Combining weighting and scatterometry: application to a levitated droplet of suspension.

D Jakubczyk*, G Derkachov, M Kolwas, K Kolwas

Institute of Physics of the Polish Academy of Sciences
Al.Lotników 32/46, 02-668 Warsaw, Poland

Abstract

Two optical methods of droplet radius measurement were combined with droplet weighting. The applicability of such combination to droplets of liquids and liquid suspensions was investigated. The combination was successfully tested for a mixture of two glycols. It was checked, that droplet radius evolution may be obtained with good accuracy by weighting. Since weighting is not a stand-alone method, it was calibrated in a small region with an optical method. Droplet electrical charge is the parameter obtained from the calibration. The application of the combination of methods to a droplet of suspension was demonstrated on droplets of suspensions of polystyrene nano-spheres in diethylene glycol, evolving from moderate/high concentration to a nearly dry agglomerate particle. A detailed analysis of the results obtained from all the three methods may provide information on the changing density, effective refractive index, electric charge and the internal structure of the droplet.

Keywords: levitated droplet, Mie scattering, droplet radius measurement, droplet weighting, droplet charge

1. Introduction

Mie theory was developed for spheres of optically homogeneous, isotropic and linear material and continuous plane wave illumination [1]. Measuring the radius of a droplet with the aid of Mie-theory-based methods may be very precise within these limitations. In many cases it is even possible to work around...
these limitations with the aid of generalised Lorenz-Mie theory (GLMT) (see eg. [2, 3]). There are also many other methods of finding the scattered light distribution (see eg. [4]). However, an operating measurement method always requires solving a difficult inverse problem. There are well established interferometric techniques, which are used for particle characterisation eg. in sprays. Not exhausting the subject, a few examples are: global rainbow technique (GRT), laser imaging for droplet sizing (ILIDS), interferometric particle imaging (IPI), Mie scattering imaging (MSI), interferometric Mie imaging (IMI), etc. (see eg. [5] and references therein). We also developed a variant of this class and used successfully in experiments with water (see e.g. [6]) and with slowly evaporating liquids (see e.g. [7]). In favourable cases the accuracy is as high as ±10 nm. Since we solve the inverse problem by comparing the experimentally obtained scattered light distributions with the lookup table of Mie-theory-generated patterns, we adopt the name: Mie scattering lookup table method (MSLTM).

On the other hand, interferometric methods are not very suitable for a droplet of suspension. Such particle may be substantially inhomogeneous, the interference fringes become distorted, and exact solving of an inverse scattering problem becomes excessively difficult. In many cases the inverse problem may be solved approximately (compare eg. [8]). In case of MSLTM, introducing an effective refractive index (usually as a simple volume fraction average, compare Lorentz-Lorenz equation) can still yield some consistent results when the interference fringes are still partially visible in the scattered light, as illustrated in the left inset in figure 4, (small inhomogeneity, e.g. few, small suspended particles or low contrast of refractive indices).

There exist optical methods which are even more resistant to interference fringes distortion (see eg. [9, 10, 11]), however at the cost of further loss of accuracy. We have developed a variant of an approximate interferometric method, based on scattered light angular frequency determination. Thus we adopt the name: angular frequency of scattered light method (AFSLM). This method yields radius even for small, highly inhomogeneous particles (see right inset in figure 4). Some interpretation difficulties arise, however, for non-isotropic or/and non-spherical particles.

For any particle, its radius can also be inferred from the particle mass and its density (distribution). Most naturally, mass can be found by weighting. We will refer to this method as to droplet radius from droplet mass method (DRDMM). Generally, DRDMM can be more precise than approximate optical methods but it can not be used as a completely self-standing method of radius measurement. However, used in combination with optical methods it can provide valuable infor-
mation on droplet parameters and internal structure. In order to combine DRDMM with optical methods it is convenient to use an electrodynamic trap, also known as electrodynamic levitator, or, more significantly, as electrodynamic balance (EDB).

On top of that, as long as the polarised light is used for scatterometry, the (integral degree of) depolarisation can be measured, which provides additional information on the observed particle (internal) structure. Methods based on depolarisation analysis [12, 13, 14, 15] are robust and very promising, however beyond the scope of this work, so we only mention them here and intend to address this issue in a separate paper.

2. Experimental apparatus and sample preparation

The experimental setup schematic view is presented in figure 1. We applied the sizing techniques, mentioned in previous section, to single droplets levitated in an electrodynamic quadrupole trap. Electrodynamic trapping is a well-established experimental technique (compare e.g. [16, 17, 18, 19, 20, 21, 22]) using a combination of alternating (AC) and static (DC) electric fields to constrain particle(s) to a small volume of “free” space, ideally to a point. A variant of a quadrupole trap was developed in our lab, too (see eg. [7] and references therein). The trap was kept in a small (\(~10 \text{ cm}^3\)) thermostatic chamber with dry nitrogen atmosphere at 25°C. Droplets were injected into the trap with the droplet-on-demand injector (a variant developed in our lab as well; similar to e.g. [23, 24]) kept at chamber temperature. The droplets were charged by charge separation in the external field of the trap, on emerging from the injector nozzle (no additional charging electrodes were used). Thus, the sign and the value of the charge was, to some extent, determined by the injection timing versus the phase of the trapping AC field. Two coaxial, counter propagating laser beams were used simultaneously for droplet illumination: green (532.07 nm) p-polarised (horizontal) and red (654.25 nm) s-polarised (vertical). The droplet was in the focus of the lens with NA=0.28 and the scattered light was collected around the right angle in the horizontal scattering plane. The entirely defocused image of the droplet (see photographs in insets in figures 3 and 4) was used for scatterometry. The distortions of frequency and shape of the interference fringes (spherical aberration and other geometrical effects; clearly visible in inset in figure 3) were corrected numerically in post-processing. Simultaneously, the focused image of the droplet was used for droplet position stabilisation. The vertical position of the (evaporating) droplet was maintained at the trap centre with a PID type stabilising loop, applying a balancing DC voltage between the top and bottom electrode. No secular (macro) motion was
allowed or observed. In lateral directions, non-absorbing droplets performed only trap-constrained Brownian motions. Neither photophoresis nor thermophoresis nor radiation pressure effects were observed.

In experiments presented in this work we produced droplets of: (i) diethylene glycol (DEG) (Fluka, BioUltra, 99.99 GC area %) and triethylene glycol (TEG) (Fluka, BioUltra, anhydrous, 99.96 GC area %) 10:1 solution, (ii) suspensions of 200-nm-diameter polystyrene (PS) nano-spheres (3200A, Thermo Scientific, "contains trace amount of surfactant") in DEG: (a) $\sim$1:100 and (b) $\sim$1:20 mass fraction. In case (b) $\sim$0.1% of surface active agent (sodium dodecyl sulfate (SDS) (Sigma-Aldrich, ACS Reagent, $\geq$ 99.0%) was added. The suspension was prepared by mixing DEG with suspension of PS nano-spheres in water and sonicating. In case of suspension (a) in bulk, formation of mm-sized (fractal-like) aggregates (leading to highly inhomogeneous suspension) was observed within several minutes after sonication. In case of (b) in bulk, only minor sedimentation was visible after several days. After the injection of a micro-droplet into the dry-nitrogen atmosphere, the water fraction evaporates in a fraction of the first second (compare [7, 25]) leaving the PS in DEG suspension. The bulk properties of substances used in experiments are presented in table 1.

### 3. Droplet radius measurements

The temporal evolution of the droplet radius $a(t)$, was obtained by analysing the angular distribution of scattered light irradiance (angle-resolved static light
<table>
<thead>
<tr>
<th>substance</th>
<th>density [kg/m³]</th>
<th>refractive index @ 532.07 nm</th>
<th>refractive index @ 654.25 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>diethylene glycol (DEG)</td>
<td>1114</td>
<td>1.448</td>
<td>1.445</td>
</tr>
<tr>
<td>triethylene glycol (TEG)</td>
<td>1121</td>
<td>1.456</td>
<td>1.453</td>
</tr>
<tr>
<td>polystyrene (PS) microspheres</td>
<td>1050</td>
<td>1.588</td>
<td>1.582</td>
</tr>
</tbody>
</table>

Table 1: Density and refractive indices of substances used in experiments. Densities @25°C taken from [26], n_D20 values provided by the manufacturers of the chemicals. Dispersion curve for PS taken from [27] and for DEG and TEG adapted after ethylene glycol from [28].

scattering, see eg. [5, 9, 29] and references therein) for every acquired frame and (simultaneously) by weighting.

In all figures, the evolution of droplet radius \( a(t) \) is presented in \( a^2(t) \) form. Such representation is advantageous, since in case of large, single component droplets \( a^2 \) evolution is linear in \( t \) (the, so called, "D^2-law", compare eg. [25]). In case of mixtures, characteristic "kinks" can be observed. They correspond to a phenomenon which is well-known from distillation: different components usually evaporate consecutively. The flat region to the right of the last "kink", if present, corresponds to non-evaporating droplet/particle. In the present case it is a solid particle. However, in general it can be a droplet of solution, in equilibrium with its environment.

3.1. Mie scattering lookup table method

MSLTM bases on fitting (with gradientless, lookup table method) the complete Mie theory predictions to the experimentally obtained scattering patterns (see inset in figure 3). In favourable cases (slowly evaporating liquids, refractive index known a priori), the method yields droplet radius with accuracy up to ±10 nm. The trap/chamber configuration that we used enabled observation of scattering within \( \sim 16^\circ \) half apex angle around the right angle, with \( \sim 0.05^\circ \) angular resolution. This makes possible droplet radius measurement in the range from \( \sim 500 \) nm to \( \sim 30 \) \( \mu m \), but in practice doesn’t allow for simultaneous finding of refractive index. The scattering pattern around right angle is more sensitive to droplet radius changes but less sensitive to refractive index changes than around the "rainbow angle". Small changes of scattering pattern around the right angle versus droplet radius and versus refractive index are in practice indistinguishable. Simultaneous accessing with high accuracy both radius and refractive index of the droplet requires observation in a wider angle encompassing the "rainbow angle".
An example of results obtained by application of this method to a droplet of 10:1 mixture of DEG and TEG is presented in figure 2 in open circles. The refractive index was assumed constant at the value corresponding to TEG; spectral dispersion between red and green light was accounted for. The data are presented unprocessed (see also inset) to illustrate high accuracy of the method. Examples of results obtained for droplets of suspensions are also shown in open circles in figures 4 and 5. The MSLTM is particularly sensitive to deformation of scattering patterns near Mie resonances, thus yielding data points severely missing the trend. Off resonance the method is less sensitive, but the more deformation the more information on phase and amplitude contained in scattering patterns is lost and data point get dispersed among possible evolution "branches".

![Figure 2: An example of an evolution (evaporation) of a droplet of 10:1 solution of DEG and TEG, polluted with non-volatile component(s). Unprocessed droplet radius evolution obtained with MSLTM, in radius-square form, shown in open circles. Boxed region magnified in inset. Stabilising DC voltage evolution shown in solid (red) dots. Droplet radius evolution obtained with DRDMM shown in solid (blue) line.](image)

### 3.2. Angular frequency of scattered light method

The AFSLM bases on general observation that the droplet radius is approximately proportional to the characteristic angular frequency of the scattering pattern for s polarisation. For observation around right angle, AFSLM can be treated as insensitive to scattering particle refractive index. The characteristic frequency was conveniently obtained with FFT of angular irradiance distribution (compare [9, 10, 11]). AFSLM yields droplet radius with ±200 nm accuracy only, but is
much more resistant to interference fringes distortion than MSLTM. Examples of results obtained by application of this method to droplets of suspensions are given in figures 4 and 5 in (red) triangles. This method seems applicable even to highly inhomogeneous, solid particles.

3.3. Droplet radius from droplet mass method

Obtaining the droplet radius $a$ from the droplet mass $m$ at a moment $t$ involves the relation, which for spherically symmetric droplets can be expressed as:

$$ m(t) = 4\pi \int_0^{a(t)} \rho(r,t)r^2 dr, \quad (1) $$

where $\rho(r,t)$ is the droplet density distribution temporal evolution and $m$ can be found by weighting. Weighting in electrodynamic trap bases on balancing the charged droplet weight $mg$ with the electrostatic field $E_{DC}$:

$$ mg = qE_{DC} = qkU_{DC}. \quad (2) $$

$U_{DC}$ is the DC voltage applied between the top and bottom electrode. Factor $k$ can be calculated with the finite-element method from general equations of electrostatics and the geometry of the trap. The droplet charge $q$ is unknown and can be obtained with an auxiliary method, like, for example, analysing of particle trajectories [30], analysing the dynamics of particle in the trap (spring point method [31, 20, 32, 33], drag force method [34, 20, 35, 36]) or controlled discharging of particle [37, 38, 39]. We, however, utilised the calibration with an optical method.

As the stabilisation loop maintains the constant vertical position of the droplet in the trap by varying $U_{DC}$ (see $U(t)$ shown in (red) solid dots in figure 2), the temporal evolution of $(m/q)(t)$ (droplet mass-to-charge ratio) can be immediately obtained. If at a moment $t_0$ (or better: an interval) where the droplet density distribution $\rho(r,t_0)$ can be assessed, an optical method yields an unambiguous droplet radius $a(t_0)$, then equation 1 yields $m(t_0)$ and $q(t_0)$ can be found from equation 2. For micron-sized liquid/colloidal particles, $q$ changes only in acts of Coulomb explosion [40, 41] and only then it must be recalculated. Furthermore, our experimental technique favours moderately charged droplets. As a consequence, we rarely observe Coulomb explosions, and thus usually $q$ remains constant during the whole evolution. Usually also, the initial density distribution $\rho(r,t_0)$ is uniform throughout the droplet and can be assessed. In case of most mixtures (solutions and suspensions), the temporal evolution of average density can be fairly
easily modelled analytically. The temporal evolution of spatial density distribution \( \rho(r,t) \) of suspensions can be modelled numerically and sometimes inferred from droplet radius measured with an optical method [42, 43].

The accuracy of weighting depends primarily on the accuracy of stabilising loop, which, in turn, via PID parameters, depends on \( m/q \) value. Since PID parameters of the stabilising loop can not be optimised to fit all \( m/q \) values equally well, the noise present in \( a(t) \) obtained with weighting changes during the evolution (as well as among experimental runs). Further improvement of weighting technique requires a more advanced control strategy (we have begun experiments with the Kalman filter).

An example of finding \( q \) for an evaporating droplet of DEG/TEG solution (data corresponding to figure 2) is presented in figure 3. Stabilising DC field strength \( E_{DC} \) calculated from \( U_{DC} \) is drawn versus droplet weight calculated from droplet radius obtained with an optical method. No Coulomb explosions were observed so \( q \) was constant through all the evolution. Densities of DEG and TEG differ only by 0.6%. Therefore, all data points lie around one straight line (solid, red) which can be found with least squares method. According to equation 2, the directional coefficient of this line is \( 1/q \).

Examples of radius evolution found with DRDMM are shown in figures 2, 4 and 5 in (blue) solid line.

![Figure 3: Open circles: stabilising DC field strength \( E_{DC} \), calculated from \( U_{DC} \) as \( E_{DC} = kU_{DC} \), drawn versus droplet weight, calculated from droplet radius obtained with MSLTM from data corresponding to figure 2 as \( mg = 4\pi a^3 \rho g/3 \). Solid (red) line represents linear fit. An example of Mie scattering image for a clear liquid shown in inset.](image-url)
4. Discussion

4.1. Pure liquids

For pure liquids, the droplet density is the bulk liquid density and the droplet radius obtained with DRDMM is the geometrical radius. It coincides with the one obtained with MSLTM (see open circles and (blue) solid line in figure 2). Figure 2 makes an example of rather high weighting noise.

![Figure 2](image-url)

Figure 2: Example of rather high weighting noise.

4.2. Moderate concentration suspension

For a droplet of suspension (a) presented in figure 4 (~1:100 initial concentration) the noise of weighting was low, and the radius evolution obtained with DRDMM is excellent. In the region where the droplet was only moderately inhomogeneous ($t < 300$ s), the MSLTM yielded quite satisfactory results, which enabled very good calibration of DRDMM. For $t > 370$ s MSLTM is practically useless, while AFSLM seems to work even for (nearly) solid particles. It is significant that though during the evolution the suspension concentration grows steadily, which is visible as a slight upward deviation from the "D$^2$-law" represented with (green) dashed line, there is no corresponding steady deterioration of
results yielded by this method. The deterioration of results builds up rapidly when a rapid transition in scattering image from (distorted) fringes to speckles occurs (compare left and right inset in figure 4). We expect (compare [42, 43]) that this transition is associated with high inhomogeneity developing at the droplet surface, since for a droplets of considered size the cavity modes energy density is highest near the surface (compare: whispering gallery modes) and the near-surface region plays a vital role in light scattering. The dispersed phase probably forms a maximal cluster in the droplet then and the nano-spheres begin to protrude from the surface. Further drying leads to the compression of maximal cluster and finally to a dry (or nearly dry) agglomerate particle. A dramatic decrease in evaporation rate ("kink") can be observed for $t \approx 460$ s. Careful examination of data obtained from weighting indicates that the particle was still drying. Probably a nearly dry agglomerate particle is reached at that point. It is well-known that porous materials (nano-spheres agglomerate) dry very slowly, due to slow internal diffusion of liquid and reduced evaporation area. It is also possible that a low permeability crust is formed (compare [42, 44, 45]).

The density of PS and DEG is very similar (1.05 and 1.12 g/cm$^3$ respectively, see table 1), so as long as the pores of an agglomerate particle are filled with liquid, the particle radius found with DRDMM is unaffected by changes in composition. On the other hand, the refractive index of PS is higher than of DEG (1.59 and 1.45 respectively, see table 1). Thus, an increase of PS concentration leads to an increase in effective refractive index. AFSLM is nearly totally insensitive to refractive index changes. On the other hand, as long as the evolution of the effective refractive index is not accounted for, MSLTM is expected to slightly overestimate the radius. However, the comparison with the radius obtained with DRDMM indicates that this small effect is hardly detectable within the experimental accuracy. The only hint of the effect is visible for $300 < t < 400$ s as an additional branch of solutions (the branch of open circles lying just above the solid (blue) line).

It is also noticeable, that for $t > 300$ s the approximate optical method seems to yield smaller droplet radius than weighting and in the region of nearly dry agglomerate particle it clearly does. This effect is more pronounced in figure 5. However, the accuracy of the approximate method is too low to draw any conclusions.

4.3. High concentration suspension

A nearly limiting case of application of the described set of methods to a droplet of suspension is presented in figure 5. The initial suspension concentration was $\sim 1:20$ (section 2 suspension (b)), which quickly led to a "wet" agglomerate
Figure 5: Evaporation of a droplet of suspension of polystyrene nano-spheres in diethylene glycol. The initial concentration was $\sim 1:20$ (high). Droplet radius obtained with: MSLTM (every 50th data point) - open circles, AFSLM - (red) triangles and DRDMM - solid (blue) line. Dashed (green) line corresponds to the "$D^2$-law" prediction. All data points obtained with the MSLTM are shown in inset.

Particle. All data points obtained with the MSLTM are presented in inset in figure 5. Only after reducing the number of points (taking every 50th, see main figure) the most probable evolution branches become recognisable, but no leading branch can be easily pointed to. In such case additional data are required.

AFSLM seems to work most reliably for $530 < t < 850$ s, where AFSLM results coincide with the prominent branch yielded by MSLTM. This region was used for calibration of DRDMM. The radius found with DRDMM enables to identify one of the evolution branches yielded by MSLTM as the leading one. Simultaneously it indicates that AFSLM is also prone to hopping between the solution branches.

Using all the three methods together enabled finding the droplet radius evolution quite reliably. For $t > 850$ s no evolution branches are recognisable with MSLTM. The results yielded by AFSLM also seem to deteriorate. Similarly as in figure 4, this point can be associated with build up of surface corrugation. It can be noticed, that the deviation from the "$D^2$-law" ((green) dashed line) is larger then observed in figure 4, which is natural for higher suspension concentration. However, there is no distinct "kink", corresponding to transition to (nearly) dry agglomerate particle, visible in droplet radius evolution yielded by DRDMM. It might be attributed to the presence of surface active agent (SDS) which suppresses
formation of a low permeability crust.

5. Conclusions

The application of the combination of two optical methods of droplet radius measurement with droplet weighting enables efficient analysis of the evolution of droplets of suspensions. Droplets of suspensions of high concentration evolving towards "wet" agglomerates can be handled. Apart from droplet/particle radius evolution, its electrical charge and the evolution of its effective refractive index can be found. Some information on the internal structure of the droplet/particle can be inferred as well. Still more information is expected to be feasible to extract by adding analysis of scattered light depolarisation.

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References


