Brownian Motion, Dynamic Light Scattering and the Use of Viscosity Or . . . .

Would You Argue with Albert Einstein about how to use Viscosity in the DLS Formula?

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Particle Size and Characterization Instrumentation

Application Note

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Particle Size Measuring Instrumentation

Brownian Motion and Dynamic Light Scattering

Brownian motion is an effect that develops as result of fluid molecules colliding with particles and causing their movement. According to the Stokes-Einstein formula shown below, the particles are treated as point objects having no mass or density. The movement of particles gives rise to diffusion through the suspension where the rate of diffusion is more rapid for small particles. The velocity of the particles during diffusion is size dependent. Particles moving under these conditions results in shifts in the frequency of interacting light. Measurement or determination of the frequency shifts occurring when light interacts with various size particles allows for their size calculation. The determination of frequency shifts and ensuing calculation to obtain particle size is termed Dynamic Light Scattering (DLS).

$$\textbf{Stokes-Einstein Formula: } \textit{D = kT/6}\pi\eta\,\textit{R}_h$$

D = Diffusion co-efficient   *k = Boltzmann constant*   *T= Temperature* *η = dynamic viscosity R= hydrodynamic radius*

Note that the formula calls for use of Dynamic Viscosity (cP for example). The Nanotrac can accept either Dynamic or Apparent viscosity values since the same type of viscometer is used. This paper attempts to explain why the best approach is to use the dynamic viscosity so that adherence to DLS science is complied with. At present there are no physical chemistry principles outlining or explaining the use of apparent viscosity for DLS. Dynamic viscosity is well-founded and based within the Stokes-Einstein formula.

Dynamic Viscosity

There is a DLS requirement that the particles move freely and independently without impact on their velocity. There are two primary phenomena that affect such free movement: viscosity and particle interactions. As viscosity increases, the velocity of particles is slowed. This is true whether particle size measurements are performed by DLS or sedimentation. The importance of viscosity is shown in the Stokes-Einstein Equation for DLS and is a necessary physical property for calculation by Stokes-Einstein. The viscosity value used in the equation is that of the suspending fluid and not the suspension. At times this has been a cause for confusion, but violation of using the clean, suspending fluid viscosity would be a violation of the basic tenets of Einstein and Stokes.

Viscosity is also important to measurements of zeta potential as determined by light scattering methods such as Zetatrac.

There are several types of viscosity representations used to describe the non-flowability of pure fluids and suspensions. Of special importance to DLS is **Dynamic (Absolute) viscosity**. The unit system used by Microtrac instruments is centipoises (cP). Other units include centistokes (cS), SSU, and milliPascal·Second (mPa·s) while conversion from one set of units to cP is available on various websites or conversion texts. Dynamic viscosity is a measurement determined by use of various types of viscometers. Viscosity is a measure of resistance of flow due to internal friction when one layer of fluid is caused to move relative to another layer. A liquid with a dynamic viscosity of one Poise requires a force of 1 dyne to maintain a velocity differential of cm/sec over a surface of $1cm^2$ (other units include $1Ns/m^2$ and Pa.s). Dynamic viscosity is the value obtained for Newtonian fluids such as water, gasoline, milk, many oils, organic solvents, etc. These substances are termed Newtonian since their viscosity does not change with rate of agitation or stirring. In technical terms, a Newtonian fluid exhibits constancy of the ratio of shear stress to shear rate.

Apparent Viscosity

Another value is termed **Apparent Viscosity.** This is determined by using the same instrumental methods and equations as is used for dynamic viscosity. However, the application of the terminology is for NON-Newtonian fluids which are nearly always <u>suspensions</u> such as peanut butter, blood, paint, shampoo, toothpaste, hand creams, etc. These materials in a chemical sense are mixtures and not pure fluids as required by the Stokes-Einstein Equation. Since Apparent Viscosity changes as particulate concentration changes, it has great use for determining rheological characteristics of many suspensions but its use in DLS is not founded scientifically. It also has use in understanding certain physical phenomenon and explains the behavior of a substance such as the action of quicksand. The faster and harder movement is applied to escape the quicksand, the greater the apparent pull of the suspension of the mud particle system to retard or prevent escape. Thus quicksand is termed thixotropic. Thixotropic is a term used to describe a system that increases in viscosity as the rate of stirring or agitation increases. A similar suspension can be prepared from water and corn starch.

Using the apparent viscosity can result in considerable error by shifting the particle size by 30% or more for narrow distributions having a width less than one decade. As distributions widen and become broader, the error can be expected to increase. In the case of patent applications where dynamic light scattering particle size is

used, correct application of viscosity and use of Stokes-Einstein concept is mandatory and can help protect the patent contents when particle size and zeta potential are included.

Some information cites using the Apparent Viscosity to obtain repeatable data at high concentrations. Close scrutiny of the data show that at those specific concentrations, the data has shifted significantly from measurements obtained in dilute suspension where the data were obtained using Dynamic Viscosity according to Stokes-Einstein formula. Thus the error can be high and misleading since the repeatability exists only over a limited range of concentrations. Since the repeatability will occur at only certain dilutions, it would seem ill-advised to perform measurements using Apparent Viscosity. Similarly, the use of apparent viscosity for DLS is akin to manufacturing desirable data without regard and conformance to sound scientific and engineering discipline (compliance with Stokes-Einstein) and review. Additionally, logic dictates that if using Apparent Viscosity were valid, it could be used over the entire range of possible viscosities.
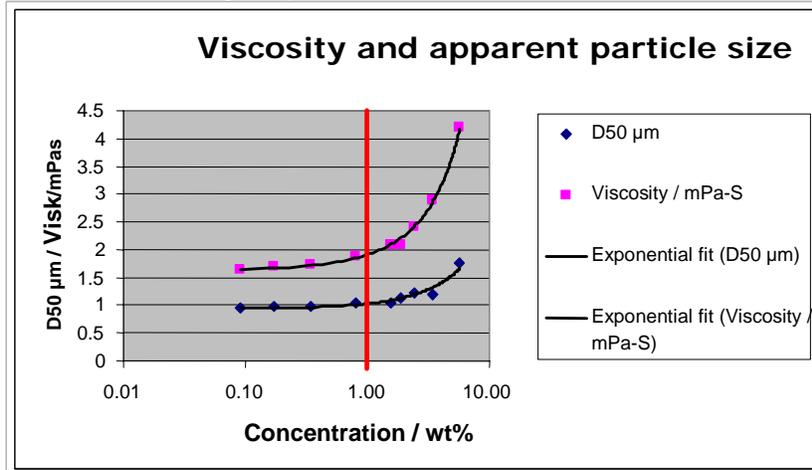
Courtesy: Dr. Hanno Wachernig and Margret Boeck, Particle Metrix, Gmbh, Düsseldorf, Germany. Shows a material (non-dairy) where viscosity changes rapidly with concentration. Note that the Newtonian range may end at concentrations as low as 1% solids or as high as 40% solids.

The use of Apparent Viscosity requires the constant measurement of viscosity of the suspension, thus concomitantly requiring the purchase of ancillary viscometer equipment and the attendant need for training and certifications. In addition, because the apparent viscosity will change, it becomes difficult to establish which Apparent Viscosity value should be used. As well, there becomes the decision as to when should the operator change over to using dynamic viscosity (very low concentrations?) and at what point concentration of particulate increases viscosity too high for DLS measurement. Using only the Dynamic viscosity will resolve these issues.

Using Apparent Viscosity can be viewed as a means of some instrument methods to justify measuring high concentration suspensions not normally possible due to optical design.

ISO Particle Size Standard for Dynamic Light Scattering (ISO 22412) specifically notes Dynamic viscosity of the suspending fluid as the proper value to be used. In lieu of using the suspending fluid, the Apparent Viscosity can be used, but a fixed finite particle concentration must be used for quality control purposes necessitating the requirement of accurate solids determination. Using this method, accuracy of size reported will be affected without such determination.

Particle – Particle Interactions and Multiple Scattering

For instruments using <u>less than</u> 180 ^{o} (Nanotrac and Zetatrac use 180 ^{o} pure back-scatter), the untoward effects of high viscosity and non-Newtonian fluids might become complexed with multiple scattering or other particle interactions. These effects include hindering of particle movement, overlapping of the electrostatic double layers of the particles, presence of polymer structures, and partial agglomeration and aggregation, When the number of particles increases to a very high level, the Brownian motion (free particle diffusion) movement may be affected. This occurs due to interactions among the particles caused by close packing. While light may still be scattered by the particles, the frequency shifts needed for Dynamic Light Scattering calculations are impacted by the changed velocity or movement of the particles. Usually particle-particle interactions impede movement causing the size reported to be erroneously large since diffusion and velocity of the particles is decreased. For *non-backscatter* detection (proven back-scatter detection is at 180°), the impeded movement is usually an effect that occurs after multiple scattering has occurred. Multiple scattering is a process caused by light being scattered too many times resulting in data changes. Nanotrac, and Zetatrac instruments detect frequency-shifted scattered light at 180 degrees and avoids multiple scattering effects that occur at high concentrations. Both multiple scattering and
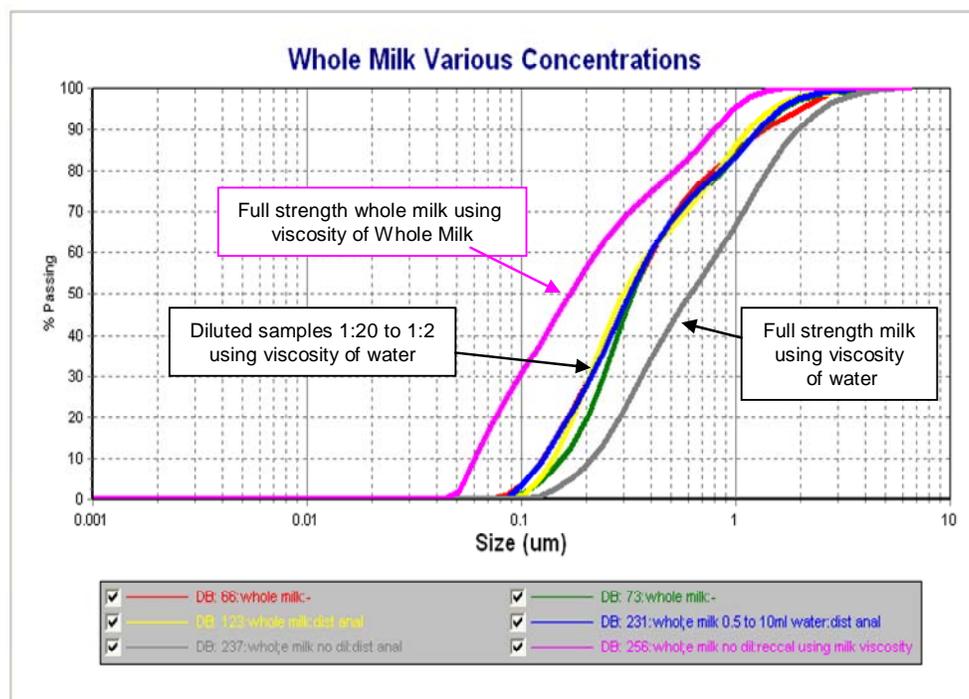
particle-particle interactions can be avoided by dilution of the sample suspension. Individually, multiple scattering effects can be avoided by instrument design; however, there is no design or scientifically mathematical means to avoid the effects of particle-particle interactions thus necessitating dilution of the sample.
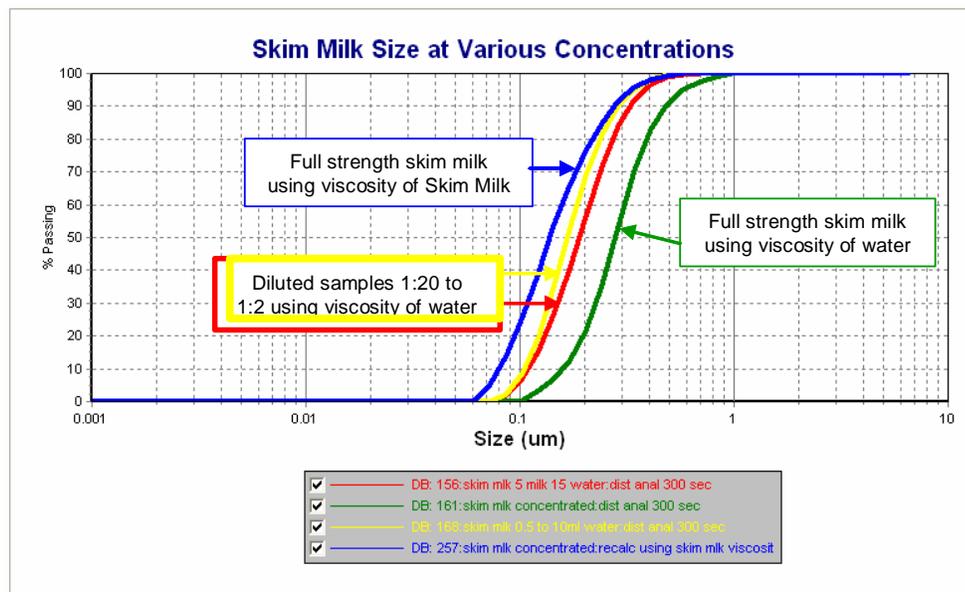
Milk – a Newtonian fluid

Milk is an emulsion that becomes a stable emulsion following homogenization. Data are shown for homogenized whole milk and skim milk. Both of these are known to be Newtonian fluids and not subject to viscosity changes as a result of shear as found with Non-Newtonian fluids. In each case when the viscosity of water is used and the milk product is concentrated (full strength), the particle size distribution is larger than when the sample is diluted. The following table shows viscosity data used (Brookfield viscometer) and the resulting particle size for diluted and full strength milk product.

The results show that the size obtained over a wide range of dilutions (5 to 50% dilution) can be properly reported. Measurement of full strength milk (high concentration of approximately 10% solids) using the viscosity of either water or milk impacts reported particle size results.

Product	Expected Size um	Measured D50 Diluted and measured using viscosity of water	Measured D50 Concentrate measured using viscosity of water	Measured D50 measured using product viscosity	Viscosity (cP) @ 4C	Viscosity (cP) @ 21C
Whole Milk	0.4	0.33	0.62	0.18	3.8	2.2
Skim Milk	0.2	0.18	0.28	0.15	3.4	1.9

The graphs show the actual distributions obtained by using water viscosity values for all samples except that the concentrated sample was also calculated using the viscosity of the actual sample of skim milk or whole milk. Note that measurement of the concentrated sample when using the actual sample viscosity, provided size distributions smaller than the distributions for the diluted samples.

Skim Milk Size at Various Concentrations

Full strength skim milk using viscosity of Skim Milk

Full strength skim milk using viscosity of water

Diluted samples 1:20 to 1:2 using viscosity of water

DB: 156:skim mlk 5 milk 15 water:dist anal 300 sec
DB: 161:skim milk concentrated:dist anal 300 sec
DB: 168:skim milk 0.5 to 10ml water:dist anal 300 sec
DB: 257:skim milk concentrated:recalc using skim mlk viscosit

Considering that the particle size values of the water-diluted milk products is similar to literature values, the effect of using actual (apparent) viscosity is ill-advised since results may be in error. This can cause the distributions to be reported as smaller than generally expected. Broadening and particle size shift exhibited by multiple scattering are not present. This suggests two possibilities for the effect and associated errors - each corollary to the other. One possibility for the effect is that using a correction employing the viscosity (apparent) of sample (and not viscosity of suspending fluid) can cause unexpected and possibly uncontrollable error. A second effect is causing the concentrated sample to be reported larger than expected, which may be caused by particle-particle interactions or other effects not investigated. Neither sample viscosity (apparent), nor particle-particle interactions can be compensated by present dynamic light scattering instruments. For correct particle size, the range of concentrations allowed by the instrument, while maintaining the concepts of Brownian motion physics as proffered by the Stoke's-Einstein formula, must be followed for accurate, defensible, meaningful measurements.

Dilutions and Effects of Measuring High Concentration Suspensions

Dilution of a sample to 40% solids or less will allow measurement of particle size and zeta potential in Microtrac instruments. The amount of dilution necessary is determined by testing various concentrations. Automotive emulsion coatings have been successfully measured at 30% concentration using a pure solvent diluent. The dilution overcomes the effects of particle-particle interactions. Multiple scattering issues are avoided since the path-length of scattered light in 180° Nanotrac and Zetatrac is very short and light has little opportunity for re-scattering that occurs in typical non-backscatter instruments. The need for such high concentration measurements is to avoid potential effects of dilution which can destabilize the particle system. While de-stabilization does not always occur, it is an issue that requires some investigation. Microtrac Customer Support staff is available with advice in these tests or customers may send samples for test per the life-time support concept begun 35 years ago.

Dilutions should be performed by a fluid that is compatible with the sample. For aqueous systems, water quite often will suffice while in some situations the diluent must be the actual clean, suspending fluid. This diluent is used also for blank measurement termed Set Zero in Microtrac instruments. These values are stored in memory and subtracted from sample signals and avoid issues of contaminants in diluents. This is a unique feature of Microtrac DLS instrumentation. When additives exceed approximately 2-4% in a fluid of the particle system, then background becomes important since the dissolved solids can enhance or retard Brownian motion and thereby affect particle size results. For zeta potential measurements, the requirement for diluting with clean suspending fluid is more critical in obtaining accurate data since the ionic environment can be strongly affected which in turn affects the developed potential field in the suspension.

The purpose of analysis is to provide indication or evidence that the product has changed in some manner. Without diluting the sample to a prescribed amount of solids, measurement may indicate that the particle size has changed. However, the resulting particle size may be affected by several factors: multiple scattering by non-back-scatter DLS instruments, particle-particle interactions, change in ionic strength, suspending fluid viscosity, soluble components (surfactants, salts, etc) or actual change in particle size. One method to test whether the particle size has changed is to apply Stokes-Einstein in the defined state of using dynamic viscosity of the suspending fluid for

samples at lower concentrations and lower sample viscosity values. Dilution will remove the effects of soluble components, particle-particle interactions, and other effects. ISO 22412 proposes a method where extrapolation techniques to zero concentration can be used to investigate effects. This is often a time-consuming and tedious approach. Alternatively, if the measured particle size is within expected limits, some factor other than size change should be suspected as causing a change in the product. Another useful technique is to dilute the sample with a surrogate clean fluid that maintains Newtonian characteristics. An example would be a fluid that contains the approximate concentration of all salts, surfactants, etc except for the particles to be measured. This can be prepared or obtained from the sample suspension by filtration or centrifugation.

In some cases data from using Apparent Viscosity can be used for quick indication of reported size or general quality conformance. Using data affected by high concentration measurement may be useful in such a quality control environment but recognition must be given to the potential for particle size error. Care should be taken that under this condition, particle size reported may be within tolerances and specifications, but the product may fail overall quality as identified by other tests. This can occur if the particle size has changed, but compensation by another ingredient, e.g. salt content, has unknowingly occurred. For example, consider the countering effects of a size increase along with a change in salt concentration resulting in an increase in particle velocity (decrease in size). Overall compensation has unknowingly occurred that hides the increase in actual particle size. Beyond the Newtonian regime, Quality Control measurements can allow the use of both viscosity values, but the sample system must be well understood and the chemical composition must not change when using Apparent Viscosity.

Summary
Using heterodyne technology, only Nanotrac has the best mathematical solution for using back scattering at 180 degrees. This geometry allows measurements at the highest possible concentrations. That highest level is only limited by the non-Newtonian viscosity limit. See Applications Note SL-AN-05 "*High Concentration Sub-micron Particle Size Distribution by DLS"* and SL-AN14 Rev C *"Nanoparticles Sizing: Dynamic Light Scattering Analysis in the Frequency Spectrum Mode".*

There is no simple relationship between particle size and viscosity of highly concentrated suspensions. According to the Stokes-Einstein formula which is the basis for all DLS instrumental light scattering measurements, viscosity is an important physical parameter that requires careful consideration. The viscosity value used in the formula is Dynamic Viscosity and *not* Apparent viscosity. This lack of simplicity of a relationship would be especially true if non-180° scattering designs contribute to multiple scattering. A reported size change may be caused by many different reasons. One obvious reason is that the size has (in reality) changed. Other effects may also result in the reported size change such as incorrect viscosity, multiple scattering, molecular networking, ingredient change, ionic environment, particle-particle interactions, etc. The interpretation as to the cause of size change at higher concentrations is therefore dangerous and should be avoided. If used as a QC tool, it is recommended to use dynamic viscosity of the diluent. The importance of using dynamic viscosity in the Newtonian regime should not be understated in the effort to report the most accurate particle size and zeta potential data. Back-scatter at 180° provides the best means of avoiding effects of high-concentration measurements.

Nanotrac can be used in a manner proscribing viscosity for non-Newtonian fluids but Microtrac does not endorse this philosophy due to its lack of a sound scientific basis. Experimental measurements, such as those for milk, demonstrate that using correct viscosity of the suspending, particle free fluids where minimum dilution is needed, can provide accurate measurements using Nanotrac and Zetatrac instruments where 180° back-scatter is used. The effect on data is insignificant over the range of dilutions examined. Higher concentrations may also be measured but investigation should be conducted.

Using the viscosity of the particle free fluid (water in the case of this paper), promotes the best approach to DLS measurements. The exact reason for the particle size change for some materials not diluted, is not always well understood and may be caused by any one or combination of several factors that may or may not be accounted for by using the *apparent* viscosity. As a result, when high concentrations cause data shifts for any particle distribution, the dynamic viscosity should be used, for best scientifically represented data. Should zeta potential be measured on the non-diluted sample that shows size-shift effects, the same issues apply. The concepts of using viscosity when considering Newtonian and non-Newtonian fluids (clear fluids or suspensions) should be respected for size determination, zeta potential or other particle charge determinations.

With these thoughts in mind, would it make sense to argue with Dr. Albert Einstein about the use of dynamic viscosity values in the DLS formula?

References:
    Website: www.foodsci.uoguelph.ca/dairyedu/homogenization.html
    Website: www.ars.usda.gov/services/docs.
    Website: brookfieldengineering.com/education/application/laboratory-milk.asp
    ISO Particle Size Standard for Dynamic Light Scattering (ISO 22412)