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Neutron scattering from aerosols: Intraparticle structure factor, Guinier analysis of particle speed, and crossed beam kinematics

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A theoretical formalism for neutron scattering from systems of particles is applied to liquid nanodroplet aerosols. A term arising from intraparticle, intermolecular correlations is identified. The kinematical theory of two body scattering is recast into a form convenient for interpreting the results of experiments with crossed beams of neutrons and aerosol particles. Based on a theoretical analysis of the scattered intensity in the Guinier region, a method for determining the particle velocity directly from the experimental data is outlined. The method is not restricted by assumptions about particle shape, composition, uniformity, or size distribution.

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I. INTRODUCTION

Small angle neutron scattering (SANS) is an important technique for studying the structure of materials at the nanometer scale [1]. When applied to aerosols containing nanoparticles, SANS permits the *in situ* determination of the aerosol size distribution and particle characteristics. This information can lead to improved understanding of aerosol formation processes, which are of great interest for both fundamental and practical reasons [2]. Quite recently, aerosols generated by homogeneous condensation have been studied with SANS using a supersonic nozzle to generate a steady aerosol flow directly in the path of the neutron beam [3,4].

The analysis of these crossed beam scattering measurements depends, in part, on the resolution of an interesting complication stemming from the relative motion of the neutrons and aerosol particles. The aerosol particles in these experiments are massive, typically containing more than 10^4 water molecules. The nozzle flow field is essentially one dimensional, and the mean particle velocity normal to the flow direction is less than 1% of the flow velocity. Consequently, for scattering orthogonal to the flow direction, the aerosol particles are effectively stationary, while, for scattering along or against the flow direction, the high speed particles produce larger neutron momentum transfers. In effect, the momentum of the scattered neutrons is Doppler shifted along the direction of particle motion, and the resulting laboratory scattering patterns are anisotropic. As shown below, this Doppler shift can be used directly to measure the particle speed by means of a suitable Guinier analysis [1,5].

This paper is organized as follows. Section II reviews and extends the formalism for the scattered neutron intensity for a stationary aerosol in terms of single particle, intraparticle, and interparticle contributions. The relative importance of each type of contribution is briefly discussed. Section III summarizes the key equations relating the scattered intensities in the center of mass (COM) and laboratory (LAB) frames. These equations also provide the basis for determining the aerosol particle speed by a Guinier analysis of the scattered intensities, and the theoretical results needed to carry out the Guinier analysis are developed here. A summary of the results and the conclusions is given in Sec. IV. The Appendix contains a short reprisal of the kinematics of two body scattering in the COM and LAB frames, with the results cast in a form directly applicable to the aerosol SANS experiments. Some of these results have been obtained previously in the context of crossed molecular beam scattering [6,7].

II. SCATTERED INTENSITY IN THE ABSENCE OF FLOW

A. General considerations

Consider N particles suspended in a scattering volume V. Collectively, the particles and solvent are assumed to have no net momentum, i.e., there is no net flow velocity. The coherent scattered neutron intensity per unit scattering volume, I_0 (units are cm^{-1}), is given by the following general expression [8]

$$I_0(q) = V^{-1}\left\langle \left| \sum_{j=1}^{N_n} b_j \exp(i\mathbf{q}\cdot\mathbf{r}_j) \right|^2 \right\rangle, \tag{2.1}$$

where N_n is the total number of nuclei in the sample, $\mathbf{r}_j$ is the position vector of the jth nucleus, b_j is its bound coherent scattering length, and $\mathbf{q}$ is the momentum transfer wave vector. The angular brackets denote a thermal equilibrium average over all nuclear positions with an appropriate configuration space distribution function. As explained in the Appendix, $I_0(q)$ is equivalent to the coherent component of the differential scattering cross section per unit volume. The validity of Eq. (2.1) rests on the first Born approximation, which in effect neglects multiple scattering events. In the recent aerosol SANS experiments [3,4], the total volume fraction of aerosol particles is $<10^{-5}$, the total number density of particles is about $10^{12}\ \mathrm{cm}^{-3}$, and the neutron path length through the aerosol is about 1 cm, so multiple scattering is truly negligible.

As shown by a number of authors [1,9–13], this equation for I_0 may be cast into a more practical form that identifies the contributions to the scattered intensity arising from individual particles and the correlations between particles. Here a similar exercise will be carried out, but with a more detailed analysis of the single particle contributions to draw attention to the intraparticle, intermolecular correlation terms not considered in these other expositions.

As in the work of Kotlarchyk and Chen [9], the analysis of Eq. (2.1) begins by decomposing V into N cells, each containing one particle. Thus $I_0(q)$ may be expressed as

$$I_0(q)=\sum_{c=1}^{N}\left[I_c(q)+\sum_{d\neq c} I_{cd}(q)\right], \tag{2.2}$$

where $I_c(q)$ is the scattered intensity from intracell correlations,

$$I_c(q)=V^{-1}\left\langle\left|\sum_{j=1}^{N_c} b_j \exp(i\mathbf{q}\cdot\mathbf{r}_j)\right|^2\right\rangle, \tag{2.3}$$

and $I_{cd}(q)$ is the scattered intensity from correlations between two different cells:

$$I_{cd}(q)=V^{-1}\left\langle\sum_{j=1}^{N_c}\sum_{k=1}^{N_d} b_j b_k \exp(i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k))\right\rangle. \tag{2.4}$$

The sums in the two preceding equations now run over only the numbers N_c and N_d of nuclei located in these cells.

B. Single particle and intraparticle terms

The intracell correlations term may first be broken into sums over the same and different nuclei,

$$I_c(q)=V^{-1}\sum_{j=1}^{N_c}\left[b_j^2+\left\langle\sum_{k\neq j} b_j b_k \exp(i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k))\right\rangle\right]. \tag{2.5}$$

In general, each cell may contain several types of nuclei, and $N_{\alpha c}$ will denote the number of nuclei of type α in cell c, such that $\Sigma_\alpha N_{\alpha c}=N_c$. Next each term of the thermal average in Eq. (2.5) may be rewritten as

$$\langle\exp(i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k))\rangle=\left\langle\int_c\int_c \exp(i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r}''))\delta(\mathbf{r}_j-\mathbf{r}')\times\delta(\mathbf{r}_k-\mathbf{r}'')d\mathbf{r}'d\mathbf{r}''\right\rangle, \tag{2.6}$$

using the properties of δ functions. The symbol $\int_c$ indicates that the integrals are performed over the cell volume V_c. Now we introduce site-site pair distribution functions $g_{\alpha_\beta}(\mathbf{r}',\mathbf{r}'')$ for nuclei of type α and β. These functions are defined as

$$\rho_\alpha(\mathbf{r}')\rho_\beta(\mathbf{r}'')g_{\alpha_\beta}(\mathbf{r}',\mathbf{r}'')=\sum_{j=1}^{N_{\alpha c}}\sum_{k=1}^{N_{\beta c}}\langle\delta(\mathbf{r}_j-\mathbf{r}')\delta(\mathbf{r}_k-\mathbf{r}'')\rangle\times(1-\delta_{jk}\delta_{\alpha_\beta}), \tag{2.7}$$

where $\rho_\alpha(\mathbf{r}')$ is the number density of type α nuclei at $\mathbf{r}'$, the sums run over all of the type α and type β nuclei in the cell, $\delta(\mathbf{r})$ is a three-dimensional δ function, and the pair of Kronecker deltas is introduced to exclude terms with the same nucleus. Because of the presence of the particle-solvent interface, each cell is an inhomogeneous subsystem, and the number densities are functions of position. Similarly, g_{α_β} depends on the positions of both nuclei and not just on the distance between them as in a homogeneous system.

After the terms in the double sum of Eq. (2.5) are rewritten using Eq. (2.6), then regrouped according to nucleus type and replaced using Eq. (2.7), we introduce the identity $g_{\alpha\beta}=g_{\alpha\beta}-1+1$. The terms associated with the $+1$ are easily resummed to give $|\int_c\rho_b(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}|^2$, where $\rho_b(\mathbf{r})$ is the scattering length density at position $\mathbf{r}$ of the cell:

$$\rho_b(\mathbf{r})=\sum_\alpha b_\alpha\rho_\alpha(\mathbf{r}). \tag{2.8}$$

Finally, we replace $\rho_b(\mathbf{r})$ with the scattering length contrast density $\Delta\rho_b(\mathbf{r})$,

$$\Delta\rho_b(\mathbf{r})=\rho_b(\mathbf{r})-\rho_b^s, \tag{2.9}$$

where ρ_b^s is the mean scattering length density in the bulk solvent (s), $\rho_b^s=\Sigma b_\alpha\rho_\alpha^s$, which is independent of position. The result of these manipulations is that $I_c(q)$ can be written as

$$I_c(q)=V^{-1}[\langle f_c^2(\mathbf{q})\rangle_\Omega+N_c\overline{b^2}S_c(q)+\langle f_c f_c^{s*}+f_c^s f_c^*\rangle_\Omega+f_c^s f_c^{s*}], \tag{2.10}$$

which is the sum of a form factor $\langle f_c^2(\mathbf{q})\rangle_\Omega$, a term involving a molecular structure factor $S_c(q)$, and several other terms that turn out to be unimportant, as shown below. The subscript Ω on the angular brackets in Eq. (2.10) indicates that a random orientational average should be taken if the result of the cell volume integrals is not spherically symmetric.

In Eq. (2.10), the particle form amplitude $f_c(\mathbf{q})$ for cell c is

$$f_c(\mathbf{q})=\int_c\Delta\rho_b(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}. \tag{2.11}$$

The form scattering term arises essentially from the shape of the particle as defined by the scattering length contrast density. Since $\Delta\rho_b(\mathbf{r})$ generally differs from zero only within each particle and in its surrounding interfacial zone, Eq. (2.11) provides an operational definition of a particle's boundary that includes the effects of a diffuse interfacial region on the observed scattering.

The last three terms in Eq. (2.10) involve a solvent form amplitude $f_c^s(\mathbf{q})$,

$$f_c^s(\mathbf{q})=\rho_b^s\int_c\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}, \tag{2.12}$$

which is proportional to a delta function $\delta(\mathbf{q})$ when the cell volume is sufficiently large, as in applications to dilute aerosols or colloids. For a very concentrated system, this condition will not be satisfied. However, it is intuitively plausible that, due to cancellation of positive and negative contributions at nonzero q, the sum of these terms over all cells also reduces to a δ function contribution, which is thus ignorable.

The second term in Eq. (2.10) arises from interatomic correlations on molecular length scales both within the particle and the solvent and, as a result, is not usually considered in discussions of small angle scattering. Nevertheless, its analysis may be of some interest because aerosol particles often occur under conditions that would be considered extreme for bulk liquid samples. For example, in the supersonic nozzle experiments [3,4] the liquid D_2O nanodroplets are supercooled and have high internal pressures. Hence higher q scattering experiments could potentially provide new information about the structure and behavior of liquids at these unusual conditions.

The structure factor $S_c(q)$ is analogous to the observable structure factor for a homogeneous liquid mixture [14]. It is defined by the expression

$$\begin{aligned}S_c(q)=1+(N_c\overline{b^2})^{-1}\sum_\alpha\sum_\beta b_\alpha b_\beta\Big\langle\int_c\int_c\rho_\alpha(\mathbf{r}')\rho_\beta(\mathbf{r}'')\\ \times[g_{\alpha_\beta}(\mathbf{r}',\mathbf{r}'')-1]\exp(i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r}''))d\mathbf{r}'d\mathbf{r}''\Big\rangle_\Omega ,\end{aligned} \tag{2.13}$$

where $\overline{b^2}$ is the mean square scattering length for the cell:

$$\overline{b^2}=N_c^{-1}\sum_{j=1}^{N_c} b_j^2 . \tag{2.14}$$

By invoking an arbitrary, but physically reasonable, definition of a particle boundary, $S_c(q)$ may be split into separate structure factors for the particle (p) and solvent (s) regions plus a third structure factor for cross correlations between solvent and particle sites. The particle boundary imagined here is a surface surrounding the particle on which all the densities ρ_α have reached their bulk solvent values. The volume enclosed by this surface should be a minimum in the sense that the surface represents the first points at which the density condition is satisfied along trajectories starting in the particle and ending in the solvent. Obviously, other definitions are possible. One disadvantage of this definition is that it may differ slightly from the one described after Eq. (2.11). One advantage of it is that the entire solvent phase is now a homogeneous system, which allows its structure factor to be simplified. Equation (2.13) may now be rewritten as

$$\begin{aligned}N_c\overline{b^2}S_c(q)=N_c^p\overline{b_{pc}^2}S_c^p(q)+N_c^s\overline{b_{sc}^2}S_c^s(q)\\ +2N_c^s\overline{b_{sc}}N_c^p\overline{b_{pc}}H_c(q),\end{aligned} \tag{2.15}$$

where the numbers of nuclei in each region are defined as

$$N_c^s=V_c^s\sum_\alpha \rho_\alpha^s , \tag{2.16}$$

$$N_c^p=N_c-N_c^s , \tag{2.17}$$

and the solvent volume V_c^s in the cell is determined by subtraction once the particle volume V_c^p is determined using the above definition, $V_c^s=V_c-V_c^p$. The mean square scattering lengths for the particle and solvent, $\overline{b_{pc}^2}$ and $\overline{b_{sc}^2}$, respectively, are defined by equations similar to Eq. (2.14), and the mean scattering lengths, $\overline{b_{pc}}$ and $\overline{b_{sc}}$, are defined as, e.g., $\overline{b_{sc}}=\Sigma_j^s b_j/N_c^s$, where the superscript s on Σ indicates that only nuclei in the solvent phase are summed over.

The particle and solvent structure factors appearing in Eq. (2.15) are explicitly defined as

$$\begin{aligned}S_c^p(q)=1+(N_c^p\overline{b_{pc}^2})^{-1}\sum_\alpha\sum_\beta b_\alpha b_\beta\Big\langle\int_p\int_p\rho_\alpha(\mathbf{r}')\rho_\beta(\mathbf{r}'')\\ \times[g_{\alpha_\beta}^p(\mathbf{r}',\mathbf{r}'')-1]\exp(i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r}''))d\mathbf{r}'\,d\mathbf{r}''\Big\rangle_\Omega ,\end{aligned} \tag{2.18}$$

$$\begin{aligned}S_c^s(q)=1+(\overline{b_{sc}^2})^{-1}\sum_\alpha\sum_\beta b_\alpha b_\beta x_\alpha^s x_\beta^s\rho^s\\ \times\int_s\int_s[g_{\alpha_\beta}^s(r)-1]\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r},\end{aligned} \tag{2.19}$$

where x_α^s is a solvent atom fraction and ρ^s is the total solvent atom number density. This expression for $S_c^s(q)$ is now equivalent to that for a bulk multicomponent fluid [14]. The cross correlation structure factor $H_c(q)$ is defined as

$$\begin{aligned}H_c(q)=(N_c^s\overline{b_{sc}}N_c^p\overline{b_{pc}})^{-1}\sum_\alpha\sum_\beta b_\alpha b_\beta\\ \times\rho_\alpha^s\Big\langle\int_s\int_p\rho_\beta(\mathbf{r}'')[g_{\alpha_\beta}^{sp}(\mathbf{r}',\mathbf{r}'')-1]\\ \times\exp(i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r}''))d\mathbf{r}'\,d\mathbf{r}''\Big\rangle_\Omega ,\end{aligned} \tag{2.20}$$

where $\mathbf{r}'$ always lies within V_c^s and $\mathbf{r}''$ always lies within V_c^p. Although the integrations in Eq. (2.20) include the full particle and solvent volumes in the cell, the effective range of integration in each phase is limited to a thin zone flanking the particle-solvent interface, since both $\mathbf{r}'$ and $\mathbf{r}''$ must be close to the interface to have $g_{\alpha_\beta}^{sp}\neq 1$. This term thus has the character of a thin shell scatterer and should be less important than either $S_c^p(q)$ or $S_c^s(q)$. Based on results for bulk atomic liquids and clusters [14,15], $S_c(q)$ will not be important at the small q values for which scattering is dominated by the particle form factor, and will be observable only at larger q. In aerosol applications, the solvent (gas) density is very low, and the $S_c^s(q)$ and $H_c(q)$ terms are negligible. Standard treatment of experimental data by subtraction of the scattered intensity from particle free solvent would in any case eliminate the contribution from $S_c^s(q)$. This leaves only the $S_c^p(q)$ term at high q and raises the interesting possibility of its experimental measurement, which has also been suggested for small atomic clusters by Fosmire and Bulgac [15]. Thus the main intracell contribution to the observable scattered intensity becomes

$$I_c(q)=V^{-1}[P_c(q)+N_c^p\overline{b_{pc}^2}S_c^p(q)], \tag{2.21}$$

where the particle form factor is defined as

$$P_c(q)=\langle f_c^2(\mathbf{q})\rangle_\Omega . \tag{2.22}$$

C. Interparticle terms

To complete this formal development, the intercell correlation terms defined by Eq. (2.4) must be considered. Except for a tiny fraction of solvent sites (those lying very close to the boundary of two adjacent cells), distances between sites in different cells will be too large to exhibit atomic level correlation effects. Thus only particle-particle correlations are of potential importance, and we may proceed along the lines of earlier authors [9–13] to analyze them. First, recalling that in Eq. (2.4) $\mathbf{r}_j$ refers only to nuclei in cell c and $\mathbf{r}_k$ refers only to those in cell d, these vectors may be replaced by the sum of two new vectors,

$$\mathbf{r}_j = \mathbf{R}_c + \mathbf{X}_j, \tag{2.23}$$

where $\mathbf{R}_c$ is the center of mass vector of the particle in cell c, and $\mathbf{X}_j$ is the position of nucleus j relative to the center of mass. With this substitution, Eq. (2.4) may immediately be rewritten as

$$I_{cd}(q) = V^{-1}\langle f_c(\mathbf{q}) f_d^*(\mathbf{q}) \exp(i\mathbf{q}\cdot(\mathbf{R}_c - \mathbf{R}_d))\rangle, \tag{2.24}$$

where several terms involving the solvent form amplitude f_c^s have been dropped for reasons similar to those used in simplifying Eq. (2.10). This equation is quite general, applying to polydisperse systems of particles of any shape, but an analysis of it that accounts for orientational correlations between different particles is not needed in the present case. The liquid aerosol particles studied recently [3,4] are large enough (radius ~ 10 nm) that the action of surface tension should ensure a spherical shape, at least on average. For spherical particles, the form amplitudes depend only on the magnitude of $\mathbf{q}$, and they may be factored from the angular brackets in Eq. (2.24). The particles now differ only in their size and compositional structure (average composition and density profiles). Let there be N_l particles of type l and N_m of type m, etc. in the volume V, and let n_l be the number density of type l particles, $n_l = N_l/V$. The sums over cells in Eq. (2.2) may now be rewritten as sums over particle types, and the total scattered intensity may then be put into the form

$$I_0(q) = \sum_l n_l N_l^p \overline{b_{pl}^2} S_l^p(q) + nP(q) S_i(q), \tag{2.25}$$

where N_l^p, $\overline{b_{pl}^2}$, and $S_l^p(q)$ now refer to a particular particle type, but their meanings are otherwise the same as before. In the second term of Eq. (2.25), which is dominant at lower q, n is the total particle density N/V, $P(q)$ is the number average particle form factor,

$$nP(q) = \sum_l n_l P_l(q), \tag{2.26}$$

where $P_l(q)$ is defined similarly to Eq. (2.22), and $S_i(q)$ is an interparticle structure factor defined as

$$S_i(q) = 1 + (P(q))^{-1} \sum_l \sum_m x_l x_m f_l(q) f_m^*(q) n \times \int (g_{lm}(R) - 1) \exp(i\mathbf{q}\cdot\mathbf{R}) d\mathbf{R}, \tag{2.27}$$

where x_l $(= n_l/n)$ is the fraction of type l particles in the system, and $g_{lm}(R)$ is the usual pair distribution function [12] for a particle of type l and another of type m whose centers are separated by the distance R. The aerosols investigated so far have had relatively narrow size distributions that are fit well by a Gaussian with a standard deviation of about 25% of the mean particle radius [3,4]. For pure particles, or if a similar spread of compositional variations is assumed for mixed particles, it should be reasonable to use what is sometimes called the decoupling approximation and replace $g_{lm}(R)$ by a mean $g(R)$ that is independent of the types of particles. In this case, $S_i(q)$ simplifies to the following well-known results [9–13]

$$S_i(q) = 1 + B(q)[S(q) - 1], \tag{2.28}$$

where

$$S(q) = 1 + n \int (g(R) - 1) \exp(i\mathbf{q}\cdot\mathbf{R}) d\mathbf{R}, \tag{2.29}$$

and

$$B(q) = \sum_l \sum_m x_l x_m f_l(q) f_m^*(q) / P(q). \tag{2.30}$$

D. Aerosol considerations

The total scattered intensity given by Eq. (2.25) contains contributions from both intraparticle scattering and interparticle correlations. Because the aerosols under consideration here are so dilute, the mean interparticle separation will be about 10^3 nm. Thus the main contribution from $S_i(q)$ should occur at values of q two orders of magnitude smaller than those of experimental interest [3,4], and in the q region of interest it is expected that $S_i(q) \approx 1$. In the future, this assumption will be checked by more thorough calculations of $S_i(q)$. Since the interparticle correlations are very weak, the scattered intensity should be very well approximated by just the contributions from individual particles, and if the high q contributions from the S_l^p terms are also neglected, Eq. (2.25) reduces to

$$I_0(q) = nP(q). \tag{2.31}$$

This relatively simple result for $I_0(q)$ is one of the basic working equations for the analysis of aerosol SANS experiments.

In Sec. III, where the effects of aerosol flow on the scattered intensity are treated, the small q expansion of Eq. (2.31) is needed. To simplify the analysis of the interparticle correlation terms, the particles were assumed to be spherical, but since these terms do not affect the total scattering, no such restrictions apply to Eq. (2.31), which holds generally. It suffices to consider only the behavior of $P_l(q)$. After Eq. (2.11) is substituted into Eq. (2.22) and a random average is performed over all orientations of $\mathbf{r}$ $(= \mathbf{r}' - \mathbf{r}'')$ with respect to $\mathbf{q}$, $P_l(q)$ is given by a general result known as the Debye equation [1,16]:

$$P_l(q)=\int_{V_l}\int_{V_l}\Delta\rho_b(\mathbf{r}')\Delta\rho_b(\mathbf{r}'')\frac{\sin qr}{qr}d\mathbf{r}'\,d\mathbf{r}''. \tag{2.32}$$

The integrals are taken over the volume of the particle, V_l, defined as the region in which $\Delta\rho_b\neq 0$. Now expand $\sin qr$ to obtain another familiar and general result [1] to leading order in q^2,

$$P_l(q)=(V_l\overline{\rho_{bl}})^2(1-q^2r_{Gl}^2/3), \tag{2.33}$$

where the radius of gyration r_{Gl} for a particle of type l is defined as

$$r_{Gl}^2=(V_l\overline{\rho_{bl}})^{-1}\int_{V_l}\Delta\rho_b(\mathbf{r}_1)r_1^2\,d\mathbf{r}_1. \tag{2.34}$$

The position vector $\mathbf{r}_1$ in Eq. (2.34) is measured from the center of ''mass'' $\mathbf{r}_0$ of the particle defined as $\mathbf{r}_0=(V_l\overline{\rho_{bl}})^{-1}\int_{V_l}\Delta\rho_b(\mathbf{r}')\mathbf{r}'\,d\mathbf{r}'$, where the origin for $\mathbf{r}'$ [and $\mathbf{r}''$ in Eq. (2.32)] is arbitrary. Finally, the mean scattering length density $\overline{\rho_{bl}}$ appearing in the above equations is defined as

$$V_l\overline{\rho_{bl}}=\int_{V_l}\Delta\rho_b(\mathbf{r}_1)d\mathbf{r}_1. \tag{2.35}$$

III. SCATTERED INTENSITY WITH FLOW

The aerosol particles are now assumed to move with a speed v_p in the positive x direction of a right-handed three-dimensional Cartesian coordinate system with the scattering volume at the origin. Neutrons, moving with speed v_n, approach the particles from the negative z direction and are scattered into the positive z direction. The scattering direction in the LAB frame is defined by the polar angle θ with respect to the LAB z axis, and by the azimuthal scattering angle ϕ measured from the x axis in the detector plane. As shown in the Appendix, for this right-angle crossed beam geometry the LAB scattered intensity I is related to the scattered intensity I_0 in the COM frame by the equation

$$I(q)=I_0(q_0)\frac{(\xi+\sqrt{1+\xi^2})^2}{\sqrt{1+\xi^2}}, \tag{3.1}$$

where

$$\xi=s\sin\theta\cos\phi, \tag{3.2}$$

and

$$s=v_p/v_n. \tag{3.3}$$

The parameter ξ contains both the particle-to-neutron speed ratio s and $\cos\phi$ as key factors. The momentum transfer magnitudes, q and q_0, in the respective LAB and COM frames are equal, and are expressed in laboratory variables as

$$q^2=q_0^2=2k^2[1+(\xi-\cos\theta)(\xi+\sqrt{1+\xi^2})], \tag{3.4}$$

where the incident neutron wave vector k is related to the neutron wavelength λ in the usual way:

$$k=2\pi/\lambda. \tag{3.5}$$

Equations (3.1)–(3.4) are valid for the elastic scattering of neutrons by very massive aerosol particles. They are used extensively in analyzing the experimental aerosol SANS data [3,4], a task requiring that the value of s be known. One way to determine s is by a Guinier analysis [1,5] of the small q behavior of $I(q)$, in which one plots the logarithm of the scattered intensity versus q^2. At small q the plot is linear, with a slope that is ordinarily proportional to the radius of gyration. Here the slope also depends on s.

For fixed λ, small q is equivalent to very small values of θ and, hence, ξ, since the speed ratio s never exceeds 2 in the experiments [3,4]. Thus we use Eqs. (2.26), (2.31), and (2.33), and expand Eq. (3.1) for small values of q and ξ to obtain, in lowest order,

$$I(q)=I(0)[1-q^2r_G^2/3][1+2\xi+3\xi^2/2], \tag{3.6}$$

where the (extrapolated) scattered intensity at $q=0$ is

$$I(0)=\sum_l n_l(V_l\overline{\rho_{bl}})^2, \tag{3.7}$$

and the effective radius of gyration is

$$r_G^2=\sum_l n_l(V_l\overline{\rho_{bl}}r_{Gl})^2. \tag{3.8}$$

Since q itself depends on the as yet unknown particle velocity, it is not a useful independent variable. To surmount this difficulty, we expand Eq. (3.4) for small θ to find

$$q^2=q_i^2(1+\xi+s^2\cos^2\phi), \tag{3.9}$$

where q_i is the nominal momentum transfer wave vector based on the incident (i) neutron wavelength,

$$q_i=(4\pi/\lambda)\sin(\theta/2). \tag{3.10}$$

One can also think of q_i as the value of q for stationary aerosol particles $(v_p=0)$. After combining Eqs. (3.6) and (3.9) and neglecting unimportant higher terms, we obtain

$$\frac{I(q_i)}{I(0)}=1+2\xi+\frac{3\xi^2}{2}-\frac{q_i^2r_G^2}{3}(\xi+(1+2\xi)(1+s^2\cos^2\phi)) \tag{3.11}$$

for the explicit velocity dependence of the scattered intensity at small q_i. An important feature of this equation is the $\cos^2\phi$ term, which strongly affects the shape of the anisotropic scattering pattern. It also affects the slope in Guinier plots based on data point averaging procedures that eliminate odd powers of $\cos\phi$.

After averaging Eq. (3.11) to find the averaged intensity $\overline{I}(q_i)$, we expand $\ln\overline{I}(q_i)$ to find

$$\ln\overline{I}(q_i)=\ln I(0)-q_i^2r_G^2[1+(1-9(\lambda/\pi r_G)^2/8)as^2]/3, \tag{3.12}$$

where

$$a=\overline{\cos^2\phi},\tag{3.13}$$

and the overbar represents any average for which $\overline{\cos^p\phi}=0$ for odd p. Since θ is very small, $\sin\theta$ was replaced by $q_i\lambda/(2\pi)$ using Eq. (3.10) to obtain Eq. (3.12). This result shows that a Guinier plot of $\ln\overline{I}(q_i)$ versus q_i^2 yields a velocity dependent slope whose value depends on the type of average performed. For example, a circular average (c) over the azimuthal angle ϕ at constant θ (or q_i) yields the value $a_c=1/2$, and a ''horizontal'' average (h), taken by averaging pairs of intensities at $\phi=0$ and π, gives $a_h=1$. One can then solve the resulting pair of equations to find the values of r_G^2 and s^2 from the two slopes. However, for essentially all particle sizes of interest we have $(\lambda/\pi)^2\ll r_G^2$, and Eq. (3.12) simplifies to the form

$$\ln\overline{I}(q_i)=\ln I(0)-q_i^2r_G^2(1+as^2)/3,\tag{3.14}$$

in which the λ^2 term is gone. The ratio of any two Guinier slopes is now independent of r_G^2 and depends only on the known a values and on the unknown s^2, which can then be determined much more easily. It is clear that, to find s by these means, no assumptions about the shape, composition, uniformity, and size distribution of the particles are required. Recently, this method was used to experimentally determine the particle velocity [4].

IV. SUMMARY AND CONCLUSIONS

A theoretical formalism for neutron scattering was analyzed for application to the interpretation of crossed beam aerosol SANS experiments. To treat the Doppler shift in the scattered neutron momentum, the kinematic theory of two body scattering was put into a form that is directly applicable to the experimental crossed beam scattering geometry. The theory correctly predicts the observed anisotropy in the scattered neutron intensity in the LAB frame due to the Doppler shift [3,4]. Furthermore, with a Guinier analysis of the scattered intensity in the low q region, it was shown how the anisotropy in the signal can be exploited to measure the actual particle velocity.

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APPENDIX: KINEMATICAL SCATTERING THEORY

To interpret the measured scattered intensity properly, it is necessary to relate the differential scattering cross sections for the COM and LAB frames. This task requires that q be expressed in terms of laboratory variables and parameters for the appropriate scattering geometry. It also involves properly accounting for the differences in solid angles subtended at the detector by the scattered neutrons as viewed in the COM and LAB frames. Much of Sears's [17] notation will be used, and his kinematic analysis will be followed initially. Only elastic scattering will be considered.

The absolute scattered neutron intensity (units are cm^{-1}) in the LAB frame, $I(\theta,\phi)$, is defined as

$$I(\theta,\phi)=\frac{1}{V}\frac{d\sigma}{d\Omega},\tag{A1}$$

where θ is the usual LAB scattering angle; ϕ is the azimuthal scattering angle measured in the detector plane from the x axis, which coincides with the direction of particle motion; V is the scattering volume; and $d\sigma/d\Omega$ is the differential scattering cross section for the aerosol particles measured in the LAB frame. Note that, as defined here, σ is directly proportional to the total number of aerosol particles in V. Thus the quantity $I(\theta,\phi)d\Omega$ represents the total number of neutrons scattered into the differential solid angle $d\Omega(\theta,\phi)(=\sin\theta d\theta d\phi)$ normalized by the scattering volume and the incident neutron flux J.

In the LAB frame, the neutrons and aerosol particles are moving, respectively, with velocities $\mathbf{v}_n$ and $\mathbf{v}_p$ before the collision, and J simply equals the product of the average number density of neutrons in the beam, c, and the LAB neutron speed

$$J=cv_n=c|\mathbf{v}_n|.\tag{A2}$$

Quantities in the COM frame will be designated with the subscript ''0.'' Because the absolute number of scattered neutrons in the two frames must be identical, the differential scattering cross sections in the two frames are related by

$$J\frac{d\sigma}{d\Omega}d\Omega=J_0\frac{d\sigma_0}{d\Omega_0}d\Omega_0,\tag{A3}$$

where J_0 depends on v, the relative speed of the neutrons and aerosol particles:

$$J_0=cv=c|\mathbf{v}_n-\mathbf{v}_p|.\tag{A4}$$

To relate I and I_0, we combine Eqs. (A1) and (A3) to find

$$I=I_0\frac{J_0}{J}\frac{d\Omega_0}{d\Omega},\tag{A5}$$

where

$$I_0=\frac{1}{V}\frac{d\sigma_0}{d\Omega_0}.\tag{A6}$$

Equation (A5) is useful because I_0 is only a function of θ_0, the COM scattering angle and is relatively easy to calculate. To use Eq. (A5) it is necessary to express θ_0 in terms of LAB variables and to evaluate $d\Omega_0/d\Omega$. To do this, we use an algebraic approach based on the conservation of momentum and energy [17].

In the LAB frame, the wave vectors $\mathbf{k}$ and $\mathbf{K}$ of the neutrons and aerosol particles, respectively, are defined as

$$\hbar\mathbf{k}=m_n\mathbf{v}_n,\tag{A7}$$

$$\hbar\mathbf{K}=m_p\mathbf{v}_p,\tag{A8}$$

where m_n and m_p are the neutron and particle masses, respectively, and $\hbar$ is Planck's constant divided by 2π. With a prime denoting values after the collision, the conservation of momentum and energy are simply expressed as

$$\mathbf{k}+\mathbf{K}=\mathbf{k}'+\mathbf{K}' \tag{A9}$$

and

$$\frac{k^2}{m_n}+\frac{K^2}{m_p}=\frac{(k')^2}{m_n}+\frac{(K')^2}{m_p}. \tag{A10}$$

In the COM frame, the scattering problem reduces to the motion of a single particle with reduced mass μ,

$$\mu=m_n m_p/(m_n+m_p), \tag{A11}$$

with wave vectors $\mathbf{k}_0$ and $\mathbf{k}_0'$ before and after the collision:

$$(m_n+m_p)\mathbf{k}_0=m_p\mathbf{k}-m_n\mathbf{K}, \tag{A12}$$

$$(m_n+m_p)\mathbf{k}_0'=m_p\mathbf{k}'-m_n\mathbf{K}'. \tag{A13}$$

To evaluate $d\Omega_0/d\Omega$, we borrow an argument from Sears (p. 31) [17]. First, we substitute Eq. (A9) into Eq. (A13) to obtain

$$\mathbf{k}_0'=\mathbf{k}'-\mu(\mathbf{k}+\mathbf{K})/m_p. \tag{A14}$$

Since $\mathbf{k}$ and $\mathbf{K}$ are constant vectors, any change in $\mathbf{k}'$ produces a corresponding change in $\mathbf{k}_0'$, and the differential wave vector volume elements d^3k' and d^3k_0' must be equal. If we use spherical coordinates appropriate to the LAB and COM frames, this equality takes the form

$$(k')^2 dk'\, d\Omega=(k_0')^2\, dk_0'\, d\Omega_0, \tag{A15}$$

from which we see that

$$\frac{d\Omega_0}{d\Omega}=\left(\frac{k'}{k_0'}\right)^2\frac{dk'}{dk_0'}. \tag{A16}$$

At this point, we depart from Sears's analysis and express k' and k_0' in terms of k and K, the incident neutron and particle momenta in the LAB frame. To do this, we first use Eq. (A9) to form the dot product of $\mathbf{K}'$ with itself. After substituting this result into Eq. (A10) and noting for our right-angle crossed beam and detector geometries that $\mathbf{k}\cdot\mathbf{K}=0$, $\mathbf{k}\cdot\mathbf{k}'=kk'\cos\theta$, and $\mathbf{k}'\cdot\mathbf{K}=k'K\sin\theta\cos\phi$, we find a quadratic equation for k' that yields the physical root

$$k'=\kappa+(\kappa^2+uk^2)^{1/2}, \tag{A17}$$

where

$$\kappa=(\mu/m_p)(k\cos\theta+K\sin\theta\cos\phi) \tag{A18}$$

and

$$u=(m_p-m_n)/(m_n+m_p). \tag{A19}$$

Next, since $\mathbf{k}\cdot\mathbf{K}=0$, from Eq. (A14) we obtain

$$(k_0')^2=(k')^2-2k'\kappa+(\mu/m_p)^2(k^2+K^2), \tag{A20}$$

from which it follows that

$$k_0'\frac{dk_0'}{dk'}=k'-\kappa. \tag{A21}$$

Equations (A16) and (A21) are equivalent to earlier results obtained mainly by geometric arguments [6,7]. Once Eqs. (A16), (A17), and (A21) are substituted into Eq. (A5), the desired relationship between I and I_0 can be obtained with just a few more simplifications. We first note that for elastic collisions, energy conservation in the COM frame implies that $k_0'=k_0$. [This result may also be demonstrated explicitly using Eqs. (A9), (A10), (A12), and (A13)]. We then observe that Eqs. (A2) and (A4) for the LAB and COM neutron fluxes can be rewritten as $J=\hbar nk/m_n$ and $J_0=\hbar nk_0/\mu$. Using these three simple relations, Eq. (A5) finally emerges as

$$I=I_0\frac{m_n}{\mu}\left(\frac{k'}{k}\right)^2\frac{k}{\sqrt{\kappa^2+uk^2}}, \tag{A22}$$

which is an exact result for elastic scattering that is limited only by the assumption of a specific geometry for the incident neutron and particle beams $(\mathbf{k}\cdot\mathbf{K}=0)$. This assumption can easily be relaxed if desired.

With the help of Eqs. (A7), (A8), (A17), and (A18), Eq. (A22) provides all of the geometric corrections needed to understand the laboratory scattering intensity. What remains is to treat the additional anisotropy that arises when I_0 is expressed as a function of laboratory variables. Scattering in the COM frame is isotropic, depending only on the COM scattering angle θ_0, but θ_0 itself is a function of both laboratory scattering angles. For the systems under consideration here, I_0 is only a function of q_0, the magnitude of the momentum transfer wave vector $\mathbf{q}_0$, defined as

$$\mathbf{q}_0=\mathbf{k}_0-\mathbf{k}_0'. \tag{A23}$$

From Eqs. (A23), (A7), (A8), and (A12), and the definition of θ_0,

$$\mathbf{k}_0\cdot\mathbf{k}_0'=k_0^2\cos\theta_0, \tag{A24}$$

it follows that

$$k_0=\mu v/\hbar \tag{A25}$$

and

$$q_0=2k_0\sin(\theta_0/2). \tag{A26}$$

Naturally, q_0 depends on the reduced mass and the relative speed v of the neutrons and aerosol particles.

To express q_0 in terms of the laboratory scattering angles, we substitute Eqs. (A12) and (A13) into Eq. (A23), and use Eq. (A9) to eliminate $\mathbf{K}$ and $\mathbf{K}'$. The result, which is readily apparent on physical grounds, is that the momentum transfer wave vector in the LAB frame $\mathbf{q}$ is identical to $\mathbf{q}_0$:

$$\mathbf{q}_0=\mathbf{q}=\mathbf{k}-\mathbf{k}'. \tag{A27}$$

We next evaluate q^2 from Eq. (A27), using Eqs. (A17) and (A18), to obtain

$$q^2=k^2[1+u+2(\xi-\cos\theta)(\xi+(u+\xi^2)^{1/2})], \tag{A28}$$

where

$$\xi = \kappa / k. \tag{A29}$$

An explicit functional relationship between the COM (θ_0) and LAB (θ, ϕ) scattering angles is readily obtained by equating q_0 [Eq. (A26)] with q [from Eq. (A28)]. In the special case of stationary target particles, this relationship reduces to the well-known result [18] $\tan\theta = \sin\theta_0 / (\cos\theta_0 + m_n / m_p)$.

When we work in the massive particle limit, $m_p \gg m_n$, which is appropriate in the present situation, we find that $u = 1$ and ξ reduces to

$$\xi = (v_p / v_n) \sin\theta \cos\phi. \tag{A30}$$

In this limit, Eqs. (A22) and (A28) simplify to the results presented in Sec. III. With Eq. (A30), it is also easy to see that the Doppler shift in scatterered neutron momentum vanishes for scattering orthogonal to the direction of particle motion ($\phi = \pm \pi/2$).

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