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New Functionality in CORFUNC

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Introduction

CORFUNC is the CCP13 program suite for correlation function analysis [1]. Fundamentally, a correlation function describes how the density varies with distance along a given direction in a sample, for example a semi-crystalline polymer. Parameters that characterise the microstructure of the sample may then be derived from it.

In soft condensed matter science there are analogous functions that describe how the density, or volume fraction, of an adsorbate (such as a surfactant or polymer) varies with distance along the direction normal to an interface (such as the surface of a colloidal particle). This is illustrated schematically in Figure 1.

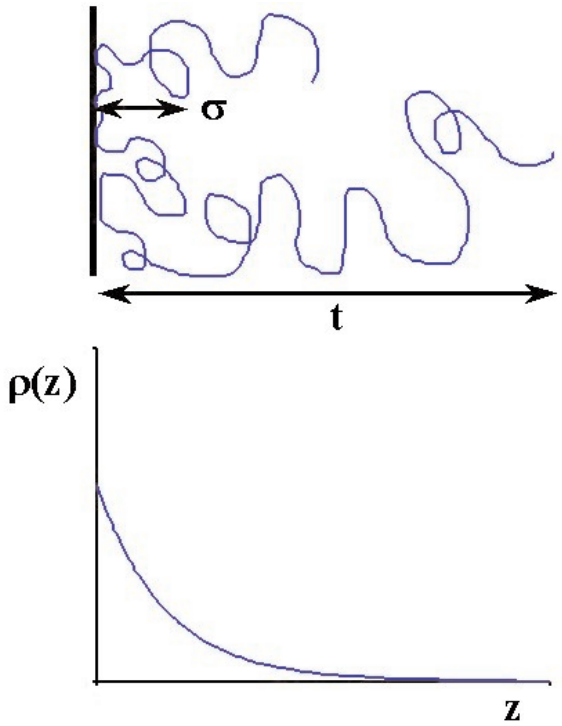

Figure 1: Schematic representation of a polymer molecule adsorbed at a solid interface and the resulting volume fraction profile.

These functions are called the *segment density distribution and volume fraction profile*, respectively, and experimentally are most conveniently measured by "Solution" Small-Angle Neutron Scattering (SANS). Examples of the sort of colloidal system for which this type of analysis is routinely conducted are dispersions of sterically stabilised pigment particles (such as are found in paint), or dispersions of sterically stabilised liquid emulsion droplets (such as are used in cosmetic, food or pharmaceutical formulations).

The volume fraction profile, $\Phi(z)$, and the segment density distribution, $\rho(z)$, are inter-related through

$$\Phi(z) = \frac{\rho(z)\ \Gamma}{\Delta} \qquad (1)$$

where Γ is the amount of surfactant/polymer adsorbed (with dimensions of mass per unit area) and Δ is the bulk density of the adsorbate (as mass per unit volume).

$\Phi(z)$ provides the most detailed description of the average internal structure of an adsorbed layer [2, 3]. In addition to showing how the adsorbate is arranged in the vicinity of the interface, it also allows several measures of the layer thickness, the adsorbed amount (from the integral under the curve) and the average fraction of segments "bound" at the interface (from the segment density within, say, the first nm) to be derived.

The Scattering from Adsorbed Layers

The SANS from a dispersion of colloidal particles (which are assumed to be spherical) with adsorbed layers may be written

$$\frac{\partial \Sigma}{\partial \Omega}(Q) = N_p\ P(Q)\ S(Q) + B \qquad (2)$$

where N_p is the number concentration of particles, *S(Q) is the interparticle structure factor* and *B* is the background signal. *P(Q)*, the *form or shape factor*, may then be expressed as [4, 5, 6]

$$P(Q) = \left[(\rho_p - \rho_m)\ F_p(Q) + (\rho_l - \rho_m)\ F_l(Q)\right]^2 \qquad (3)$$

where ρ is the neutron scattering length density (with dimensions of length^{-2}) with the subscript "m" signifying the dispersion medium and the subscript "1" the adsorbed layer, $F_p(Q)$ represents the *intraparticle form factor for the core particle and* $F_l(Q)$ represents the *intralayer form*

factor for the adsorbed polymer. $(d\Sigma/d\Omega)(Q)$ thus has dimensions of (length)$^{-1}$ and is normally expressed in absolute units of cm^{-1}. In this type of experiment it is usually arranged that S(Q) and *B* make a minimal contribution to $(d\Sigma/d\Omega)(Q)$; e.g. $N_p < 5\%$ and there is little or no free polymer in the dispersion medium.

If the curvature of the interface is small compared to Q, that is, if $QR_p >> 1$, then the bracketed term in Equation 3 may be expanded to give

$$P(Q) = \left[(\rho_p - \rho_m)^2 F_p(Q)^2\right] + \tag{4a}$$

$$\left[2(\rho_p - \rho_m)(\rho_l - \rho_m) F_p(Q) F_l(Q)\right] + \tag{4b}$$

$$\left[(\rho_l - \rho_m)^2 F_l(Q)^2\right] \tag{4c}$$

from which it can be seen that Equation 4a (here called $I_{pp}(Q)$, but also called $I_2(Q)$ or I_{gg}(Q) in the literature) describes the contribution to $P(Q)$ arising from the core particle, Equation 4c (here called $I_{ll}(Q)$, but also called $I_0(Q)$ or $I_{pp}(Q)$ in the literature) describes the contribution from the adsorbed layer, and Equation 4b (here called $I_{pl}(Q)$, but also called $I_1(Q)$ or $I_{pg}(Q)$ in the literature) is a particle-surface interference term. These three terms may be written explicitly thus

$$I_{pp}(Q) = (\delta_p - \delta_m)^2 \frac{2\pi A_p}{Q^4}\left[1 + \frac{1}{Q^2 R_p^2}\right] \tag{5}$$

$$I_{pl}(Q) = (\delta_p - \delta_m)(\delta_l - \delta_m)\frac{4\pi A_p}{Q^4} \times \left[\int_0^t \rho(z)\cos(Qz)\,dz - QR_p \int_0^t \rho(z)\sin(Qz)\,dz\right] \tag{6}$$

$$I_{ll}(Q) = (\delta_l - \delta_m)^2 2\pi A_p \times \left[\frac{1}{Q^2}\left|\int_0^t \rho(z)\exp(iQz)\,dz\right|^2 + \tilde{I}_{ll}\right] \tag{7}$$

where A_p is the surface area per unit volume of a particle, t is the maximum extent of the adsorbed layer and $\tilde{I}_{ll}$ describes fluctuations in the adsorbed layer. $\tilde{I}_{ll}$ is generally unimportant except in a few special cases, su ch as in syste ms with densely grafted layers.

It will be noted that Equation 5 is simply a modified Porod law.

When the particles are at contrast match with the dispersion medium (i.e. $\rho_p = \rho_m$), $P(Q)$ in Equations 4a - 4c reduces to Equation 7. Unfortunately, because it is the *modulus* of the integral that is measured experimentally, the transformation of the term in the brackets is complicated by the need to introduce a phase factor, $\exp(i\varphi Q)$, where φ is unknown. Fortunately the particle surface can be u sed as a phase reference point since $\rho(z) = 0$ for $z < 0$. Equation 7 is thus a causal function and this allows φ to be determined using a dispersion integral relationship between $\partial\varphi/\partial Q$ and $\partial Ln\left|\int \rho(z)\exp(iQz)\,dz\right|/\partial Q$ [4, 5]. With a knowledge of φ, $\rho(z)$ can then obtained by Hilbert transformation of the $I_{ll}(Q)$ scattering data. This normally requires that the data first be extrapolated to both low and high Q to prevent Gibbs oscillations from otherwise being introduced through premature truncation.

This procedure always generates a *possible* $\rho(z)$ that is *model-independent*. Unfortunately, the Hilbert transformation is not guaranteed to produce a *unique* distribution and so back-transformation must be treated with caution.

It is possible to obtain $\rho(z)$ by Fourier transformation of *off-contrast* $I_{pl}(Q)$ data, but experimentally this procedure involves subtracting a large background from a small signal and is thus not particularly well-conditioned. The new routines incorporated into CORFUNC and which are described below assume that the input scattering data is *on-contrast* (i.e. at contrast match).

Analysis of the Volume Fraction Profile

Invariably one has a reasonable estimate of the adsorbed amount Γ from other techniques and this allows Φ(z) to be iteratively normalised to Equation 1 given that

$$\int_0^t \Phi(z)\,dz = \frac{\Gamma}{\delta} = M \tag{8}$$

The *n*-th moment of the volume fraction profile can then be defined as

$$\langle z^n \rangle = M^{-1}\int_0^t \Phi(z)\, z^n\, dz \tag{9}$$

from which the *root-mean-square thickness*, t_{rms} , and the *second moment about the mean* (or *standard deviation*), σ, of the volume fraction profile may be defined as

$$t_{rms} = \langle z^2 \rangle^{1/2} \tag{10}$$

$$\sigma = \left[\langle z^2 \rangle - \langle z \rangle^2\right]^{1/2} \tag{11}$$

respectively. Physically, σ provides an estimate of the average distance of the centre-of-mass of the adsorbed layer from the interface.

An additional parameter that can be determined is the

bound fraction, <*p*>, given by the expression:-

$$< p > \; = \; \int_0^l \Phi(z)\, dz \Big/ \int_0^t \Phi(z)\, dz \qquad (12)$$

This is the average fraction of segments in an adsorbed surfactant/polymer molecule that are "bound" to the interface. Although intuitively it may seem sensible to choose l to be the length of one segment, say, ≤ 0.5 nm, in practice it is better to choose a larger value in order to offset the effects of any interfacial inhomogeneities. By scaling experimental data from simple systems to simulated data from contemporary mean-field theories it has been suggested that one lattice layer in a simulation corresponds to a distance of 1.3 nm [2]. On this basis the software has been coded to take a more pragmatic approach and to use l = 1 nm.

Implementation within CORFUNC

The reason for choosing to add this new functionality to *CORFUNC* was quite simply that the program suite already included tried and tested data extrapolation routines of the sort necessary to pre-process scattering data from adsorbed layers prior to Hilbert inversion.

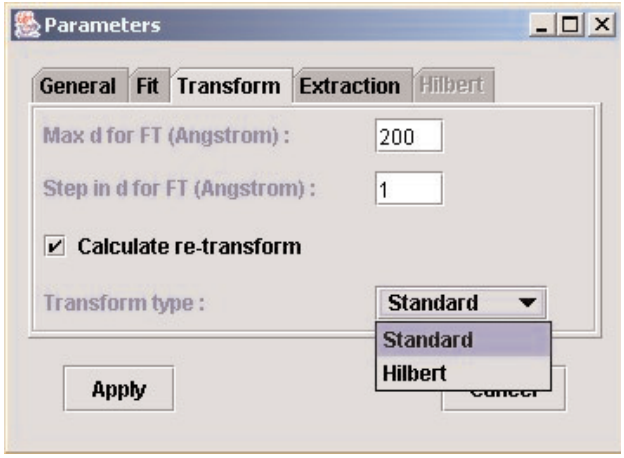

Figure 2: Two views of the new Edit - Parameters window showing how the transform type selection activates the Hilbert tab.

The software design principles necessary to incorporate the new analysis routines into *CORFUNC* have already been described [7]. Below the changes to the Graphical User Interface (GUI) are described.

The most noticeable change is the addition of an extra "tab", called **Hilbert**, to the **Edit** - **Parameters**… window. This tab is only activated if **Transform type** on the **Transform** tab is set to "Hilbert". At the same time the **Extraction** tab is disabled, see Figure 2.

To perform conventional correlation function analysis Transform type should be set to "Standard". CORFUNC will then operate as it has always done. But having selected "Hilbert" it is then necessary to enter parameters in the Hilbert tab, see Figure 3.

If the dimensions of the Q-axis are not identified correctly the normalisation of the volume fraction profile will be wrong. The Normalisation accuracy is the maximum acceptable difference between the specified Adsorbed amount and the integral of the volume fraction profile (see Equation 8).

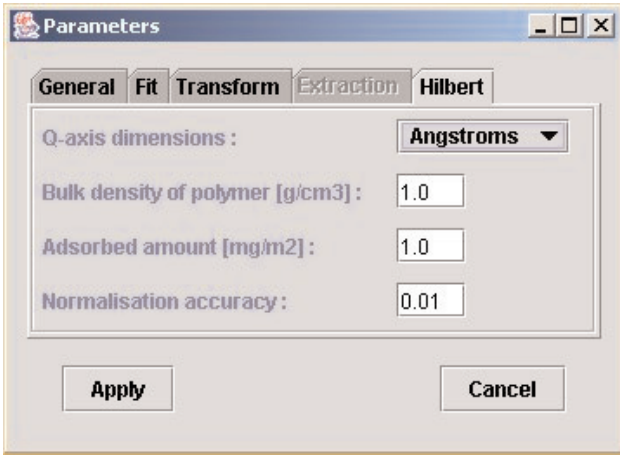

Figure 3: The Edit - Parameters - Hilbert tab.

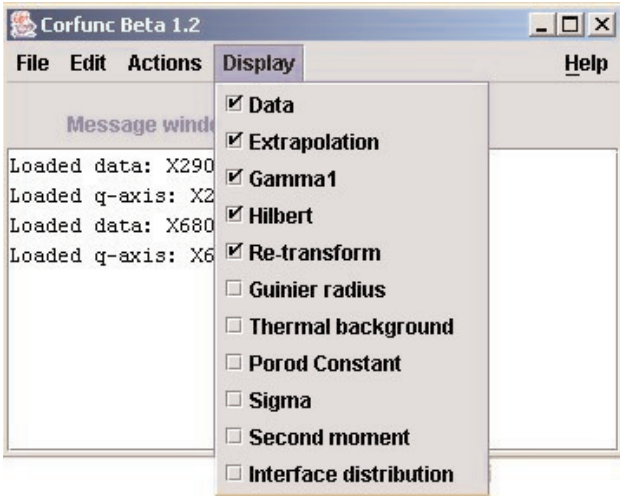

Figure 4: The Display menu.

The **Display** menu has also been updated, as shown in Figure 4. Only the **Data, Extrapolation** and **Hilbert** options have any meaning if **Transform type** is set to "Hilbert" (although the other options are not disabled).

Generating a Volume Fraction Profile

The sequence of actions necessary to generate a volume fraction profile is:

File ==> Load data...
File ==> Load q-axis...

At this point a graph of the data is drawn if **Data** *is checked in the* **Display** *menu, Figure 5.*

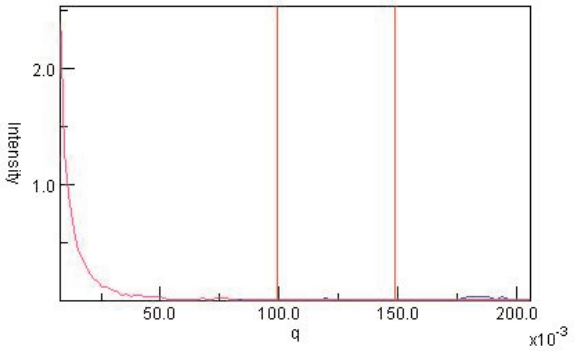

Figure 5: Typical SANS data from a sterically stabilised dispersion of colloidal particles (blue curve) overlaid by the extrapolation (purple curve).

Move the left-hand limit marker to q=0.

Move the central and right-hand limit markers to define the "tail" region of the data that is to be extrapolated to high-Q (in this example the region $50x10^{-3}$ < q < $100x10^{-3}$ would suffice).

Edit ==> Parameters...

General: select **Data scale:** "Absolute"
Fit: select **Back extrapolation:** "Guinier"
Fit: select **Tail fit:** "Porod"
Transform: uncheck **Calculate re-transform**
Transform: select **Transform type**: "Hilbert"
Hilbert: select **q-axis dimensions**
Hilbert: enter the **Bulk density**
Hilbert: enter the **Adsorbed amount**
Hilbert: enter the **Normalisation accuracy**
Click **Apply**

Actions ==> Extrapolate

At this point the extrapolated data will be drawn over the input data if **Extrapolation** *is checked in the* **Display** *menu, Figure 5.*

If the extrapolation is acceptable:

Actions ==> Transform

At this point another graph window will open displaying the volume fraction profile if **Hilbert** *is checked in the* **Display** *menu, Figure 6.*

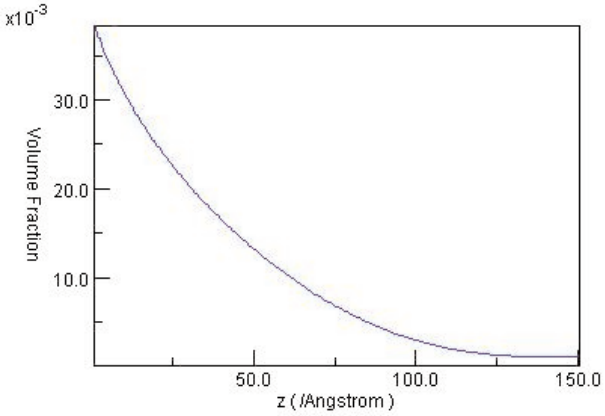

Figure 6: The volume fraction profile derived from the extrapolated SANS data in Figure 5.

Note that **Actions - Extract parameters** *has no meaningful effect when* **Transform type** *is set to* "Hilbert". *Analysis of the volume fraction profile, as described above, is performed automatically.*

Acknowledgements

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