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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

STRUCTURE AND DYNAMICS OF CHARGED FLUIDS

(Lecture V)

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Potential models

Molten Alkali Halides

a) rigid ion models (RI)

– restricted primitive model (RPM)

J.C. Rasaiah, D.N. Card and J.P. Valleau: J. Chem. Phys. 56, 248 (1972)

B. Larsen: Chem. Phys. Letters 27, 47 (1974)

– symmetric molten salt (SMS)

$$v_{\nu\mu}(r) = \frac{e^2}{\lambda}\left[\frac{1}{n}\left(\frac{\lambda}{r}\right)^n + z_\nu z_\mu \left(\frac{\lambda}{r}\right)\right]$$

$n = 9$

MC: D.J. Adams and I.R. McDonald: Physica 79B, 159 (1975)

MD: $M_+ = M_-$: J.P. Hansen and I.R. McDonald: Phys. Rev. A 11, 2111 (1975)

corresponding states law

– Huggins-Mayer potential:

$$v_{\nu\mu}(r) = \underbrace{A_{\nu\mu}\exp\{(\sigma_\nu + \sigma_\mu - r)/\rho\}}_{\text{overlap repulsion}} + \underbrace{C_{\nu\mu}\left(\frac{r_0}{r}\right)^6}_{\text{dipole-dipole}} + \underbrace{D_{\nu\mu}\left(\frac{r_0}{r}\right)^8}_{\text{dipole-quadrupole}} + \underbrace{z_\nu z_\mu \left(\frac{r_0}{r}\right)}_{\text{Coulomb}}$$

parameters determined from solid state data: M.P. Tosi and F.G. Fumi: J. Phys. Chem. Solids 25, 45 (1964)

b) polarizable ions

shell model:

M. Dixon and M.J.L. Sangster: J. Phys. C 8, L8 (1975)

G. Jacucci, I.R. McDonald and A. Rahman: Phys. Rev. A 13, 1581 (1976)

Thermodynamic properties

MC calculations for various alkali halides by K. Singer, I.R. McDonald and collaborators, using the Huggins-Mayer pot. (see e.g. the pioneering paper by L.V. Woodcock and K. Singer: Trans. Faraday Soc. 67, 12 (1971), and the NPT-ensemble computations by D.J. Adams and I.R. McDonald: J. Phys. C 7, 2761 (1974)

$u^{ex} \backsim 90\%$ electrostatic

Equilibrium structure

a) 3 p.d.f.: $g_{++}(r)$, $g_{--}(r)$, $g_{+-}(r)$

RPM and SMS: $g_{++}(r) \equiv g_{--}(r)$

For most alkali halides:

$$g_{++}(r) \backsimeq g_{--}(r)$$

$$\Rightarrow \begin{cases} g_e(r) = \frac{1}{2}\left[g_{++}(r) + g_{--}(r)\right] \\ g_u(r) = g_{+-}(r) \end{cases}$$

$$\text{or} \begin{cases} g_{NN}(r) = \frac{1}{2}\left[g_e(r) + g_u(r)\right] \\ g_{QQ}(r) = \frac{1}{2}\left[g_e(r) - g_u(r)\right] \end{cases}$$

③ b) 3 ~~three~~ partial structure factors

$$S_{\nu\mu}(k) = \delta_{\nu\mu} + \frac{\rho}{2}\int [g_{\nu\mu}(r)-1]\, e^{i\vec{k}\cdot\vec{r}}\, d\vec{r}$$

generally: $S_{++}(k) = S_{--}(k) = S_{el}(k)$

$$\rightarrow \begin{cases} S(k) \equiv S_{NN}(k) = S_{el}(k) + S_{in}(k) \\ S'(k) = S_{QQ}(k) = S_{el}(k) - S_{in}(k) \end{cases}$$

perfect screening condition:

$$\lim_{k\to 0} S'(k) = k^2/\chi^2$$

where $\chi = (4\pi\rho e^2/k_B T)^{1/2}$ (Debye)

$$\lim_{k\to 0} S(k) = \frac{1}{k_B T}\left[\left(\frac{\partial P}{\partial \rho}\right)_T\right]^{-1}$$

(X-ray or neutron diffraction) (isothermal compressibility)

c) charge ordering

see slides (I) and (II)

d) "shoulder" in $g_{el}(r)$:

RPM (Larsen)

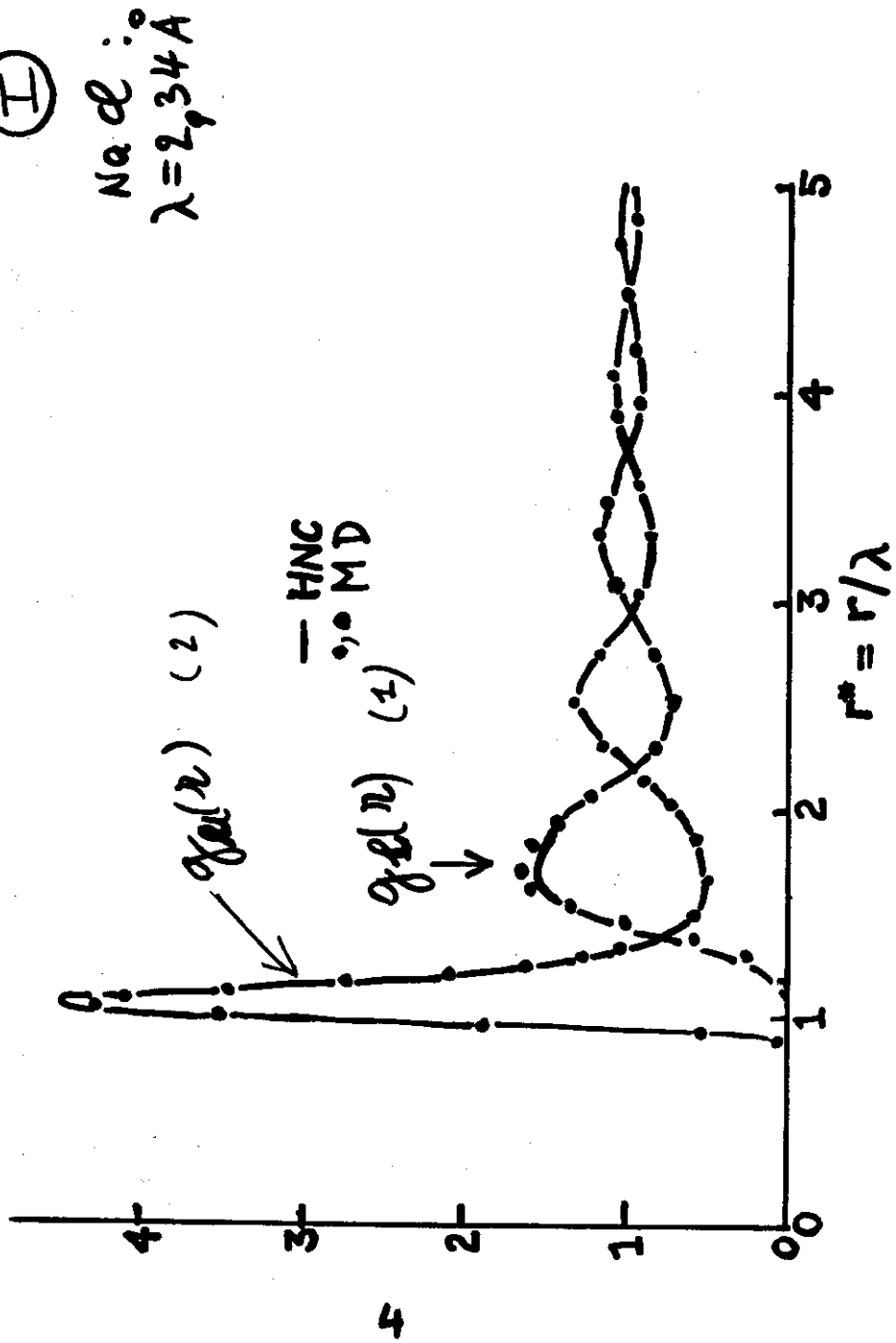
RbBr.: J.R.D. Copley and A. Rahman: Phys. Rev.

e) influence of ion polarization

NaI: Dixon and Sangster

KI, NaCl: Jacucci et al.

(H)



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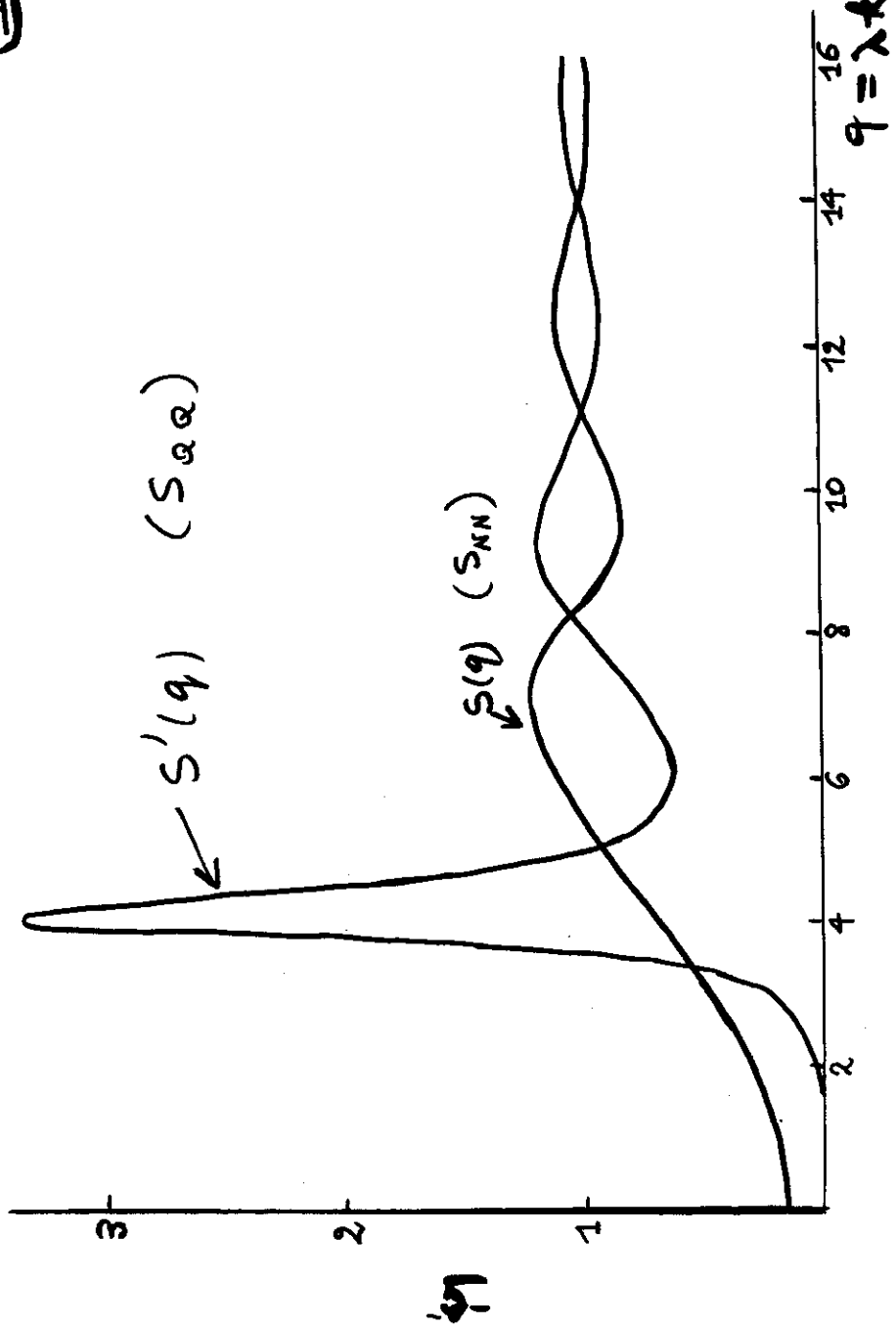
(III)



-5-

④ Self diffusion

a) 2 v.a.f.: $Z_\pm(t) = \langle \vec{v}_{i\pm}(t) \cdot \vec{v}_{i\pm}(0) \rangle$ (un-normalized)

2 diffusion coefficients:

$$D_\pm = \frac{1}{3}\int_0^\infty Z_\pm(t)\,dt = \lim_{t\to\infty} \frac{1}{6t} \langle [\vec{r}_{i\pm}(t) - \vec{r}_{i\pm}(0)]^2 \rangle$$

b) SMS: $D_+ = D_- = D$

$Z_+(t) = Z_-(t) = Z(t)$

slide (VI)

c) Huggins-Mayer RI potential:

NaCl: F. Lantelme, P. Turq, B. Quentrec and J. W. E. Lewis: Mol. Phys. 28, 1537 (1974)

LiF, NaCl, NaI, KI, RbCl, RbI: Gliccotti, G. Jacucci and I. R. McDonald: Phys. Rev. A13, 426 (1976)

slide (IV): "cage effect" (LiF)

d) ion polarization:

D_+ and D_- ↑ (Jacucci et al.)

⑤ Electrical conductivity

a) $\vec{J}(t) = \sum_{i=1}^{N} z_i \vec{v}_i(t) = \sum_{i=1}^{N_+} \vec{v}_{i+}(t) - \sum_{j=1}^{N_-} \vec{v}_{j-}(t)$

electrical current a.c.f.:

$J(t) = \langle \vec{J}(t) \cdot \vec{J}(0) \rangle$

electrical conductivity (Kubo):

$$\sigma = \frac{e^2}{3Vk_BT} \int_0^\infty J(t)\,dt$$

b) Nernst-Einstein relation:

if we assume $\langle \vec{v}_i(t) \cdot \vec{v}_j(0) \rangle = \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle \delta_{ij}$

$$\rightarrow J(t) = \frac{N}{2}\left[Z_+(t) + Z_-(t)\right]$$

$$\sigma = \frac{1}{2}\frac{Ne^2}{Vk_BT}(D_+ + D_-) \quad \text{(Nernst-Einstein)}$$

Deviation parameter Δ (cross correlations):

$$\sigma = \frac{1}{2}\frac{Ne^2}{Vk_BT}(D_+ + D_-)(1-\Delta)$$

Experimentally, for alkali halides:

$$0.1 \lesssim \Delta \lesssim 0.4$$

SMS (Hansen and McDonald):

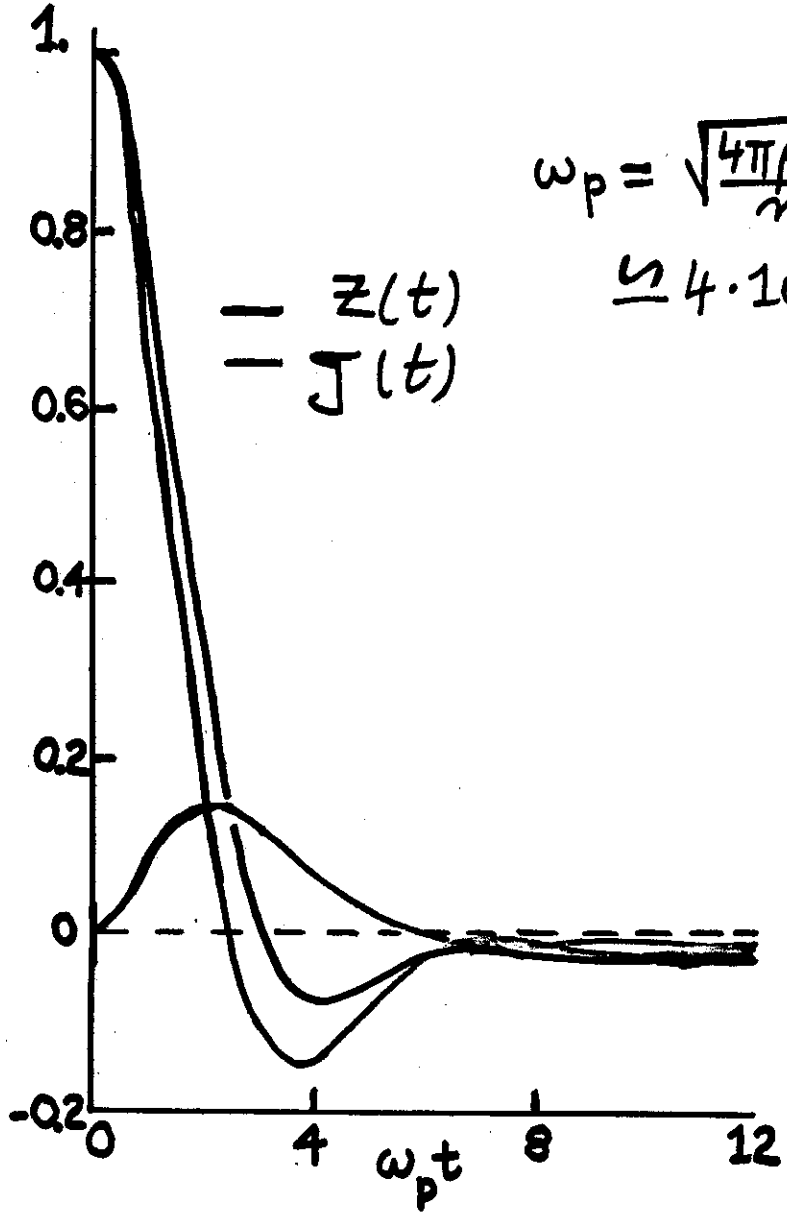
$\Delta \simeq 0.2$ ‖ R.I. model with Huggins-Mayer yields satisfactory results for σ

slide ③

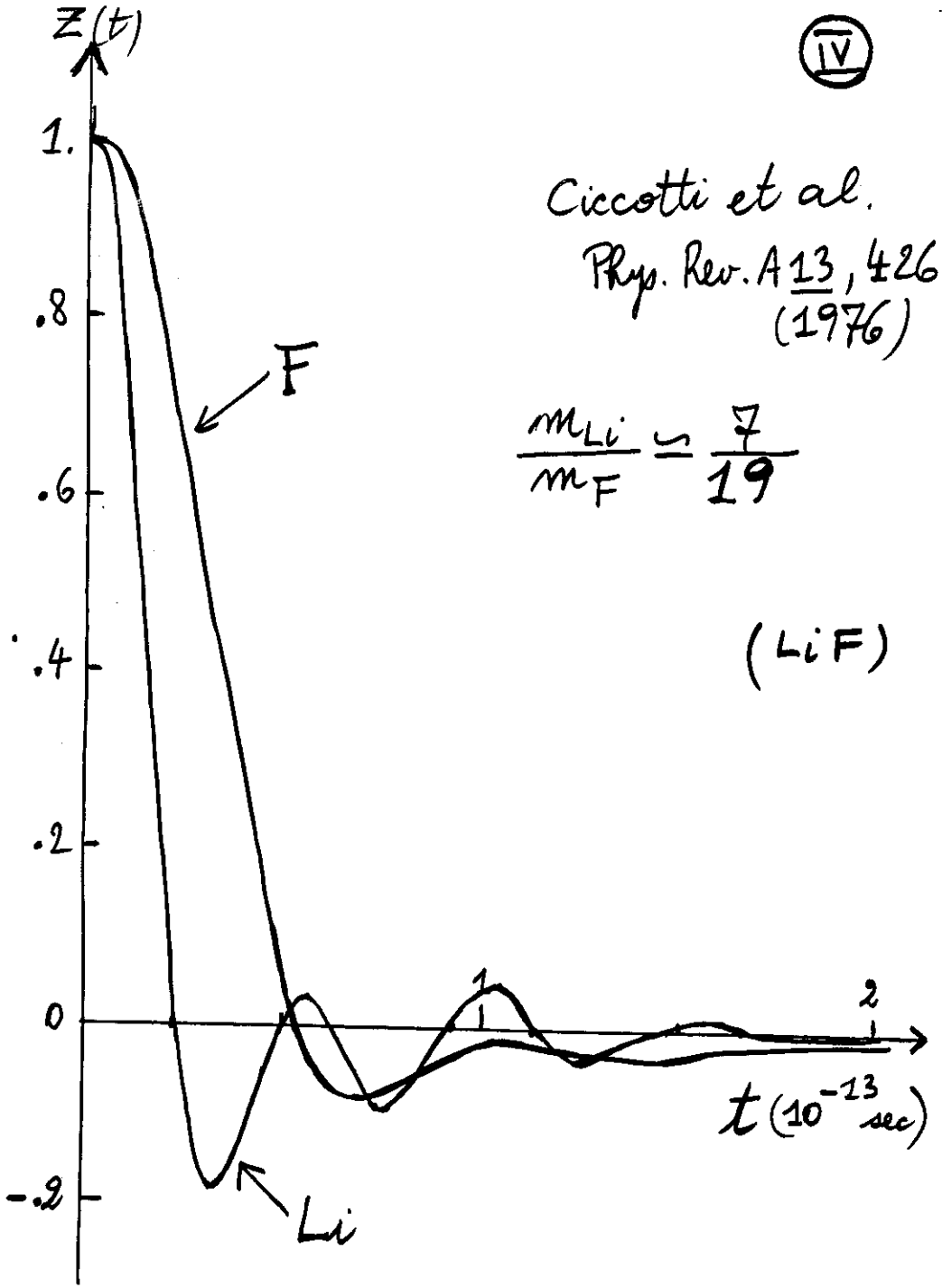
c) effects of ion polarization: (Ciccotti et al.)

negligible as regards σ

SMS ③



$$\omega_p = \sqrt{\frac{4\pi\rho e^2}{m}} \simeq 4 \cdot 10^{13}\ sec^{-1}$$



(IV)

Ciccotti et al.
Phys. Rev. A 13, 426 (1976)

$\frac{m_{Li}}{m_F} \simeq \frac{7}{19}$

(LiF)

⑥ Longitudinal collective modes
(mass and charge density fluctuations)

longitudinal coll. modes are accessible by coherent inelastic neutron scattering exp. and Rayleigh scattering in light scattering exp.
transverse coll. modes are only accessible by MD "experiments" (cf. Ciccotti et al.; Copley and Rahman)

Density operators:

partial: $\rho_{\vec{k}}^{+} = \sum_{i=1}^{N_+} e^{i\vec{k}\cdot\vec{r}_{i+}}$

$\rho_{\vec{k}}^{-} = \sum_{j=1}^{N_-} e^{i\vec{k}\cdot\vec{r}_{j-}}$

number density op.: $\rho_{\vec{k}}^{N} = \rho_{\vec{k}}^{+} + \rho_{\vec{k}}^{-}$

mass " " : $\rho_{\vec{k}}^{M} = M_+ \rho_{\vec{k}}^{+} + M_- \rho_{\vec{k}}^{-}$

charge " " : $\rho_{\vec{k}}^{a} = Z_+ \rho_{\vec{k}}^{+} + Z_- \rho_{\vec{k}}^{-}$

$= \rho_{\vec{k}}^{+} - \rho_{\vec{k}}^{-}$ (alkali halides)

Autocorrelation functions (or intermediate scattering f.):

$$F_{\nu\mu}(k,t) = \frac{1}{\sqrt{N_\nu N_\mu}} \langle \rho_{\vec{k}}^{\nu}(t)\, \rho_{-\vec{k}}^{\mu}(0) \rangle$$

⑦ Number density a.c.f.:

$$F_{NN}(k,t) = \frac{1}{N}\langle \rho^N_{\underline{k}}(t)\,\rho^N_{-\underline{k}}(0)\rangle$$
$$= \frac{1}{2}\left[F_{++}(k,t)+F_{--}(k,t)\right] + F_{+-}(k,t)$$

Mass density a.c.f.:

$$F_{MM}(k,t) = \frac{1}{N}\langle \rho^M_{\underline{k}}(t)\,\rho^M_{-\underline{k}}(0)\rangle$$

charge density a.c.f.:

$$F_{QQ}(k,t) = \frac{1}{N}\langle \rho^Q_{\underline{k}}(t)\,\rho^Q_{-\underline{k}}(0)\rangle$$
$$= \frac{1}{2}\left[F_{++}(k,t)+F_{--}(k,t)\right] - F_{+-}(k,t)$$

cross correlation functions:

$$F_{MQ}(k,t) = \frac{1}{N}\langle \rho^M_{\underline{k}}(t)\,\rho^Q_{-\underline{k}}(0)\rangle$$

etc.

Dynamical structure factors:

$$S_{\nu\mu}(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} F_{\nu\mu}(k,t)\,e^{i\omega t}\,dt$$

b_+, b_- = coherent scattering amplitudes

⇒ coherent inelastic neutron scattering cross section:

$$\frac{d^2\sigma}{d\Omega\,d\omega} = \frac{k_{out}}{4\pi k_{in}}\left[(b_+ + b_-)^2 S_{NN}(k,\omega)\right.$$
$$\left. + 2(b_+^2 - b_-^2)S_{NQ}(k,\omega) + (b_+ - b_-)^2 S_{QQ}(k,\omega)\right]$$

D.L. Price and J. R.D. Copley (Phys. Rev. A11, 2124 (1975))

Rb Br: $b_+ \simeq b_-$ ⇒ $S_{NN}(k,\omega)$

⑧ MD "experiment" on the SMS

(Hansen and McDonald)

SMS: $F_{++}(k,t) \equiv F_{--}(k,t) = F_l(k,t)$

$F_{+-}(k,t) = F_u(k,t)$

(only 2 independent correlation functions)

We shall consider:

a) $F_{NN}(k,t) \equiv F_{MM}(k,t)$ (since $M_1 = M_2$)

$= F_l(k,t) + F_u(k,t)$

b) $F_{QQ}(k,t) = F_l(k,t) - F_u(k,t)$

N.B.: $F_{MQ}(k,t) \equiv F_{NQ}(k,t) = 0$:

charge and mass density fluctuations are completely decoupled

	T	V
MD "exp."	1267 °K	41.9 cm³/mole
NaCl triple point	1073 °K	37.52 cm³/mole

time scale: $\omega_p^{-1} = \sqrt{\frac{M}{4\pi\rho e^2}} \simeq 2.5\cdot 10^{-14}$ sec.

length parameter in potential:

$\lambda = 2.34$ Å

dimensionless wave number:

$q = k\cdot\lambda$

② Density fluctuations : $S_{NN}(q,\omega)$

$0.75 \leq q \leq 7.5$
$(\sim 0.3 \text{Å}^{-1})$ $(\sim 3 \text{Å}^{-1})$

cf. slide (V)

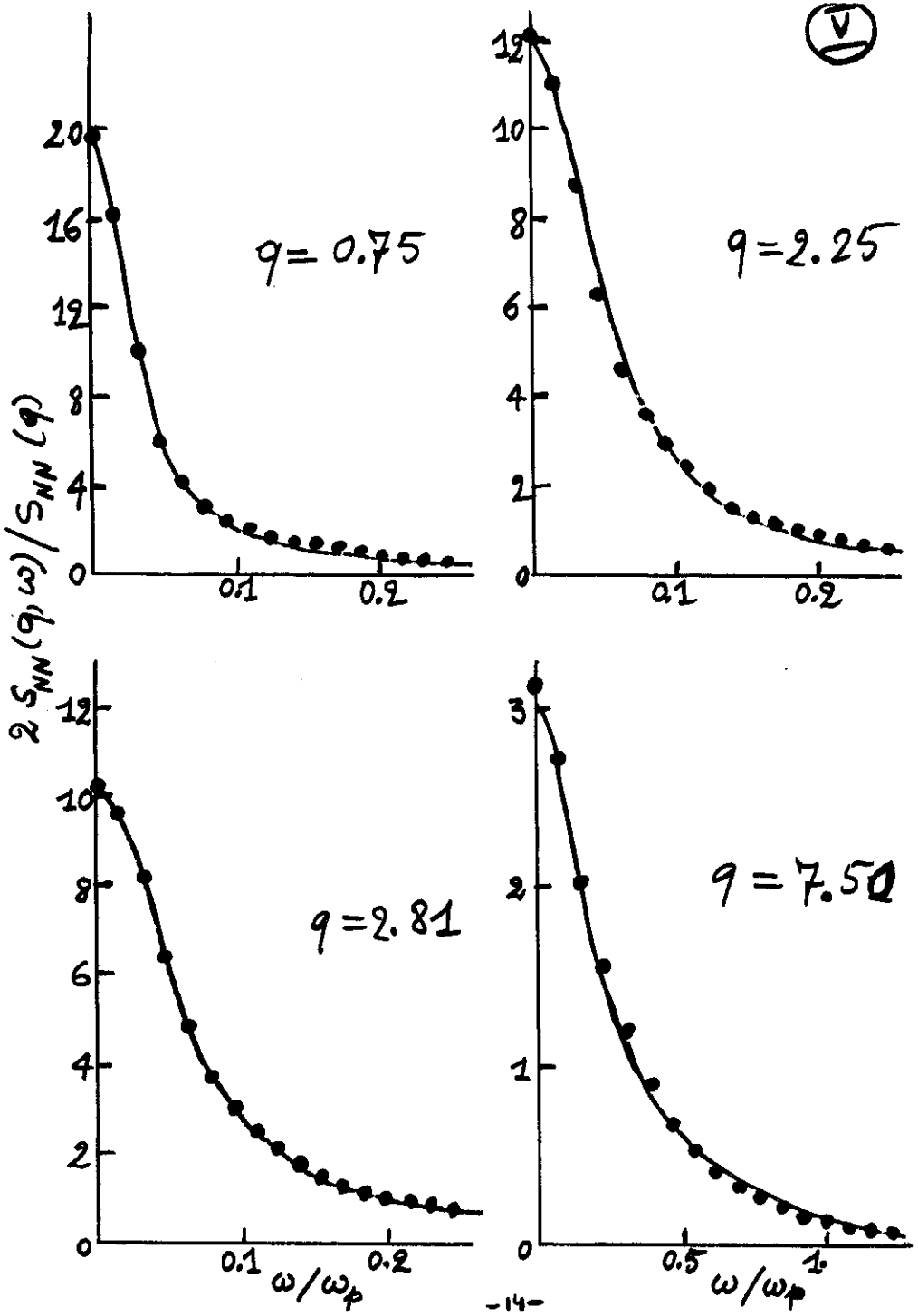
$\omega^2 S_{NN}(q,\omega) = C_{NN}(q,\omega)$ → dispersion curve of "acoustic" mode on slide (VI)

Qualitatively similar results obtained by Copley and Rahman in the case of Rb Br and by Adams et al. for Na Cl (Proc. Roy. Soc. A 357 37 (1977)

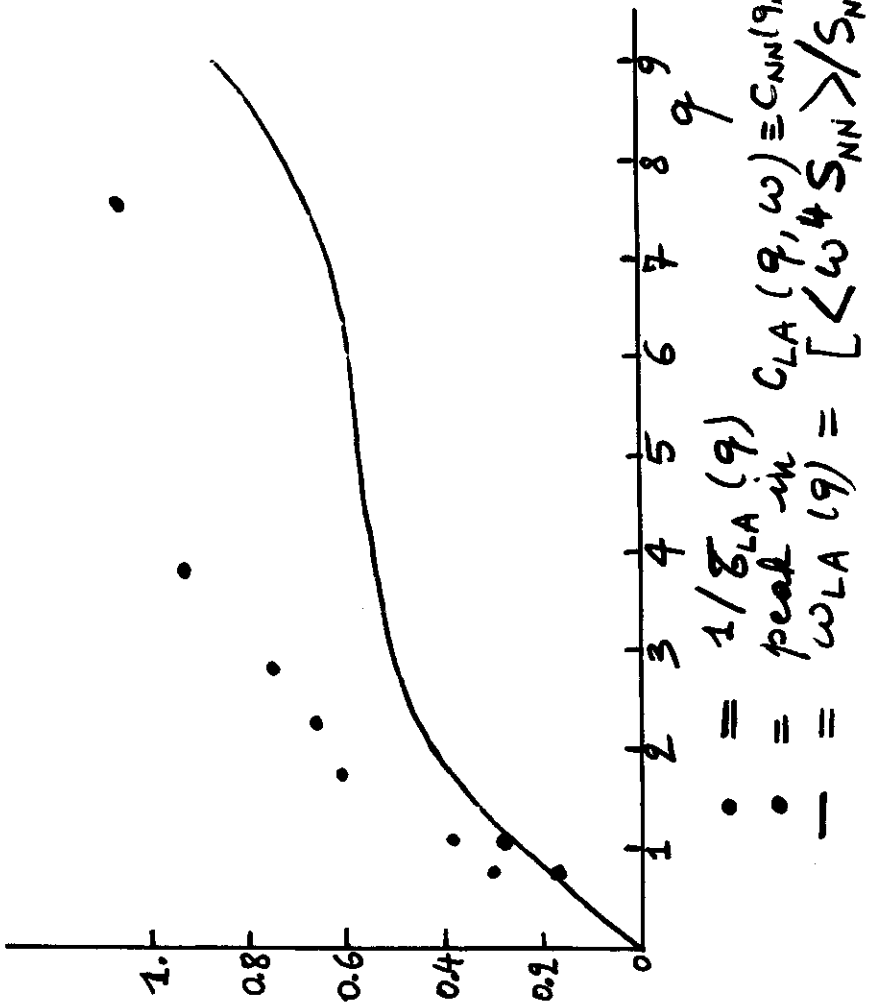
Charge fluctuations : $S_{QQ}(q,\omega)$

$q \lesssim 3$: $F_{QQ}(q,t)$ exhibits oscillations, with an angular frequency of the order of ω_p : slide (VII)

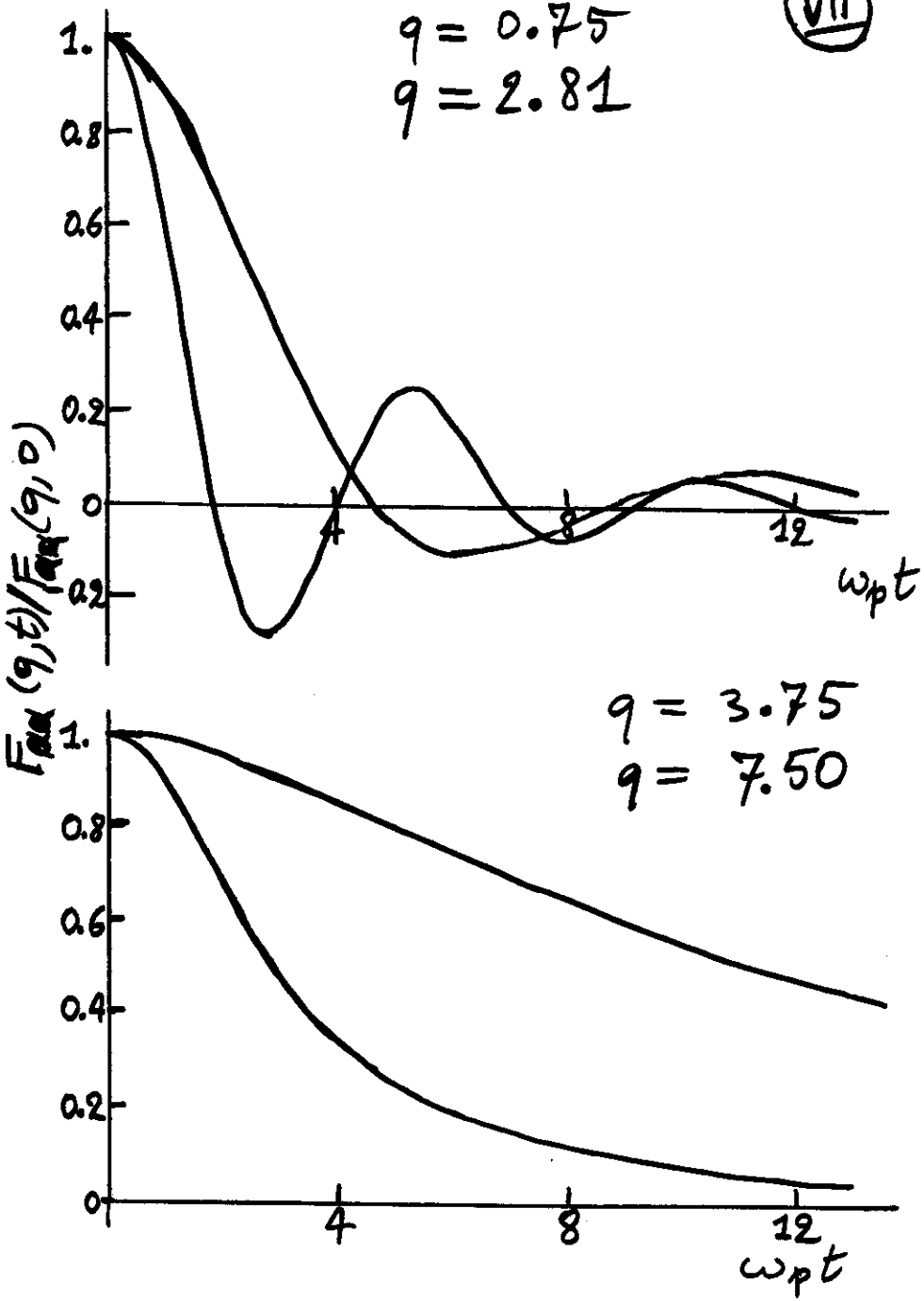
$S_{QQ}(q,\omega)$: slides (VIII), (IX), (X) : "optic" mode
- negative dispersion : slide (XI)
- peak width minimum for $q \simeq 2$ (1.5Å^{-1}) ; increases for larger and smaller q.
- theoretical fits based on exact 0th, 2d and 4th frequency moments, and on a single relaxation-time exponential memory function.



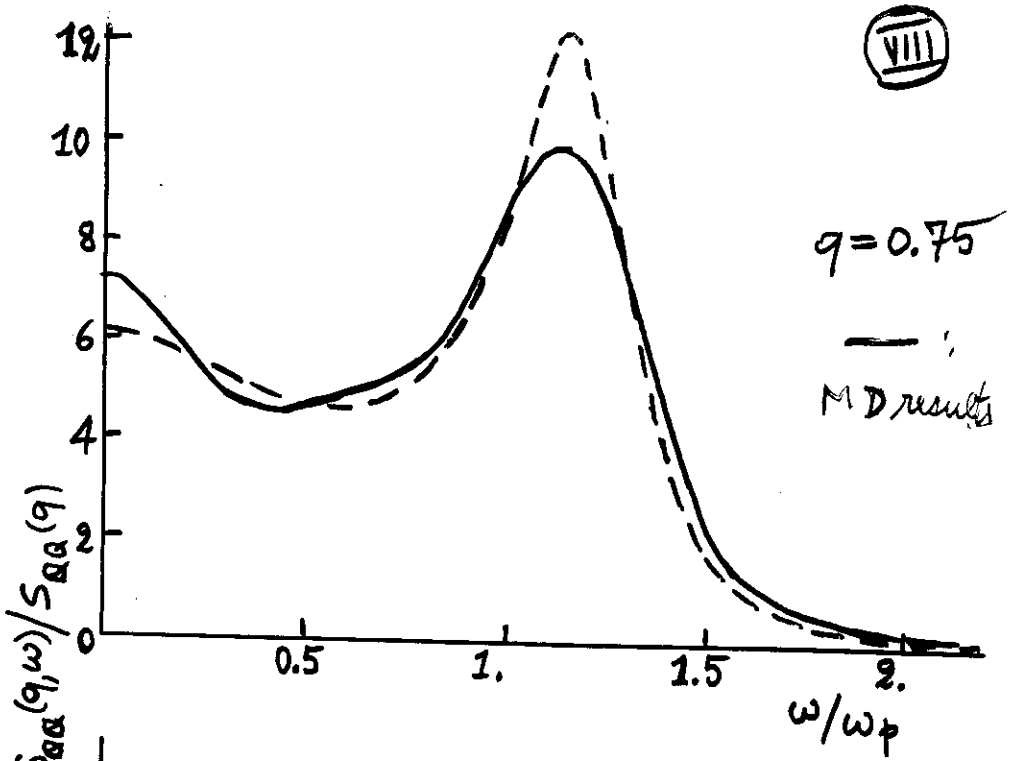
(VII)

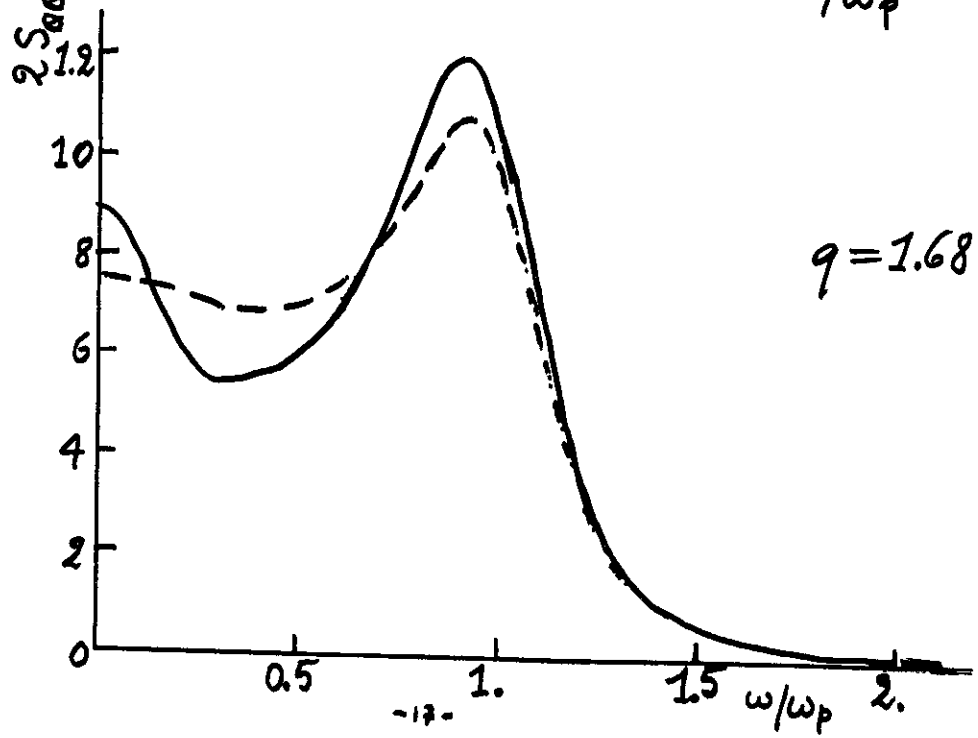

1.
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
q
• ≡ 1/ξ_LA (q)
• ≡ peak in C_LA (q,ω) ≡ C_NN(q,ω)
— ≡ ω_LA (q) = [⟨ω⁴ S_NN⟩/S_NN(q)]^1/4

(VII)

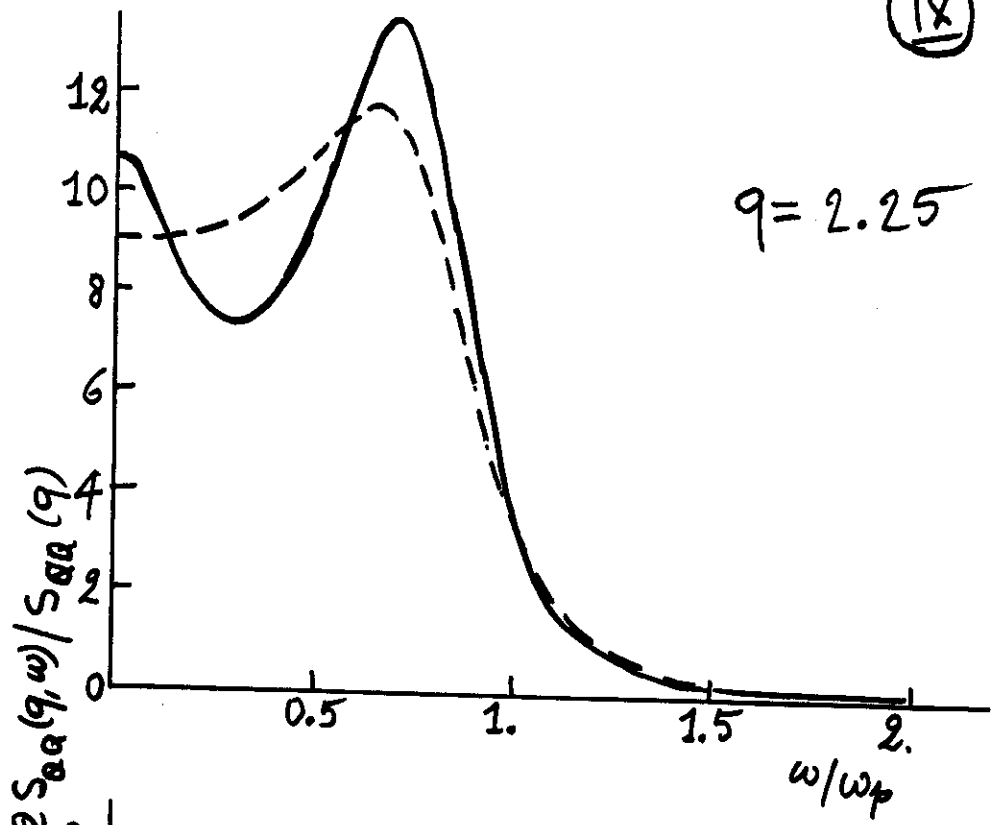

q = 0.75
q = 2.81
q = 3.75
q = 7.50
F_coh (q,t)/F_coh(q,0)
1.
0.8
0.6
0.4
0.2
0
-0.2
4
8
12
ω_p t

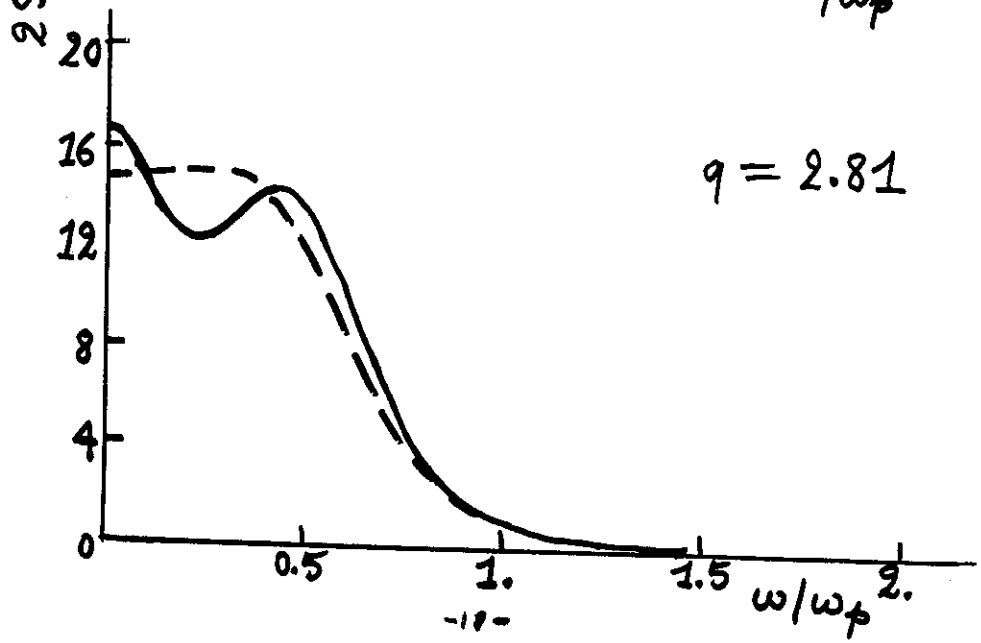
VIII


$2S_{QQ}(q,\omega)/S_{QQ}(q)$
ω/ω_p
$q = 0.75$
—: MD results

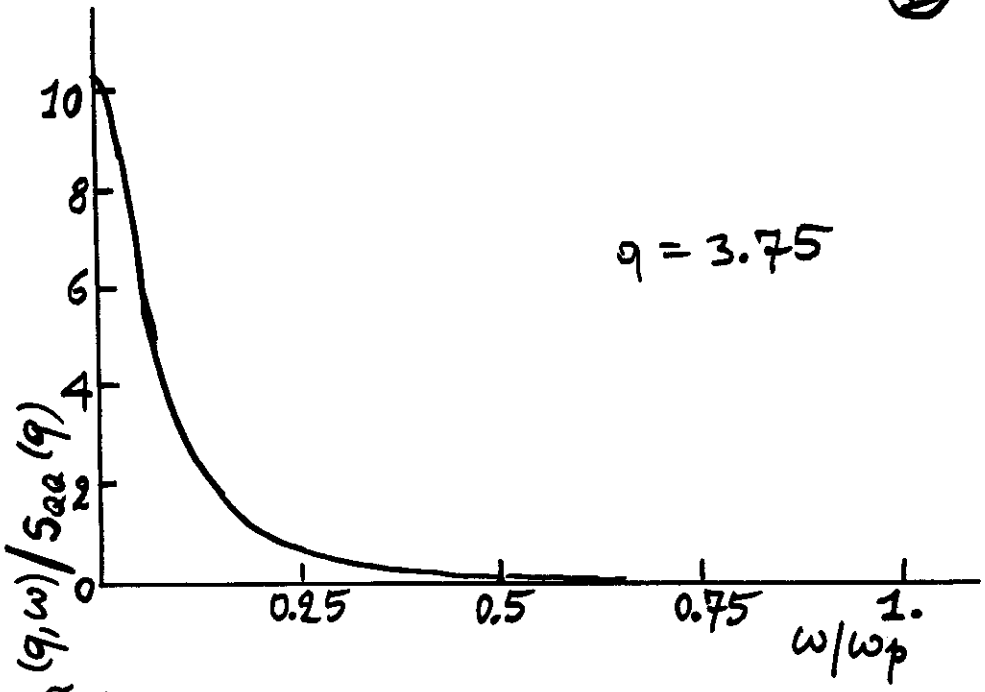

$2S_{QQ}(q,\omega)/S_{QQ}(q)$
ω/ω_p
$q = 1.68$

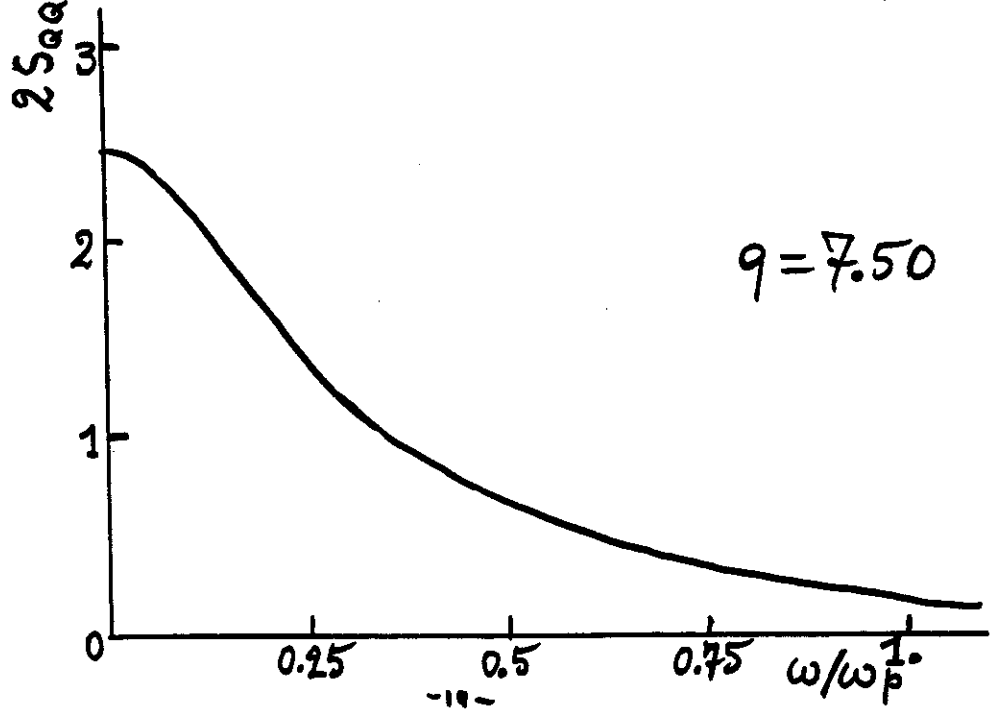
IX


$2S_{QQ}(q,\omega)/S_{QQ}(q)$
ω/ω_p
$q = 2.25$


$2S_{QQ}(q,\omega)/S_{QQ}(q)$
ω/ω_p
$q = 2.81$

(X)





(XI)

Dispersion curve "optique" of LO mode