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Some years ago Ciccariello *et al.*[1,2] have studied the effect of edges and contact points on the bulk scattering from two-phase media. Now there is a variety of systems, where the scattering length densities of the two media are equal, and only the interface scatters. Examples are foams or aqueous solutions of membrane-forming substances like surfactants and lipids. Another example is given by neutron scattering of microemulsions. If the scattering length densities of water and oil are matched by partial deuteration, only the surfactant film is observed.[3] Since many of the systems are expected to display singularities of the above mentioned type, it seems useful to supply the corresponding results for surface scattering.

We start with the definition of the surface correlation function.[4] Let $\delta_S^\epsilon(r)$ be the characteristic function for a thin sheet S^ϵ of uniform thickness ϵ approximating the surface S. For small ϵ, $\epsilon^{-1}\delta_S^\epsilon$ is an approximation to δ_S, the δ function concentrated on S. Then the surface correlation function is defined by

$$g_{ss}(\mathbf{r},\mathbf{r}') = \lim_{\epsilon \downarrow 0} \epsilon^{-2} \langle \delta_S^\epsilon(\mathbf{r}) \delta_S^\epsilon(\mathbf{r}') \rangle. \tag{1}$$

It can be proved[4] that g_{ss} is given by the following expression:

$$g_{ss}(|\mathbf{r},\mathbf{r}'|) = \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|^2} \frac{1}{V} \int_S dS \int_{C_{r,r'}} \frac{ds'}{|\hat{\mathbf{r}} \times \mathbf{n}'|}. \tag{2}$$

Here $\mathbf{r}$ ranges over S, $C_{r,r'}$ is the curve common to S and the sphere with center at $\mathbf{r}$ and radius $|\mathbf{r}-\mathbf{r}'|$, $\hat{\mathbf{r}} = (\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$, $\mathbf{n}'$ is the normal on S at $\mathbf{r}'$, and s' is the arclength of $C_{r,r'}$. For small r one finds

$$g_{ss}(r) = \frac{S}{V} \frac{1}{2r}. \tag{3}$$

For a smooth surface the next term is of order r and has been calculated in Ref. 4. Edges or contact points generate additional terms of order $O(1)$. The calculation of these terms is similar to, but simpler than the corresponding calculation in Refs. 1 and 2. Therefore we only present the results. If no contact points are present

$$\lim_{r \downarrow 0} \left[g_{ss}(r) - \frac{S}{V} \frac{1}{2r} \right] = \frac{1}{\pi V} \int_L \left(\frac{\alpha}{\sin \alpha} - 1 \right) dl, \tag{4}$$

where the line integral is performed over all the edges in V and $\pi \pm \alpha(-\pi < \alpha < \pi)$ represents the angle between the corresponding half-planes. (For $\alpha = \pm \pi$ the two half-planes coincide. For $\alpha = 0$ the surface is smooth.) For example, for a circular cylinder of radius R and height h one finds by direct evaluation for $r < \text{Min}(2R,h)$,

$$Vg_{ss}(r) = \frac{2R^2}{r} \left[\arccos \frac{r}{2R} - \frac{r}{2R} \sqrt{1 - \frac{r^2}{4R^2}} \right] + \pi R$$

$$- R \int_0^\pi \arcsin \left(\frac{r}{2R} \sin \theta \right) \sin \theta \, d\theta$$

$$+ \frac{R}{r} \int_0^\pi \frac{h - r|\cos \theta|}{\sqrt{1 - (r^2/4R^2)\sin \theta}} \, d\theta \tag{5}$$

and for small r,

$$Vg_{ss}(r) = S\frac{1}{2r} + 4R \left(\frac{\pi}{2} - 1 \right) + O(r) \tag{6}$$

which coincides with Eq. (4).

If N_c contact points per volume are present,

$$2\pi \frac{N_c}{V} \left\langle \frac{1}{\sqrt{\Delta}} \right\rangle \tag{7}$$

has to be added to Eq. (4). The average is performed over the the contact points and Δ is the Hessian of the difference surface at the contact point as defined in Ref. 2. For two spheres in contact

$$\Delta^{-1/2} = \frac{R_1 R_2}{R_1 + R_2}. \tag{8}$$

Transforming these results into q space we find for the Fourier-transform χ_{ss} of g_{ss},

$$\frac{1}{2\pi^2} \int_0^\infty \left[q^2 \chi_{ss}(q) - 2\pi \frac{S}{V} \right] dq$$

$$= \frac{1}{\pi V} \int_L \left(\frac{\alpha}{\sin \alpha} - 1 \right) dl + 2\pi \frac{N_c}{V} \left\langle \frac{1}{\sqrt{\Delta}} \right\rangle. \tag{9}$$

Note that the right-hand side is always nonnegative. For comparison I also quote the corresponding result[1,2] for the bulk correlation function

$$\frac{1}{2\pi^2} \int_0^\infty \left[q^4 \chi_{bb}(q) - 2\pi \frac{S}{V} \right] dq$$

$$= -\frac{1}{\pi V} \int_L (1 - \alpha \cot \alpha) dl - 4\pi \frac{N_c}{V} \left\langle \frac{1}{\sqrt{\Delta}} \right\rangle. \tag{10}$$

If both surface and bulk scattering can be measured by contrast matching, it can be tested whether there are sharp edges in the system. If there are edges, and any one of the three quantities, L, α, $(N_c/V) \langle 1/\sqrt{\Delta} \rangle$ is known, the other two can be determined. For hard spheres, for example, only the contact points contribute to Eqs. (9) and (10). For an attractive interaction the concentration of contact points is exponentially dependent on the interaction potential at contact. In this way the contact potential can be measured by scattering techniques.

We finally mention a type of line singularities that may not be uncommon in surfactant solutions. If there is attrac-

tion among the membranes, they will occasionally stick together in close contact over some extended regions. At the boundary they will in general depart tangentially forming a line of cusp singularities. If, for example, the membranes form flexible spheres as in vesicles or some microemulsions, an attraction may lead to dimers[5] having a finite contact area. Such lines of cusp singularities produce in bulk scattering a term $\sim q^{-(4+1/2)}$ and in surface scattering a term $\sim q^{-(2+1/2)}$ in addition to the Porod terms $\sim q^{-4}$ and q^{-2}. The coefficients are $-2\pi^{3/2}(L/V)\langle|k_1 - k_2|^{-1/2}\rangle$ and $2\pi^{3/2}(L/V)\langle|k_1 - k_2|^{-1/2}\rangle$, respectively, where L is the length of the singularity line L, $\langle\ \rangle$ is the average along L, and k_1,k_2 are the sectional curvatures normal to L of the two surfaces which join tangentially at L.

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NH₂ electron affinity

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We report the electron affinity of amidogen (NH_2), the amino radical, obtained from the photoelectron spectrum of the amide ion (NH_2^-). The literature electron affinity values from early laser photodetachment experiments have relatively large uncertainties: $EA(NH_2) = 0.744 \pm 0.022$ eV from photodetachment threshold measurements[1] and $EA(NH_2) = 0.779 \pm 0.037$ eV from photoelectron spectroscopy.[2] The development of higher resolution (5–25 meV) negative ion photoelectron spectrometers[3–6] now permits a significantly improved determination of the electron affinity as well as the observation of more detailed structure in the photoelectron spectrum. The spectrum reported here shows clear rotational bands in the photodetachment of NH_2^-. Partially resolved rotational band structure has been observed previously in photoelectron spectra[5,7] of small hydride ions such as OH^-, OD^-, SH^-, SD^-, and CH_2^-.

The photoelectron spectrometer used in this experiment has been described in detail previously.[5] NH_2^- is produced by introducing ammonia into a helium flow downstream of a microwave discharge; a beam of about 10 pA was achieved. Negative ions are extracted from the flow tube, mass selected with a Wien velocity filter, and crossed with a continuous 363.8 nm (3.408 eV) laser beam of fixed photon energy at a power of 40 W in an optical build-up cavity.[8] The kinetic energy of photodetached electrons is measured by a hemispherical electrostatic analyzer.[5] The absolute electron kinetic energy (eKE) is calibrated with O^- ions, $EA(O) = 1.461\,125 \pm 0.000\,001$ eV,[9] and the energy scale compression factor[5] of 0.6% is determined from photodetachment of W^-. The uncertainty of the eKE scale is ± 5 meV and the instrumental linewidth is 8–9 meV. The rota-

tional temperature of OH^- ions produced in this source under similar conditions is 315 ± 20 K, and the vibrational temperatures are typically 300–500 K.[8]

Figure 1 shows the $NH_2(\tilde{X}\,^2B_1, v' = 0) \leftarrow NH_2^- (\tilde{X}\,^1A_1, v'' = 0)$ vibrational origin transition in the photoelectron spectrum of NH_2^-. We also observed transitions in the symmetric stretch $NH_2(v_1' = 1) \leftarrow NH_2^- (v_1'' = 0)$ and in the bend $NH_2(v_2' = 1) \leftarrow NH_2^- (v_2'' = 0)$ which had intensities of 0.5% and 0.9% respectively relative to the vibrational origin. Weak transitions to the $\tilde{A}\,^2A_1$ state[10] of NH_2 were observed at electron kinetic energies below 1.5 eV. The rotational contour of the origin transition shows Q, P, and R branches. The Q branch has a FWHM of 8.5 meV, limited by the instrumental resolution. The rotationless origin is found from the rotational modeling to be within 1 meV of the center of the Q branch and this yields the electron affinity $EA(NH_2) = 0.771 \pm 0.005$ eV. This value for $EA(NH_2)$ falls within the range of the previous experimental determinations.[1,2] A recent theoretical value[11] is $EA(NH_2) = 0.707$ eV. We also measured the angular distribution of the ejected electron with the laser operating on the 351 nm line. This showed anisotropic detachment with asymmetry parameter β of 0.34 ± 0.05. Within experimental error the Q, P, and R branches all had the same angular distribution.

The ground electronic state of the amino radical is formed by removing an electron from the nonbonding b_1 orbital of NH_2^-. The resulting small geometry change upon photodetachment is reflected by the narrowness of the Q branch and by the weak intensities of higher vibrational transitions. The observed vibrational transitions were totally consistent with the known experimental molecular geome-