X-Ray Determination of the Orientational Distribution Function of Rod-Shaped Particles

In an important recent Letter,[1] Oldenbourg *et al.* determined the orientational distribution function (ODF) of rod-shaped tobacco-mosaic-virus (TMV) particles in solution from their small-angle x-ray diffraction pattern. They derived an integral equation relating the ODF, $f(\Gamma)$, to the measured intensity distribution $G(\Psi)$ along equatorial arcs in the pattern. A solution of this equation yields, in principle, $f(\Gamma)$ in terms of $G(\Psi)$. The equation could not, however, be solved analytically, and a model $f(\Gamma)$ had to be assumed. While the model proved to be an excellent choice in this case, an analytic solution, being unbiased and general, would be preferable. Furthermore, closely related equations have been used to determine experimentally the ODF of fibers[2] and both monomeric and polymeric thermotropic liquid crystals.[3] In all these cases the only requirement is that the intensity distribution $G(\Psi)$ due to *single*-particle scattering is measurable, and that it is free from interparticle interference effects. Indeed, such an equation could be applied to other systems composed of partially aligned, rodlike particles. One such system, grafted rods,[4] was extensively studied theoretically and arguably[5] exhibits subtle variations in the order parameter as a function of the grafting density, which may indicate a "standing up" phase transition. Thus, an analytic solution should find a wide range of applications. Such a solution has now been obtained. The derivation is outlined below and closed-form expressions for $f(\Gamma)$ and the order parameter S are given.

The equation relating the measured $G(\Psi)$ with $f(\Gamma)$ is[1]

$$G(\Psi)=\int_0^{\pi/2} I_s(\omega)f(\Gamma)\sin\omega\, d\omega\,, \tag{1}$$

where ω and Γ are the angles of the rod axis relative to the x-ray beam and the mean axis of ordering, respectively. Ψ is the angle from the equator of the diffraction pattern (see Fig. 1 in Ref. 1) and $I_s(\omega)$ is the single-particle scattering form factor. For the conventional scattering geometry[1] $\cos\Gamma=\cos\psi\sin\omega$. Changing variables in Eq. (1) first by $\omega\rightarrow\Gamma$ then by $\cos\Psi\rightarrow y$ and $\cos\Gamma\rightarrow r$ yields after some manipulations an Abel-type integral equation which can be solved[6] to give

$$f(\Gamma)=2[\pi J_s(\Gamma)\cos\Gamma]^{-1}\frac{d}{d(\cos\Gamma)}\int_0^{\cos\Gamma}[G(\Psi)/K_s(\Psi)](\cos^2\Gamma-\cos^2\Psi)^{-1/2}\cos\Psi\, d(\cos\Psi)\,. \tag{2}$$

The derivation requires that $I_s(\omega)\equiv I_s(\Gamma,\Psi)=J_s(\Gamma)\times K_s(\Psi)$. TMV in solution, as well as the other physical systems discussed above,[2,3] conforms to this requirement as do all thin rods having a uniform electron density. In this case[1] $I_s(\omega)=A/\sin\omega$ so that $J_s(\Gamma)=A/\cos\Gamma$ and $K_s(\Psi)=\cos\Psi$.

The nematic order parameter S can now be evaluated directly from the measured $G(\Psi)$ data, using Eq. (2) without having to calculate $f(\Gamma)$ explicitly. This yields, for $I_s(\omega)=A/\sin\omega$,

$$S=\langle P_2\rangle=-2\frac{\int_0^{\pi/2}G(\Psi)P_2(\sin\Psi)\cos\Psi\, d\Psi}{\int_0^{\pi/2}G(\Psi)\cos\Psi\, d\Psi}\,, \tag{3}$$

where P_2 is the second-order Legendre polynomial. Similar expressions can be derived for higher-order parameters $\langle P_l\rangle$. The numeric evaluation of Eqs. (2) and (3) for a *discrete* set of measured $G(\Psi)$ values can best be done analytically, using a functional representation such as splines or orthogonal polynomials fitted to the measured $G(\Psi)$ values.[7] Further details of the derivation of the equations above will be given elsewhere.

Using the Gaussian-model $f(\Gamma)$ of Ref. 1, Eq. (1) can be integrated directly to yield $G(\Psi)=A\exp(\beta)I_0(\beta)$, where $\beta=(\cos\Psi/2\alpha)^2$, I_0 is the modified Bessel function of order zero, and α is the width parameter of $f(\Gamma)$. These model $G(\Psi)$ and $f(\Gamma)$ can be used to check the validity of Eqs. (3) and (2) above. Finally, with the availability of a closed-form expression for $G(\Psi)$, the use of the truncated series expansion, Eq. (3) in Ref. 1, is not required, although, as discussed in Ref. 1, for the range of α concerned it closely approximates the exact result. We also note that the series can be obtained by using the asymptotic expansion[8] for I_0, in which case $\alpha'=\alpha$.

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