Study of Collective Dynamics of Fully Hydrated Phospholipid Bilayers by High Resolution Inelastic X-ray Scattering Spectroscopy

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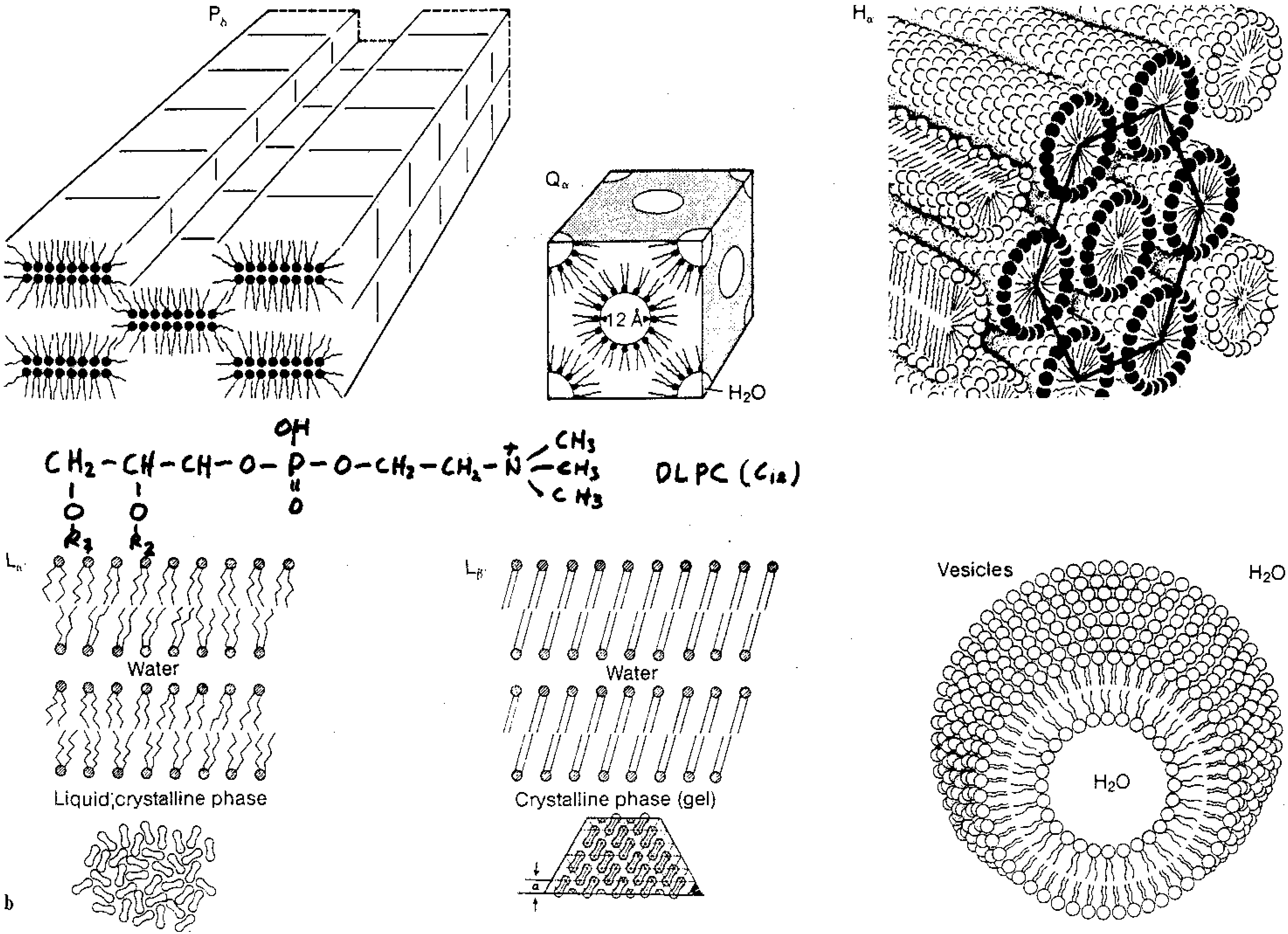
Outline

1. Analysis of IXS Data in Molecular and Supramolecular Liquids
   - Generalized three effective eigenmode theory
   - The case of water
2. Measurements with Hydrated Multi-lamellar Dilauroylphosphatidylcholine (DLPC)
   - Phase behabior of DLPC-water system
   - The analysis of data at 294 K (L-alpha phase)
   - The analysis of data at 269 K (L-beta phase)
3. Q-Dependences of the Effective Mode Parameters PRL (2000)
   - Damping of heat diffusion mode
   - Dispersion relation of the propagating density wave in bilayers
   - Damping of the density wave

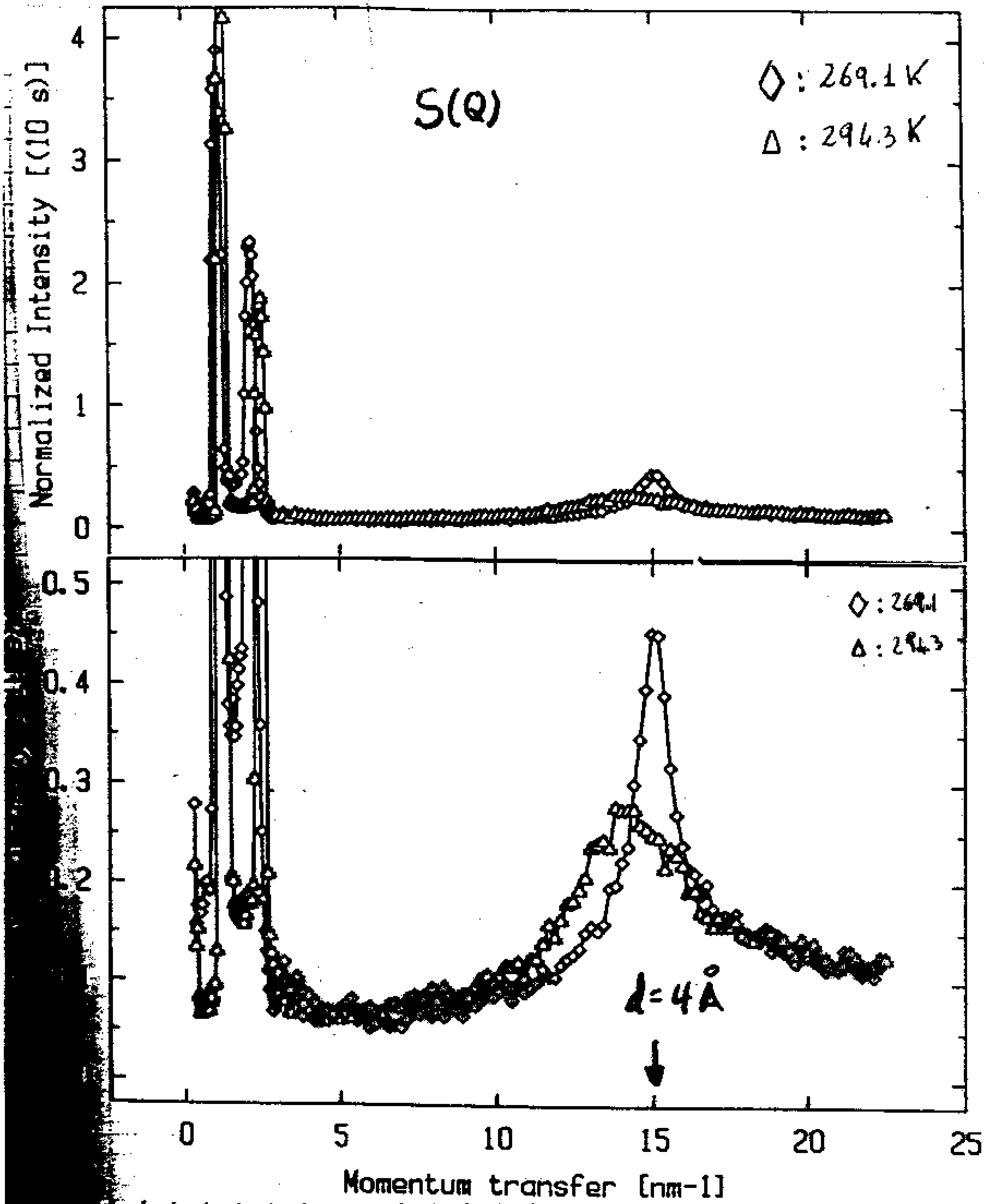
Collaborators: C.Y. Liao (MIT), H. W. Huang (Rice U.), T. Weiss (Rice U.)
M.C. Bellissent-Funel (Saclay) and F. Sette (ESRF)

An invited lecture given at a "Workshop on Scattering Studies of Mesoscopic Scale Structure and Dynamics in Soft Matter". Univ. of Messina, Italy, Nov. 22-25, 2000.

Phosphatidylcholine

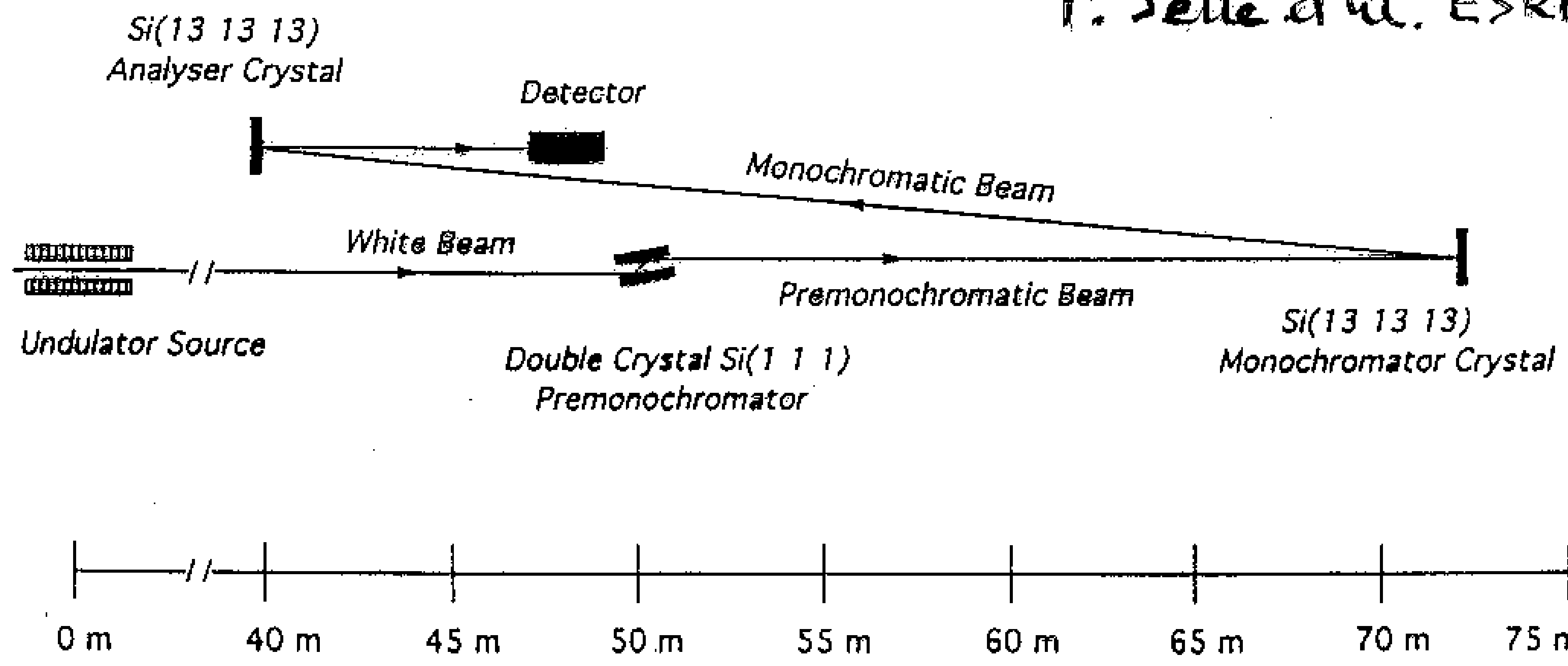


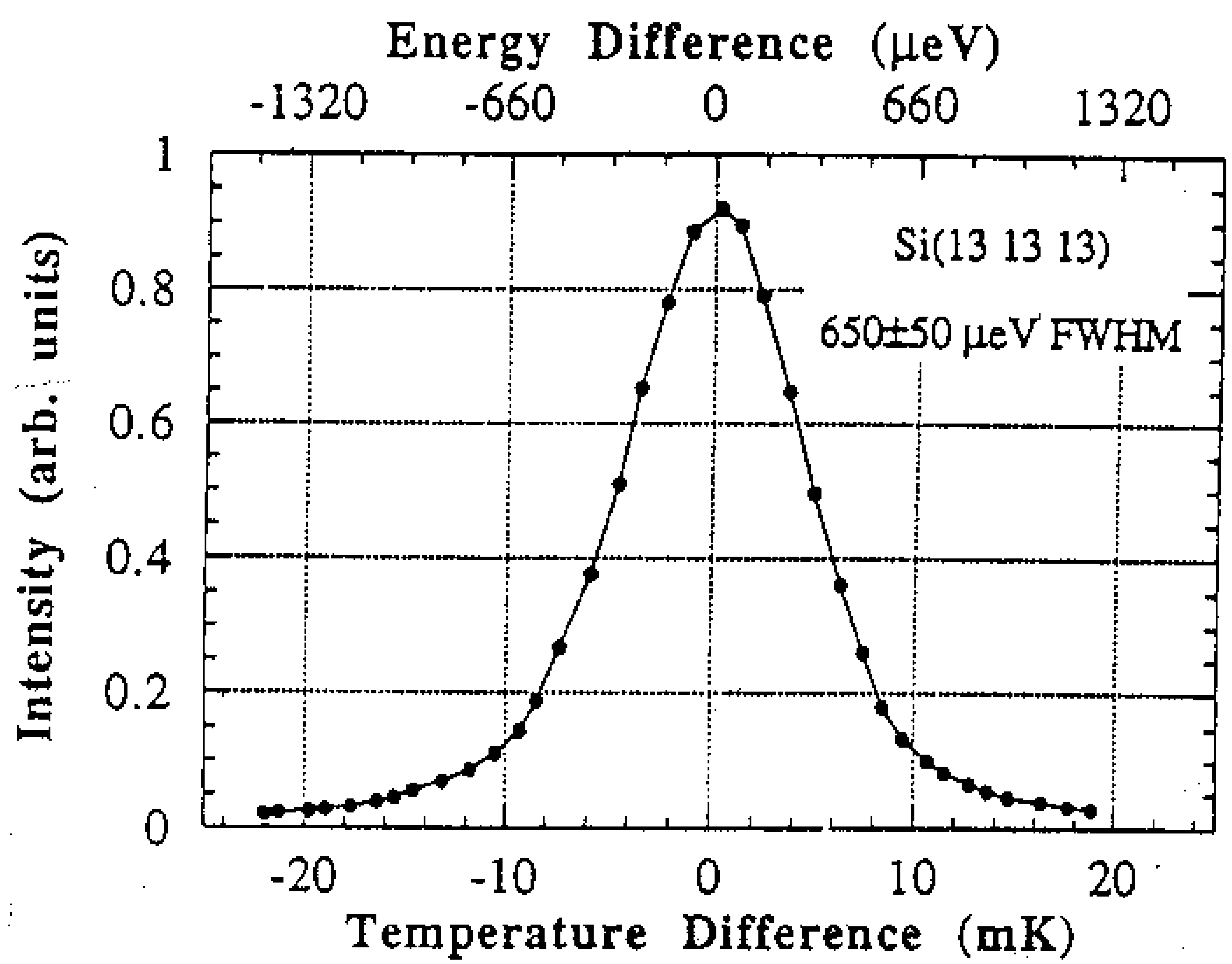
S(Q) of Lipid Sample T=269.1 and 294.3 K. sk.010 and sk.009



Experimental Lay-out Side View

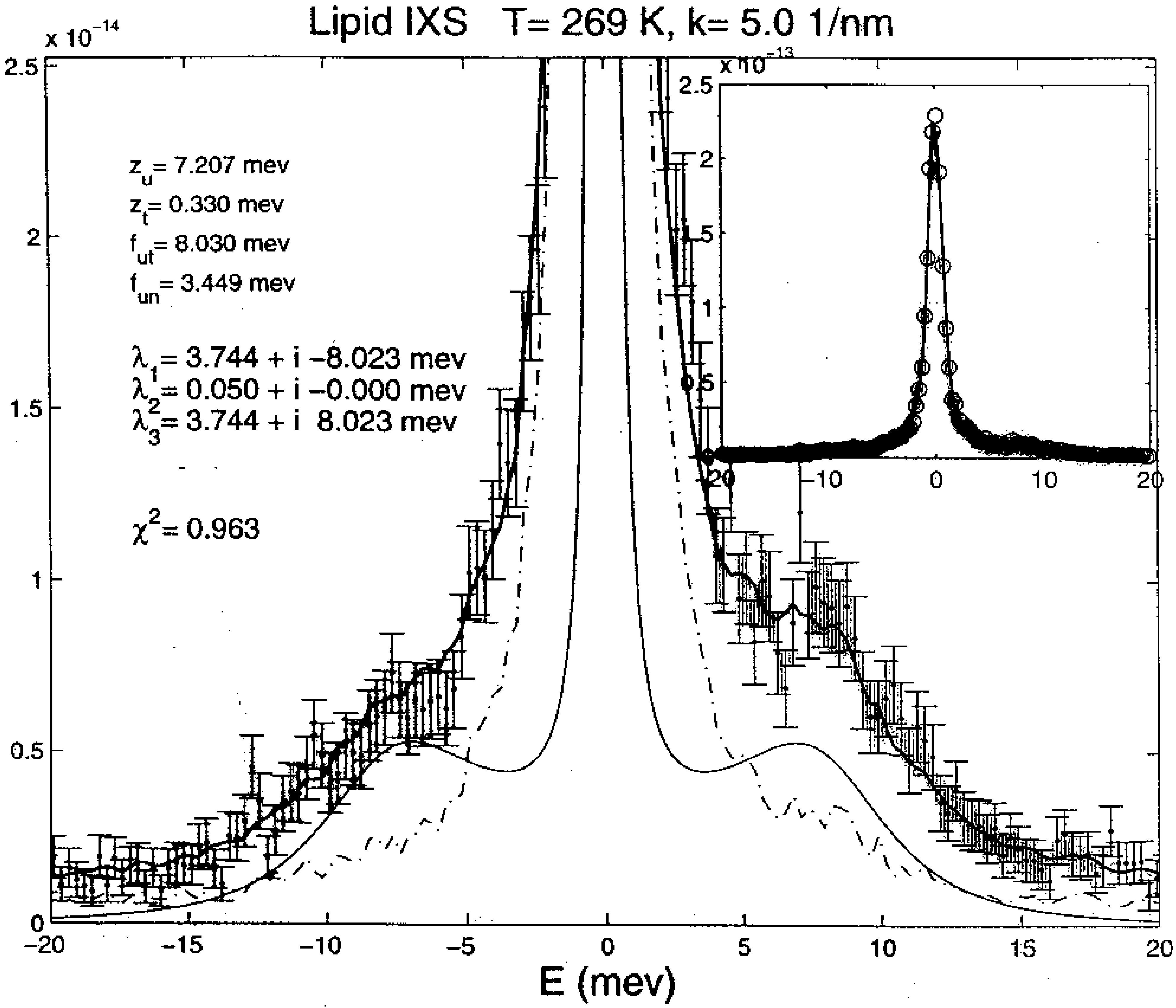
F. Sette et al. ESRF





Performances of the Very High Energy Resolution Si(h h h) Monochromator

Reflection	(7 7 7)	(8 8 8)	(9 9 9)	(11 11 11)	(12 12 12)	(13 13 13)
Energy [eV]	13840	15817	17794	21748	23725	25703
$(\Delta E)_M$ [meV]	5.3	4.4	2.2	1.02	0.73	0.5
Flux (ph /s /150 mA)	$1.4\cdot10^{10}$	$5.0\cdot10^{9}$	$1.2\cdot10^{9}$	$1.5\cdot10^{8}$	$7.5\cdot10^{7}$	$3.0\cdot10^{7}$
$(\Delta E / E)_M$	$3.8\cdot10^{-7}$	$2.8\cdot10^{-7}$	$1.2\cdot10^{-7}$	$4.7\cdot10^{-8}$	$3.0\cdot10^{-8}$	$2.0\cdot10^{-8}$



Lipid IXS T= 269 K, k= 5.0 1/nm
x 10^-14
z_u= 7.207 mev
z_t= 0.330 mev
f_ut= 8.030 mev
f_un= 3.449 mev
λ_1= 3.744 + i −8.023 mev
λ_2= 0.050 + i −0.000 mev
λ_3= 3.744 + i 8.023 mev
χ^2= 0.963
x 10^-13
E (mev)

Three Effective Eigenmode (TEE) Model

The dynamic structure factor is given as,

$$S(k,\omega) = \frac{S(k)}{\pi}\,\mathrm{Re}\left\{\frac{\vec{I}}{i\omega\vec{I} + \vec{H}(k)}\right\}_{1,1} \quad ; \quad \vec{H}(k) = \begin{pmatrix} 0 & if_{un}(k) & 0 \\ if_{un}(k) & z_u(k) & if_{uT}(k) \\ 0 & if_{uT}(k) & z_T(k) \end{pmatrix}$$

with $f_{un}(k) = \sqrt{\langle\omega^2\rangle} = kv_0/\sqrt{S(k)}$ and $z_u(k), f_{uT}(k), z_T(k)$ all real numbers.

Hydrodynamic limit ($k \to 0$):

$$f_{un}(k) = kc_s/\sqrt{\gamma}$$
$$z_u(k) = \phi k^2$$
$$z_T(k) = \gamma D_T k^2$$
$$f_{uT}(k) = kc_s\sqrt{(\gamma-1)/\gamma}$$

$$S(K,z) = \left[z + \frac{f_{un}^2(k)}{z + z_u(k) + \frac{f_{uT}^2(k)}{z + z_T(k)}}\right]^{-1}$$

$c_s = v_0(\gamma/S(0))^{1/2}$, $\gamma = c_p/c_v$, $\phi = [(4/3)\eta + \zeta]/mn$, $D_T = \lambda/nmc_p$.

The three eigenvalues, to the order of $O(k^2)$, are:

$$z_h(k) = D_T k^2 \qquad \text{(heat mode)}$$
$$z_\pm(k) = \pm ic_s k + \Gamma_s k^2 \qquad \text{(sound mode)}$$

where $\Gamma_s = \phi/2 + D_T(\gamma-1)/2$ is the sound damping.

For finite k, $z_u(k)$, $f_{uT}(k)$, $z_T(k)$ become arbitrary functions of k. However, in most cases, the eigenvalues of the matrix $\vec{H}$ consist of one real number z_h and a couple of conjugate complex numbers $\Gamma_S \pm i\omega_S$. One can therefore write The DSF in general in the hydrodynamic-like form:

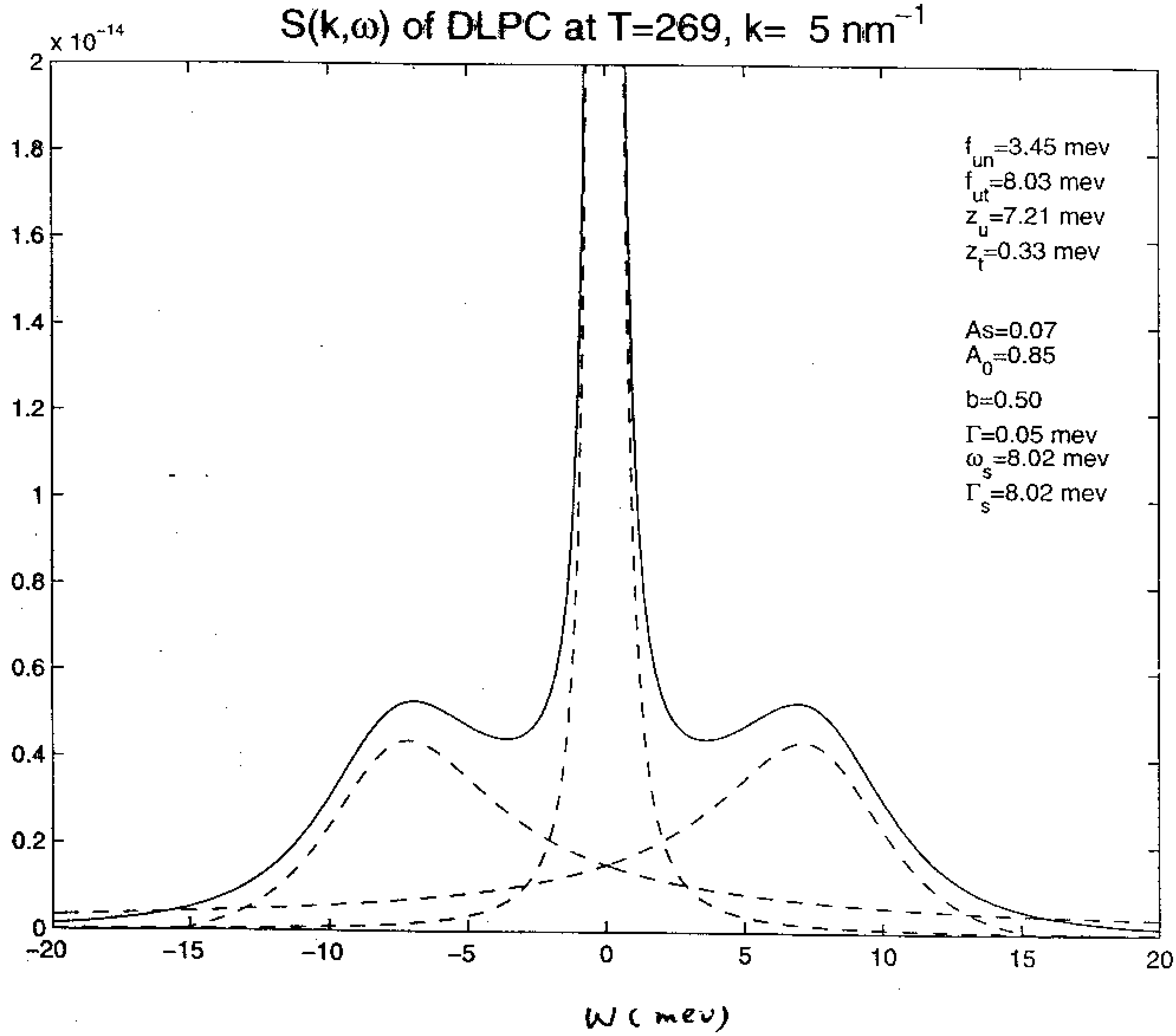
$$S(k,\omega)/S(k) = \frac{1}{\pi}\left\{A_0\frac{z_h}{\omega^2 + z_h^2} + A_s\frac{\Gamma_s + b(\omega+\omega_s)}{(\omega+\omega_s)^2 + \Gamma_s^2} + A_s\frac{\Gamma_s - b(\omega-\omega_s)}{(\omega-\omega_s)^2 + \Gamma_s^2}\right\}$$

Damped Harmonic Oscillator limit ($f_{uT}(k) = 0$)

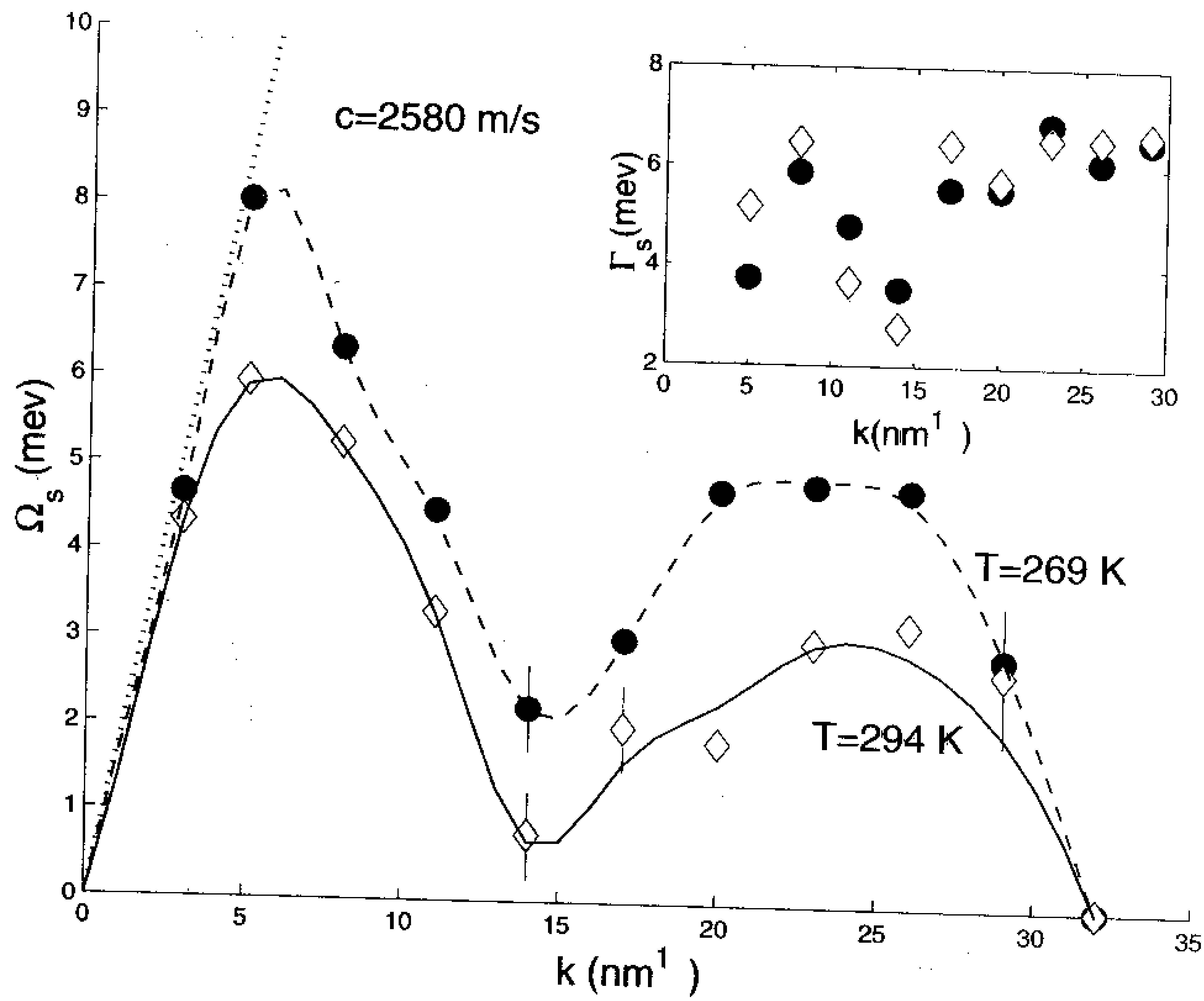
The amplitude of the central peak of $S(k,\omega)$ is zero, the side peaks can be written as:

$$S(k,\omega)/S(k) = \frac{1}{\pi}\frac{f_{un}^2(k)z_u(k)}{(\omega^2 - f_{un}^2(k))^2 + (\omega z_u(k))^2}.$$

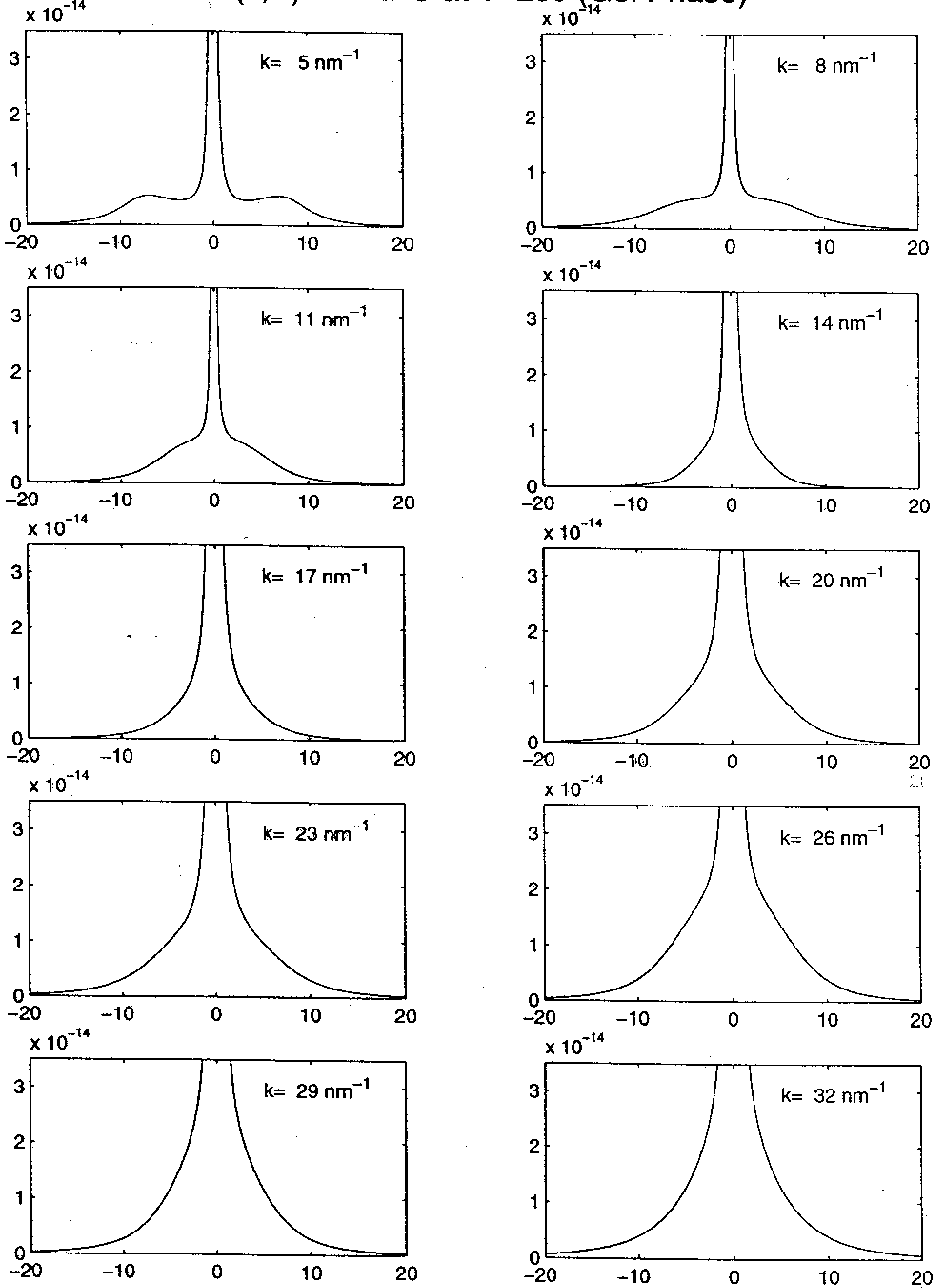
S(k,ω) of DLPC at T=269, k= 5 nm^{-1}



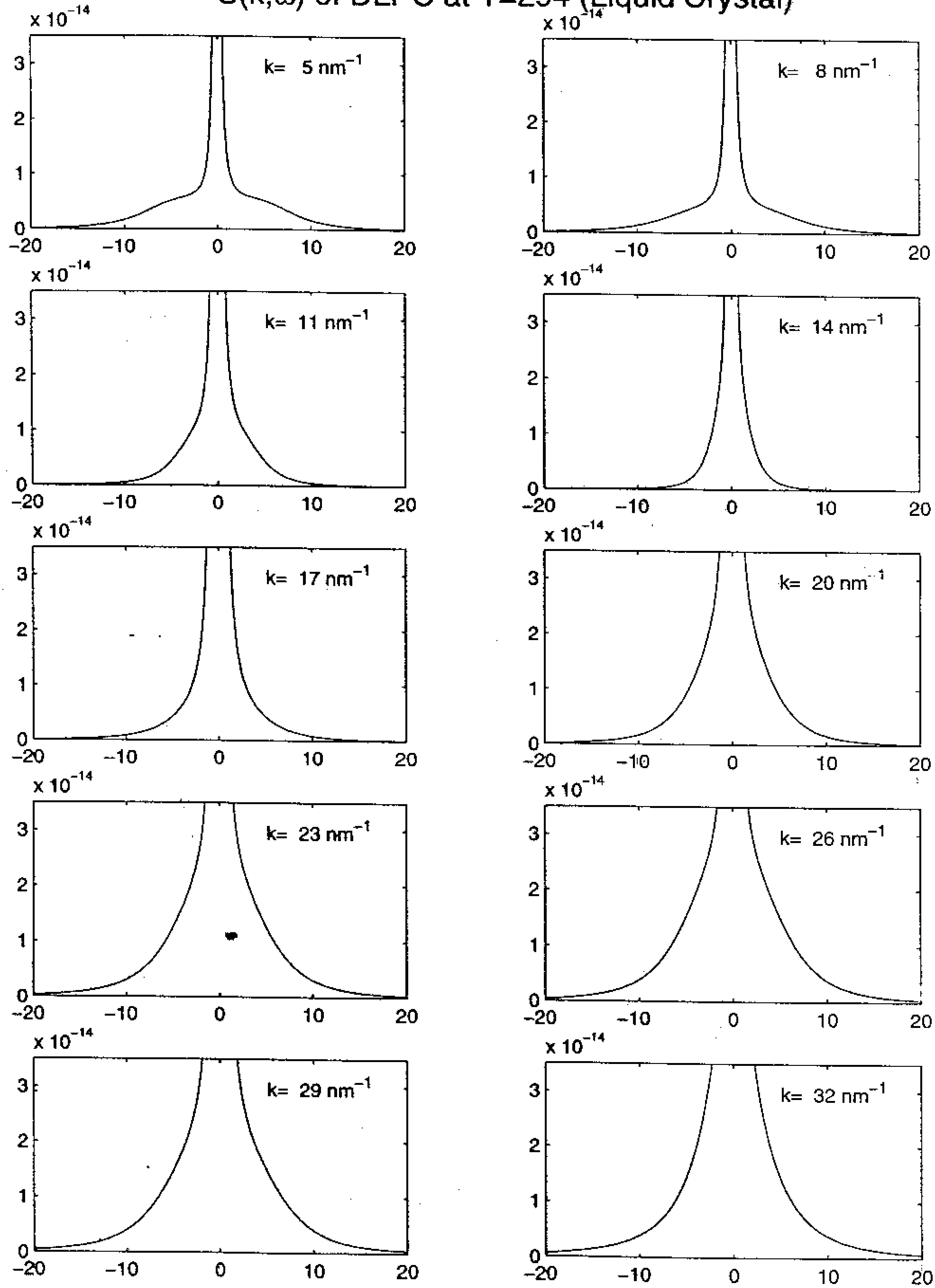
$$S(k,\omega)/S(k) = \frac{1}{\pi}\left\{ A_0 \frac{Z_h}{\omega^2 + Z_h^2} + A_s \frac{\Gamma_s + b(\omega+\omega_s)}{(\omega+\omega_s)^2 + \Gamma_s^2} + A_s \frac{\Gamma_s - b(\omega-\omega_s)}{(\omega-\omega_s)^2 + \Gamma_s^2} \right\}$$


c=2580 m/s
T=269 K
T=294 K
Ω_s (mev)
k (nm^{1})
Γ_s(mev)
k(nm^{1})

S(k,ω) of DLPC at T=269 (Gel Phase)



S(k,ω) of DLPC at T=294 (Liquid Crystal)



SUMMARY

1. We have formulated a Generalized Three Effective Eigenmode Theory (GTEE) for the analysis of IXS spectra of supramolecular liquids.

2. We measured IXS spectra from fully hydrated, semi-oriented DLPC bilayers and analyzed them using GTEE.

3. Using GTEE theory we extracted the frequency and damping of the non-propagating and propagating modes in the lipid bilayers.

4. Both the frequency and damping show a minimum at the peak of the lipid-lipid structure factor similar to simple liquids.

5. This sharp frequency dip occurring at a wavelength of inter-lipid distance in a functional bilayer may have biological significance.

6. Calculated structure factor from the second frequency moment of the GTEE model agrees with the measured structure factor.

7. The sound propagation speed is higher in $L_{\beta'}$ than that in L_{α} phase due to chain freezing.

8. GTEE analysis of proteins shows a mode softening upon hydration of the protein.