, Eq. (6) is integrated over $\boldsymbol{\Omega}$ [14, p. 20]

$$\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{r},t)=s_0(\boldsymbol{r},t)-\left[\mu_a+\frac{\partial}{c\partial t}\right]c\rho(\boldsymbol{r},t). \quad (9)$$

Multiplication of Eq. (6) with $\boldsymbol{\Omega}$, integration over $\boldsymbol{\Omega}$ and subsequent multiplication with $\boldsymbol{\nabla}$ results in

$$\frac{c}{3}\nabla^2\rho(\boldsymbol{r},t)+\left[\frac{\partial}{c\partial t}+\mu_a+\mu_s'\right]\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{r},t)=0. \quad (10)$$

Insertion of Eq. (9) in Eq. (10) yields

$$\frac{c}{3}\nabla^2\rho(\boldsymbol{r},t) +\left[\frac{\partial}{c\partial t}+\mu_a+\mu_s'\right]\left\{s_0(\boldsymbol{r},t)-\left[c\mu_a+\frac{\partial}{\partial t}\right]\rho(\boldsymbol{r},t)\right\}=0. \quad (11)$$

Introducing the optical diffusion coefficient [15] [m^2 s^{-1}],

$$D=\frac{c}{3[\alpha\mu_a+\mu_s']}, \quad (12)$$

with α describing the dependency of D on μ_a,[2] the time dependent Boltzmann transport equation can be written as [12, p. 666]

$$-D\nabla^2\rho(\boldsymbol{r},t)+[3\mu_aD+c]\frac{\partial}{c\partial t}\rho(\boldsymbol{r},t)+\frac{3D\partial^2}{c^2\partial t^2}\rho(\boldsymbol{r},t) +c\mu_a\rho(\boldsymbol{r},t)=s_0(\boldsymbol{r},t)+\frac{3D\partial}{c^2\partial t}s_0(\boldsymbol{r},t). \quad (13)$$

If a sinusoidally intensity modulated point-like light source

$$s_0(\boldsymbol{r},t)=q_{AC}\delta(\boldsymbol{r}-\boldsymbol{r}_0)\exp(-i\omega t), \quad (14)$$

with amplitude q_{AC} [s^{-1}] and angular modulation frequency ω [s^{-1}] is applied, the resulting photon density has a sinusoidal shape as well, i.e., neglecting any time-constant terms, a PDW

$$\rho(\boldsymbol{r},t)=\rho_{AC}(\boldsymbol{r})\exp(-i\omega t) \quad (15)$$

with an amplitude $\rho_{AC}(\boldsymbol{r})$ [m^{-3}] is created. The PDW is phase shifted to the light source but exhibits the same angular modulation frequency ω. Inserting Eqs. (14) and (15) in Eq. (13) and deriving with respect to time results in

$$\nabla^2\rho_{AC}(\boldsymbol{r})-\left[\frac{c^3\mu_a-3\omega^2D-3ic\omega\mu_aD-ic^2\omega}{c^2D}\right]\rho_{AC}(\boldsymbol{r}) =-q_{AC}\delta(\boldsymbol{r}-\boldsymbol{r}_0)\left[\frac{c^2-3i\omega D}{c^2D}\right]. \quad (16)$$

Eq. (16) can be solved using Green's function for the infinite space [12, p. 669]. The solution of the time-dependent photon density wave (PDW) is [14, p. 24]

$$\rho(r,t)=\frac{\rho_{AC}^0}{r}\exp(-k_1r+ik_\Phi r-i\omega t). \quad (17)$$

[1] The approximately sign is just displayed once. In further equations the equal sign is used even though approximations are applied.

[2] α is controversially discussed in literature [5,16–18]. Values applied range from 0 to 1. Here, $\alpha=1$. For the final solution $\alpha=1/3$ [15,19].