Surface modes of small particles

For a spherical particle of radius $R$ and homogeneous isotropic dielectric constant $\varepsilon(\omega)$ in a nonabsorbing medium of dielectric constant $\varepsilon_m$, the normal modes (or natural frequencies) occur when the denominators in the scattering coefficients $a_l$ and $b_l$ vanish:

$$a_l \text{ modes: } m L_l^{(\varepsilon)}(x) = \frac{\mu_1}{\mu} L_l^{(\varepsilon)}(mx);$$

$$b_l \text{ modes: } m L_l^{(\varepsilon)}(mx) = \frac{\mu_1}{\mu} L_l^{(\varepsilon)}(x),$$

where $L_l^{(\varepsilon)}$ and $L_l^{(\varepsilon)}$ are as defined earlier.

Now using power series expansion of $j_l(\rho)$ and $y_l(\rho)$ given by

$$j_l(\rho) = \frac{\rho^l}{1 \cdot 3 \cdot 5 \cdots (2l + 1)} \left[ 1 - \frac{\frac{1}{2} \rho^2}{1!(2l + 3)} + \frac{\left(\frac{1}{2} \rho^2\right)^2}{2!(2l + 3)(2l + 5)} - \cdots \right],$$

$$y_l(\rho) = -\frac{1 \cdot 3 \cdot 5 \cdots (2l - 1)}{\rho^{l+1}} \left[ 1 - \frac{\frac{1}{2} \rho^2}{1!(1 - 2l)} + \frac{\left(\frac{1}{2} \rho^2\right)^2}{2!(1 - 2l)(3 - 2l)} - \cdots \right],$$

one finds,

$$L_l^{(\varepsilon)}(\rho) = \frac{\psi_l'(\rho)}{\psi_l(\rho)} = \frac{[\rho j_l(\rho)]'}{[\rho j_l(\rho)]} \rightarrow_{\rho \to 0} \frac{(l + 1)}{\rho} \left[ 1 + O(\rho^2) \right].$$

and

$$L_l^{(\varepsilon)}(\rho) = \frac{\psi_l'(\rho) + i \chi_l'(\rho)}{\psi_l(\rho) + i \chi_l(\rho)} = \frac{[\rho j_l(\rho)]'}{[\rho j_l(\rho)]} + \frac{i[\rho y_l(\rho)]'}{[\rho y_l(\rho)]} \rightarrow_{\rho \to 0} -\frac{l}{\rho} \left[ 1 + O(\rho^2) \right].$$

Using these, one gets for $|m| x << 1, x << 1$,

$$a_l \text{ modes: } m^2 = -\frac{l + 1}{l} \left( \frac{\mu_1}{\mu} \right);$$

$$b_l \text{ modes: } \frac{l + 1}{l} = -\left( \frac{\mu_1}{\mu} \right).$$

Note that both the expressions are independent of the size parameter $x$ (provided of course $x$ is small), and if $\mu_1 = \mu$, then the $a_l$ modes are described by,

$$\frac{\varepsilon}{\varepsilon_m} = m^2 = -\frac{l + 1}{l}, \quad l = 1, 2, \cdots,$$

and the $b_l$ modes are not possible.

In general $\varepsilon(\omega)$ is complex, and therefore the $a_l$ modes are usually virtual (i.e., damped). These normal modes are usually called surface modes, sometimes referred to as (localized) particle modes, sometimes as multipolar (depending on the value of $l$) modes; for $l = 1$, these modes are called dipolar modes, and the corresponding mode frequency is determined by
The higher multipolar modes are usually not important (because, as already seen, the $a_l$s for $l > 1$ do not contribute significantly to $C_{ext}$ or $C_{sea}$).

Now writing $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, one gets the condition for dipolar modes as

$$\epsilon'(\omega) = -2\epsilon_m \quad \text{and} \quad \epsilon''(\omega) = 0.$$  

The frequency at which these conditions are satisfied, are sometimes called Fröhlich mode. However, more often than not, they are referred to as Mie modes. If one takes the view that the polarization of the particle as a whole is $\alpha(\omega)$, then

$$\alpha(\omega) = 4\pi R^3 \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m},$$

where $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, and one can rewrite this as

$$\alpha(\omega) = 4\pi R^3 \left[ 1 - \frac{3\epsilon_m}{(\epsilon'(\omega) + 2\epsilon_m) + i\epsilon''(\omega)} \right],$$

which by itself has the structure of Lorentz oscillator model.

One then gets the absorption efficiency $Q_{abs}$ as

$$Q_{abs}(\omega) = 4x\text{Im}\alpha = 12x \frac{\epsilon_m \epsilon''(\omega)}{(\epsilon'(\omega) + 2\epsilon_m)^2 + [\epsilon''(\omega)]^2}.$$  

The absorption efficiency at the Fröhlich frequency $\omega_F$ (i.e., where $\epsilon'(\omega_F) + 2\epsilon_m = 0$, and $\epsilon''(\omega_F) \approx 0$), is therefore

$$Q_{abs}(\omega_F) = 12x \frac{\epsilon_m}{\epsilon''(\omega_F)}.$$  

which can be very large since $\epsilon''(\omega_F) \approx 0$ for well defined Fröhlich modes. The exact frequency dependence of $Q_{abs}(\omega)$ can be obtained by putting in the bulk values of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ (for which the oscillator models, or the experimentally determined values are often used) in the expression for $Q_{abs}$, and it therefore depends on the detailed $\omega$-dependent structures of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ around $\omega_F$. These results are strictly valid for $x$ sufficiently small.

For corrections to account for the size effect, one has to consider again the denominator of $a_l$ (assuming again $\mu = \mu_1$), which vanish when

$$m\psi_1(mx)\xi'_1(x) = \xi_1(x)\psi'_1(mx).$$

Expanding $\psi_1$ to order $x^4$ and $\xi_1$ to order $x$, one gets the condition for dipolar modes as

$$\epsilon = -2\epsilon_m [1 + 1.2x^2], \quad \text{to order } x^2,$$

which implies lowering of Fröhlich frequency with increasing particle radius.