Mode expansion delle funzioni di autocorrelazione temporale

Una recente teoria generale circa le funzioni di correlazione di sistemi a molti corpi stabilisce che **qualsiasi** funzione di correlazione temporale è esprimibile come **una serie infinita di esponenziali** in generale di argomento complesso. Data la funzione di autocorrelazione (normalizzata)

$$b(t)=\frac{\langle A^*(0)A(t)\rangle}{\langle A^*(0)A(0)\rangle}$$

e per cui vale l'invarianza per inversione temporale

$$b(t)=b(-t)$$

è esprimibile nella forma:

$$b(t)=\sum_{k=1}^{\infty} I_k e^{z_k|t|}$$

La cui trasformata di Laplace è

$$b(z)=\sum_{k=1}^{\infty}\frac{I_k}{z-z_k}$$

Autofrequenze della correlazione

$$b(t) = \sum_{z_k = real} I_k e^{z_k |t|} + \sum_{z_k = complex} I_k e^{z_k |t|}$$

$$z_k = z_k' + i z_k'' \qquad z_k' < 0$$

Autofrequenze complesse

where I_k and z_k are amplitude and complex-frequency, respectively, of the k-th mode. When I_k and z_k are complex quantities, both the corresponding mode and its conjugate ($I_{k+1} = I_k^*$, $z_{k+1} = z_k^*$) are present and, summed together, describe an exponentially damped oscillation. When I_k and z_k are real the mode represents instead a pure exponential decay. For all modes Rez_k is negative, thus the damping is to be identified with -Rez_k.

Lo sviluppo in modi esponenziali per $F(Q,t)$, o equivalentemente in Lorentziane per lo spettro $S(Q,\omega)$, si applica ovviamente anche a questa autocorrelazione e relativo spettro.

Spettro della correlazione

$$b(\omega) = \frac{1}{\pi}\mathrm{Re}\left[LT\, b(z = i\omega)\right] = \sum_{k=1}^{\infty} b_k(\omega) = \frac{1}{\pi}\mathrm{Re}\left[\sum_{k=1}^{\infty}\frac{I_k}{i\omega - z_k}\right]$$

where $b_k(\omega)$ is a generalized Lorentzian line. If I_k and z_k are real then $b_k(\omega)$ is a true Lorentzian:

$$b_k(\omega) = I_k \frac{1}{\pi}\frac{(-z_k)}{\omega^2 + z_k^2}. \tag{3}$$

If I_k and z_k are complex, then the corresponding mode (k) and its conjugate $(k+1)$ sum together to give a pair of distorted inelastic Lorentzians:

$$\begin{aligned} b_k(\omega) + b_{k+1}(\omega) &= \frac{1}{\pi}\mathrm{Re}\left[\frac{I_k}{i\omega - z_k} + \frac{I_k^*}{i\omega - z_k^*}\right] = \\ &= \frac{I_k'}{\pi}\left[\frac{-z_k' + I_k''/I_k'(\omega - z_k'')}{(\omega - z_k'')^2 + (z_k')^2} + \frac{-z_k' - I_k''/I_k'(\omega + z_k'')}{(\omega + z_k'')^2 + (z_k')^2}\right] \end{aligned} \tag{4}$$

where the prime and double prime are used to indicate the real and imaginary parts of the complex quantities.

$$b(\omega) = \frac{1}{\pi}\left[\sum_{z_r}\frac{-I_r z_r}{z_r^{\;2} + \omega^2} + \sum_{z_c}\left(\frac{-I_c' z_c' + I_c''\left(\omega - z_c''\right)}{\left(z_c'\right)^2 + \left(\omega - z_c''\right)^2} + \frac{-I_c' z_c' - I_c''\left(\omega + z_c''\right)}{\left(z_c'\right)^2 + \left(\omega + z_c''\right)^2}\right)\right]$$

$r = real \quad c = complex$

Ricordiamoci una proprietà generale delle TF

$$f(t)=\int d\omega\,\tilde f(\omega)e^{i\omega t}$$
$$\dot f(t)=\int d\omega\,\tilde f(\omega)i\omega e^{i\omega t}$$
$$\ddot f(t)=\int d\omega\,\tilde f(\omega)(i\omega)^2 e^{i\omega t}$$
$$\dddot f(t)=\int d\omega\,\tilde f(\omega)(i\omega)^3 e^{i\omega t}$$
...

Calcolate a t=0

$$f(0)=\int d\omega\,\tilde f(\omega)=i^0\langle\omega^0\rangle$$
$$\dot f(0)=\int d\omega\,\tilde f(\omega)i\omega=i^1\langle\omega^1\rangle$$
$$\ddot f(0)=\int d\omega\,\tilde f(\omega)(i\omega)^2=i^2\langle\omega^2\rangle$$
$$\dddot f(0)=\int d\omega\,\tilde f(\omega)(i\omega)^3=i^3\langle\omega^3\rangle$$
...

Momenti dello spettro

$$\langle\omega^p\rangle=\int_{-\infty}^{+\infty} d\omega\,\omega^p\,\tilde f(\omega)$$

Ricordando che:

$$b(t)=\sum_{k=1}^{\infty} I_k e^{z_k|t|}$$

$$\Rightarrow (i)^p\langle\omega^p\rangle=\left.\frac{d^p b(t)}{dt^p}\right|_{t=0}=\sum_{k=1}^{\infty} I_k z_k{}^p\left(e^{z_k t}\right)_{t=0}=\sum_{k=1}^{\infty} I_k z_k{}^p=0$$

per *p dispari*

Regole di somma

Since we are presently considering a classical system, for which autocorrelations are even functions of time, all odd frequency moments are known and equal to zero. Moreover, being $b(t)$ normalized to unity at $t=0$, the $p=0$ sum rule is $\sum_{k=1}^{\infty} I_k = 1$.

Un'altra correlazione importante

$$c(t) = -\ddot{b}(t)$$

Spettro:

$$c(\omega) = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\ddot{b}(t) = -\frac{1}{2\pi}\left[\dot{b}(t)e^{-i\omega t}\right]_{-\infty}^{+\infty} + \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, \dot{b}(t)(-i\omega)e^{-i\omega t} =$$

$$= -\frac{i\omega}{2\pi}\left\{\left[b(t)e^{-i\omega t}\right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} dt\, b(t)(-i\omega)e^{-i\omega t}\right\} = -i^2\omega^2\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, b(t)e^{-i\omega t} =$$

$$= \omega^2 b(\omega)$$

Differenziando direttamente $b(t) = \sum_{k=1}^{\infty} I_k e^{z_k t}$ **si ha:**

$$c(t) = -\ddot{b}(t) = \sum_{k=1}^{\infty}\left(-I_k z_k^2\right)e^{z_k t}$$

$$c(\omega) = \sum_{k=1}^{\infty}\frac{1}{\pi}\mathrm{Re}\frac{\left(-I_k z_k^2\right)}{i\omega - z_k} = \omega^2 b(\omega) = \omega^2\sum_{k=1}^{\infty}\frac{1}{\pi}\mathrm{Re}\frac{I_k}{i\omega - z_k}$$

una relazione importante

$$c(\omega)=\sum_{k=1}^{\infty}\frac{1}{\pi}\mathrm{Re}\frac{\left(-I_k z_k^2\right)}{i\omega-z_k}=\omega^2 b(\omega)=\omega^2\sum_{k=1}^{\infty}\frac{1}{\pi}\mathrm{Re}\frac{I_k}{i\omega-z_k}$$

Despite its simplicity, such a relation carries the important meaning that the autocorrelation function of a dynamical variable $A(t)$ and that of its derivatives are characterized by the same time decays or complex frequencies, therefore describe essentially the same dynamics. The same generalized Lorentzians describe the spectra $b(\omega)$ and $c(\omega)$, with only different amplitudes, where those of $c(\omega)$ are readily obtained by multiplying the amplitudes of $b(\omega)$ by the negative of the squared "generalized half-width" z_k (either real or complex).

While the multi-exponential expansion applies to any correlation function, and the corresponding multi-Lorentzian representation describes the respective spectrum, the result given above is of particular importance in those cases in which two physically meaningful autocorrelation functions are linked by a double time differentiation. A well-known example is the case of the intermediate scattering function $F(Q,t)$, and the longitudinal current autocorrelation $C_L(Q,t)$

La corrente

$$\boldsymbol{j}(\boldsymbol{r},t)=\sum_{\alpha}\boldsymbol{v}_{\alpha}(t)\rho_{\alpha}(\boldsymbol{r},t)=\sum_{\alpha}\boldsymbol{v}_{\alpha}(t)\delta(\boldsymbol{r}-\boldsymbol{R}_{\alpha}(t))$$

TRASFORMATA di Fourier (spaziale):

$$\boldsymbol{j}(\boldsymbol{Q},t)=\sum_{\alpha}\boldsymbol{v}_{\alpha}(t)\rho_{\alpha}(\boldsymbol{Q},t)=\sum_{\alpha}\boldsymbol{v}_{\alpha}(t)e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_{\alpha}(t)}=$$

$$=\boldsymbol{j}_L(\boldsymbol{Q},t)+\boldsymbol{j}_T(\boldsymbol{Q},t)=\left(\boldsymbol{j}(\boldsymbol{Q},t)\cdot\hat{\boldsymbol{Q}}\right)\hat{\boldsymbol{Q}}+\boldsymbol{j}_T(\boldsymbol{Q},t)$$

Assumiamo $\hat{\boldsymbol{Q}}=\boldsymbol{k}$, versore asse *z*.

$$\boldsymbol{j}_T(\boldsymbol{Q},t)$$

$$\boldsymbol{j}(\boldsymbol{Q},t)=\boldsymbol{j}_L(\boldsymbol{Q},t)+\boldsymbol{j}_T(\boldsymbol{Q},t)=\left(\boldsymbol{j}(\boldsymbol{Q},t)\cdot\boldsymbol{k}\right)\boldsymbol{k}+\left(\boldsymbol{j}(\boldsymbol{Q},t)\cdot\boldsymbol{j}\right)\boldsymbol{j}+\left(\boldsymbol{j}(\boldsymbol{Q},t)\cdot\boldsymbol{i}\right)\boldsymbol{i}$$

Per l'isotropia di un fluido:

$$\boldsymbol{j}(\boldsymbol{Q},t)=\boldsymbol{j}_L(\boldsymbol{Q},t)+\boldsymbol{j}_T(\boldsymbol{Q},t)=\left(\boldsymbol{j}(\boldsymbol{Q},t)\cdot\boldsymbol{k}\right)\boldsymbol{k}+2\left(\boldsymbol{j}(\boldsymbol{Q},t)\cdot\boldsymbol{i}\right)\boldsymbol{i}=j_z(\boldsymbol{Q},t)\boldsymbol{k}+2j_x(\boldsymbol{Q},t)\boldsymbol{i}$$

L'autocorrelazione delle componenti della corrente

Longitudinal current-current correlation function:

$$C_L(\boldsymbol{Q},t)=\frac{1}{N}\left\langle j_L^*(\boldsymbol{Q},0)\,j_L(\boldsymbol{Q},t)\right\rangle=\frac{1}{N}\left\langle j_z^*(\boldsymbol{Q},0)\,j_z(\boldsymbol{Q},t)\right\rangle$$

Transverse current-current correlation function:

$$C_T(\boldsymbol{Q},t)=\frac{1}{2N}\left\langle j_T^*(\boldsymbol{Q},0)\,j_T(\boldsymbol{Q},t)\right\rangle=\frac{1}{N}\left\langle j_x^*(\boldsymbol{Q},0)\,j_x(\boldsymbol{Q},t)\right\rangle$$

Vogliamo dimostrare che:

$$\frac{d^2}{dt^2}\langle A(0)B(t)\rangle = -\langle \dot{A}(0)\dot{B}(t)\rangle \tag{1}$$

Occorre sfruttare la proprietà di stazionarietà per una correlazione all'equilibrio. Preliminarmente dimostriamo che

$$\langle A(0)\dot{B}(t)\rangle = -\langle \dot{A}(0)B(t)\rangle \tag{2}$$

La stazionarietà significa che $\langle A(0)B(t)\rangle = \langle A(t')B(t'+t)\rangle$ perché la media è indipendente da t' e dipende solo da t. Quindi la sua derivata rispetto a t' è zero. Calcoliamo la derivata.

$$\frac{d}{dt'}\langle A(t')B(t'+t)\rangle = \left\langle \frac{dA(t')}{dt'}B(t'+t)\right\rangle + \left\langle A(t')\frac{dB(t'+t)}{dt'}\right\rangle$$

Indicando con $\dot{A}$ e $\dot{B}$ le derivate di A e B rispetto al loro argomento, si ha

$$\frac{dA(t')}{dt'} = \dot{A}(t')$$

e anche

$$\frac{dB(t'+t)}{dt'} = \frac{dB(t'+t)}{d(t'+t)}\frac{d(t'+t)}{dt'} = \frac{dB(t'+t)}{d(t'+t)} = \dot{B}(t'+t)$$

cioè

$$\frac{d}{dt'}\langle A(t')B(t'+t)\rangle = \langle \dot{A}(t')B(t'+t)\rangle + \langle A(t')\dot{B}(t'+t)\rangle = \langle \dot{A}(0)B(t)\rangle + \langle A(0)\dot{B}(t)\rangle$$

Ma essendo questa, come detto, nulla, si ottiene

$$\langle A(0)\dot{B}(t)\rangle = -\langle \dot{A}(0)B(t)\rangle$$

che è la (2).

Adesso calcoliamo $\frac{d}{dt}\left\langle A(0)B(t)\right\rangle$. Si ha

$$\begin{aligned}\frac{d}{dt}\left\langle A(0)B(t)\right\rangle &= \frac{d}{dt}\left\langle A(t')B(t'+t)\right\rangle = \left\langle A(t')\frac{dB(t'+t)}{dt}\right\rangle = \left\langle A(t')\frac{dB(t'+t)}{d(t'+t)}\frac{d(t'+t)}{dt}\right\rangle = \\ &= \left\langle A(t')\frac{dB(t'+t)}{d(t'+t)}\right\rangle = \left\langle A(t')\dot{B}(t'+t)\right\rangle = \left\langle A(0)\dot{B}(t)\right\rangle\end{aligned} \tag{3}$$

e derivando ancora, analogamente,

$$\frac{d^2}{dt^2}\left\langle A(0)B(t)\right\rangle = \frac{d}{dt}\left\langle A(0)\dot{B}(t)\right\rangle = \left\langle A(0)\ddot{B}(t)\right\rangle \tag{4}$$

Usando la (2) con $\ddot{B}$ al posto di $\dot{B}$ si vede che questa è uguale a $-\left\langle \dot{A}(0)\dot{B}(t)\right\rangle$. Q.E.D.

Considieriamo allora

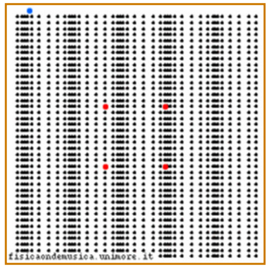
$$
\begin{cases}
F(\boldsymbol{Q},t)=\dfrac{1}{N}\left\langle \rho^{*}(\boldsymbol{Q},0)\rho(\boldsymbol{Q},t)\right\rangle \\
\dot{F}(\boldsymbol{Q},t)=\dfrac{1}{N}\left\langle \rho^{*}(\boldsymbol{Q},0)\dot{\rho}(\boldsymbol{Q},t)\right\rangle \\
\ddot{F}(\boldsymbol{Q},t)=\dfrac{1}{N}\left\langle \rho^{*}(\boldsymbol{Q},0)\ddot{\rho}(\boldsymbol{Q},t)\right\rangle =-\dfrac{1}{N}\left\langle \dot{\rho}^{*}(\boldsymbol{Q},0)\dot{\rho}(\boldsymbol{Q},t)\right\rangle
\end{cases}
$$

ma

$$
\dot{\rho}(\boldsymbol{Q},t)=\frac{d}{dt}\left(\sum_{\alpha} e^{iQ\boldsymbol{k}\cdot\boldsymbol{R}_{\alpha}(t)}\right)=
$$

$$
=iQ\boldsymbol{k}\cdot\sum_{\alpha} e^{iQ\boldsymbol{k}\cdot\boldsymbol{R}_{\alpha}(t)}\boldsymbol{v}_{\alpha}(t)=iQ\boldsymbol{k}\cdot\boldsymbol{j}(\boldsymbol{Q},t)=
$$

$$
=iQ\, j_{L}(\boldsymbol{Q},t)
$$



$$
\ddot{F}(\boldsymbol{Q},t)=-\frac{1}{N}\left\langle \dot{\rho}^{*}(\boldsymbol{Q},0)\dot{\rho}(\boldsymbol{Q},t)\right\rangle =-\frac{1}{N}\left\langle -iQ\, j_{L}^{*}(\boldsymbol{Q},0)iQ\, j_{L}(\boldsymbol{Q},t)\right\rangle =
$$

$$
=-\frac{Q^{2}}{N}\left\langle j_{L}^{*}(\boldsymbol{Q},0)\, j_{L}(\boldsymbol{Q},t)\right\rangle \Rightarrow
$$

$$
C_{L}(\boldsymbol{Q},t)=-\frac{\ddot{F}(\boldsymbol{Q},t)}{Q^{2}}
$$

Componente longitudinale

$$C_L(\boldsymbol{Q},t) = -\frac{\ddot{F}(\boldsymbol{Q},t)}{Q^2}$$

Spettro:

$$C_L(\boldsymbol{Q},\omega) = -\frac{1}{2\pi Q^2}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\ddot{F}(\boldsymbol{Q},t) = -\frac{(i\omega)^2}{Q^2}\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}F(\boldsymbol{Q},t) = \frac{\omega^2}{Q^2}S(\boldsymbol{Q},\omega)$$

E’ solo un caso particolare della relazione generale già trovata, i.e.:

$$\begin{pmatrix} c(t) = -\ddot{b}(t) \\ c(\omega) = \omega^2 b(\omega) \end{pmatrix}$$

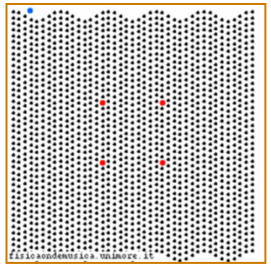
$$c(t) = -\ddot{b}(t) = \sum_{k=1}^{\infty}\left(-I_k z_k^2\right)e^{z_k t}$$

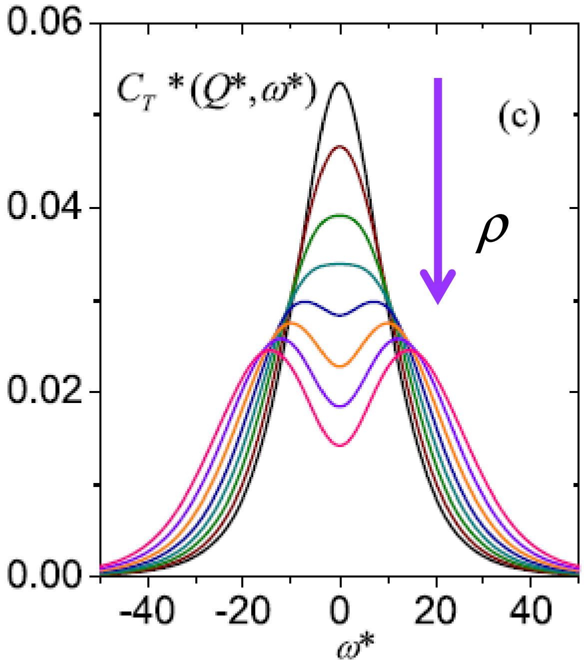
$$c(\omega) = \sum_{k=1}^{\infty}\frac{1}{\pi}\mathrm{Re}\frac{\left(-I_k z_k^2\right)}{i\omega - z_k} = \omega^2 b(\omega) = \omega^2\sum_{k=1}^{\infty}\frac{1}{\pi}\mathrm{Re}\frac{I_k}{i\omega - z_k}$$

La corrente longitudinale **non porta** in realtà **nuova informazione** sulla dinamica collettiva, rispetto a quanto fornito dalla funzione intermedia di scattering e dal suo spettro.

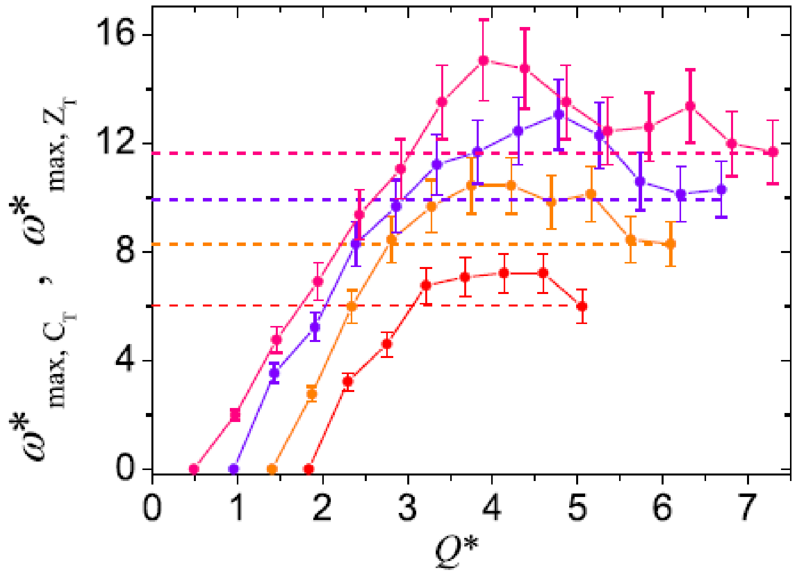
Componente trasversa

Diversamente dalla componente longitudinale, la correlazione della corrente trasversa non è accoppiata con le fluttuazioni di densità, pertanto fornisce informazioni su altre proprietà dinamiche del liquido. In particolare, sonda i modi di shear che possono propagarsi nel fluido.





(*Q* fissato)



Andamenti limite

	$S(Q,\omega)$	$S_s(Q,\omega)$	$C_T(Q,\omega)$
$Ql \ll 1$	Triplet of “lorentzians”	Lorentzian of $HWHM=DQ^2$	Lorentzian of $HWHM=(\eta/m\rho)Q^2$
$Ql \gg 1$	Gaussian of $\sigma^2=(k_B T/m)Q^2$	Gaussian of $\sigma^2=(k_B T/m)Q^2$	Gaussian of $\sigma^2=(k_B T/m)Q^2$

Andamenti limite

$$S(Q,\omega)\big|_{\text{i.g.}} = \left(\frac{m}{2\pi k_B T Q^2}\right)^{1/2} \exp\left(-\frac{m\omega^2}{2k_B T Q^2}\right)$$

$$S_s(Q,\omega)\big|_{\text{hyd}} = \frac{1}{\pi}\frac{D_s Q^2}{\omega^2 + \left(D_s Q^2\right)^2}$$

From Fick diffusion law

$$S_s(Q,\omega)\big|_{\text{i.g.}} = S(Q,\omega)\big|_{\text{i.g.}}$$

In the kinetic limit, correlations between distinct atoms are lost

$$C_T(Q,\omega)\big|_{\text{hyd}} = \frac{k_B T}{m\pi}\frac{(\eta/\rho m)Q^2}{\omega^2 + \left((\eta/\rho m)Q^2\right)^2}$$

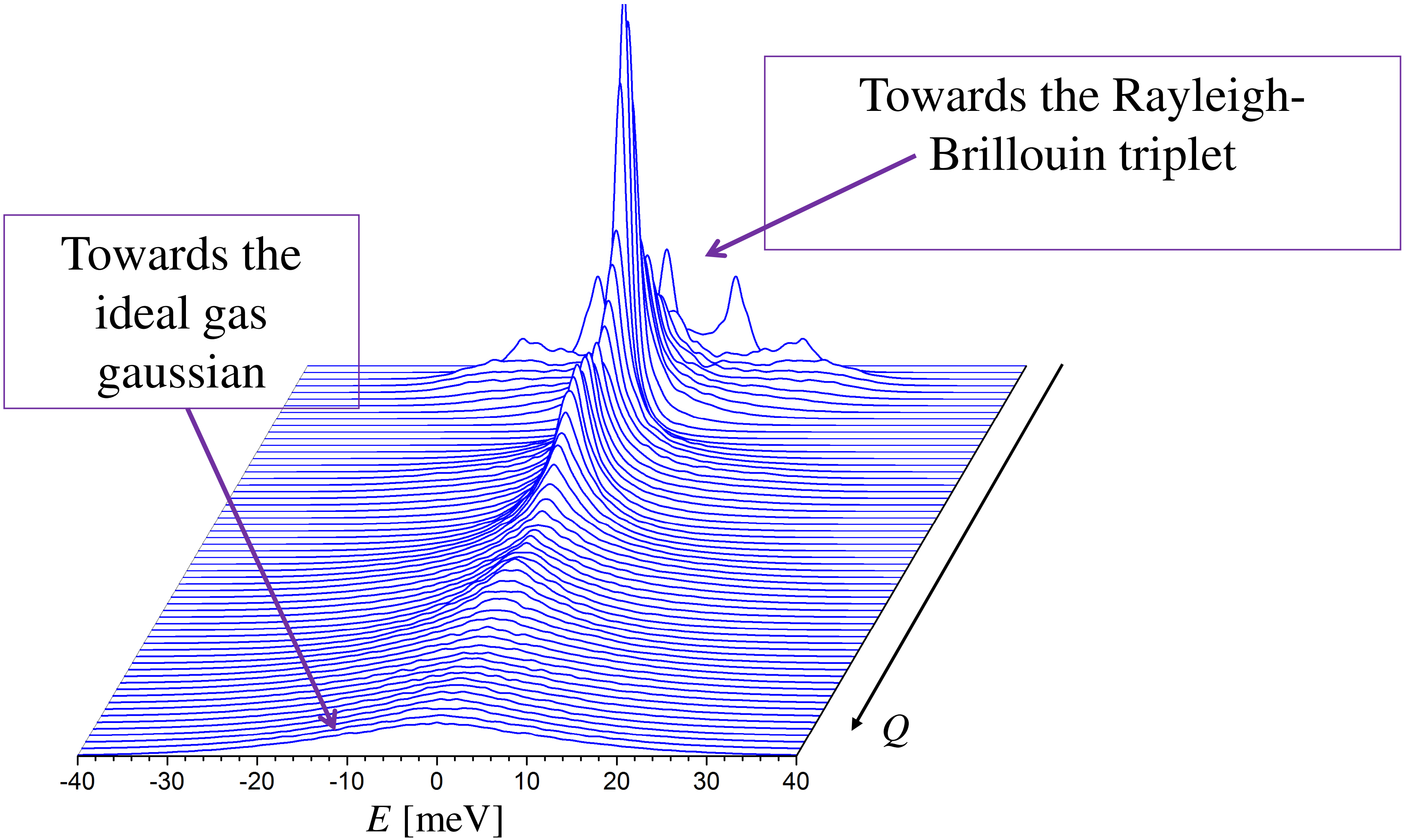
No propagating transverse sound waves. At a macroscopic level the fluid is unable to resist shear forces

$$C_T(Q,\omega)\big|_{\text{i.g.}} = \left(\frac{k_B T}{2\pi m Q^2}\right)^{1/2} \exp\left(-\frac{m\omega^2}{2k_B T Q^2}\right)$$

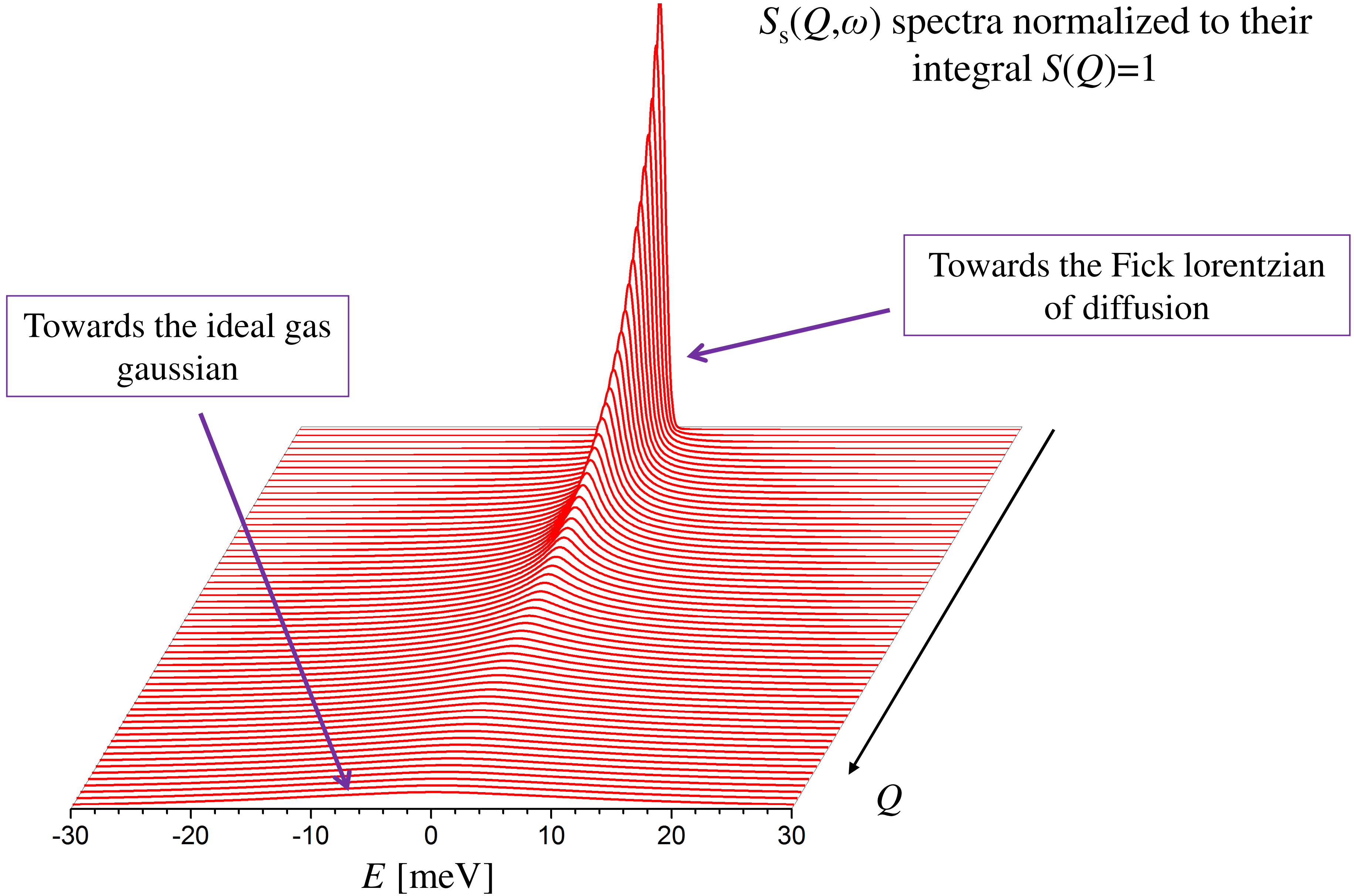
Same expression as for $S(Q,\omega)$ apart from a normalization factor $k_B T/m$.

Typical $S(Q,\omega)$ of a liquid

$S(Q,\omega)$ spectra normalized to their integral $S(Q)$, i.e. the structure factor



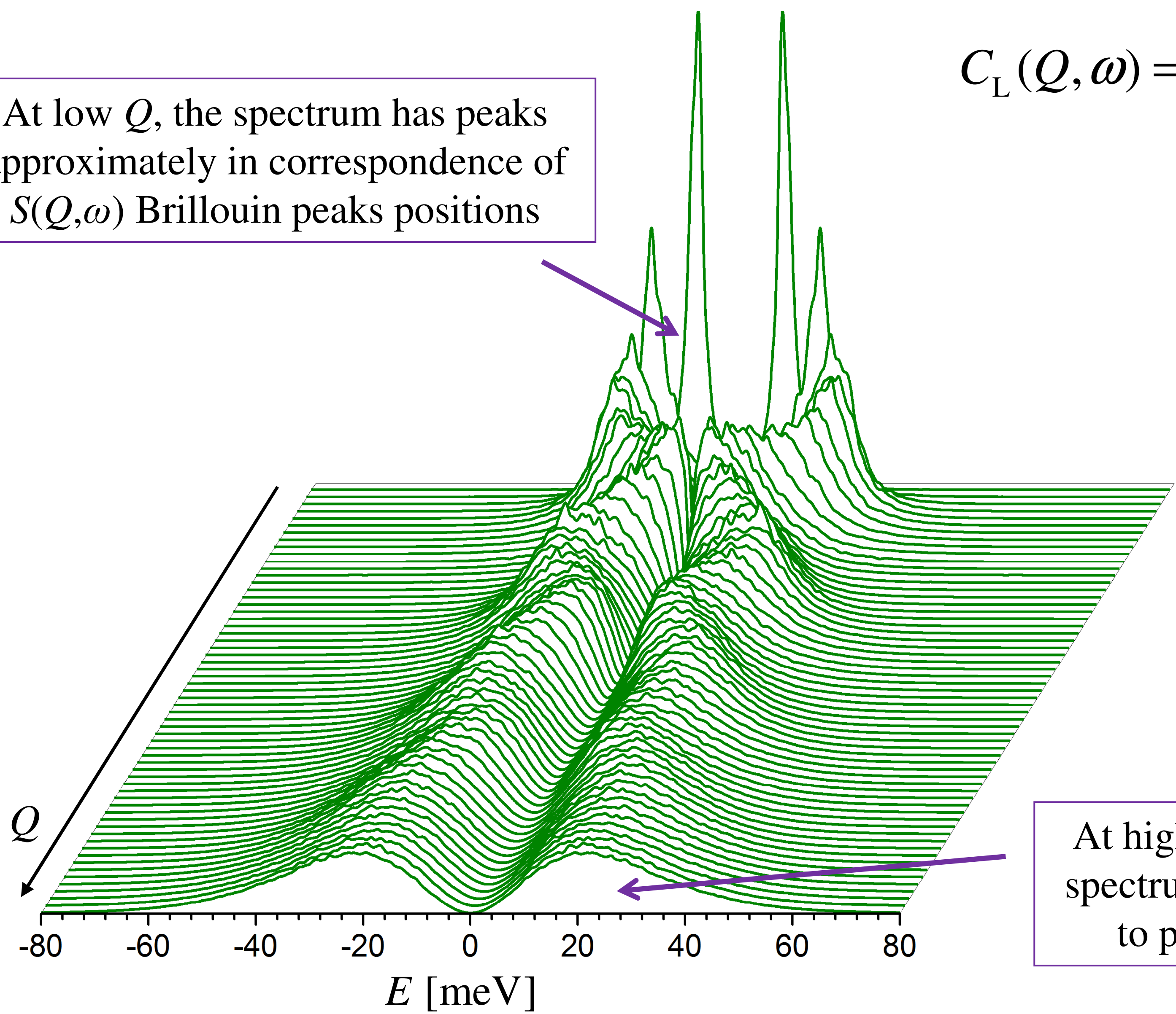
Typical $S_s(Q,\omega)$ of a liquid



Typical $C_L(Q,\omega)$ of a liquid

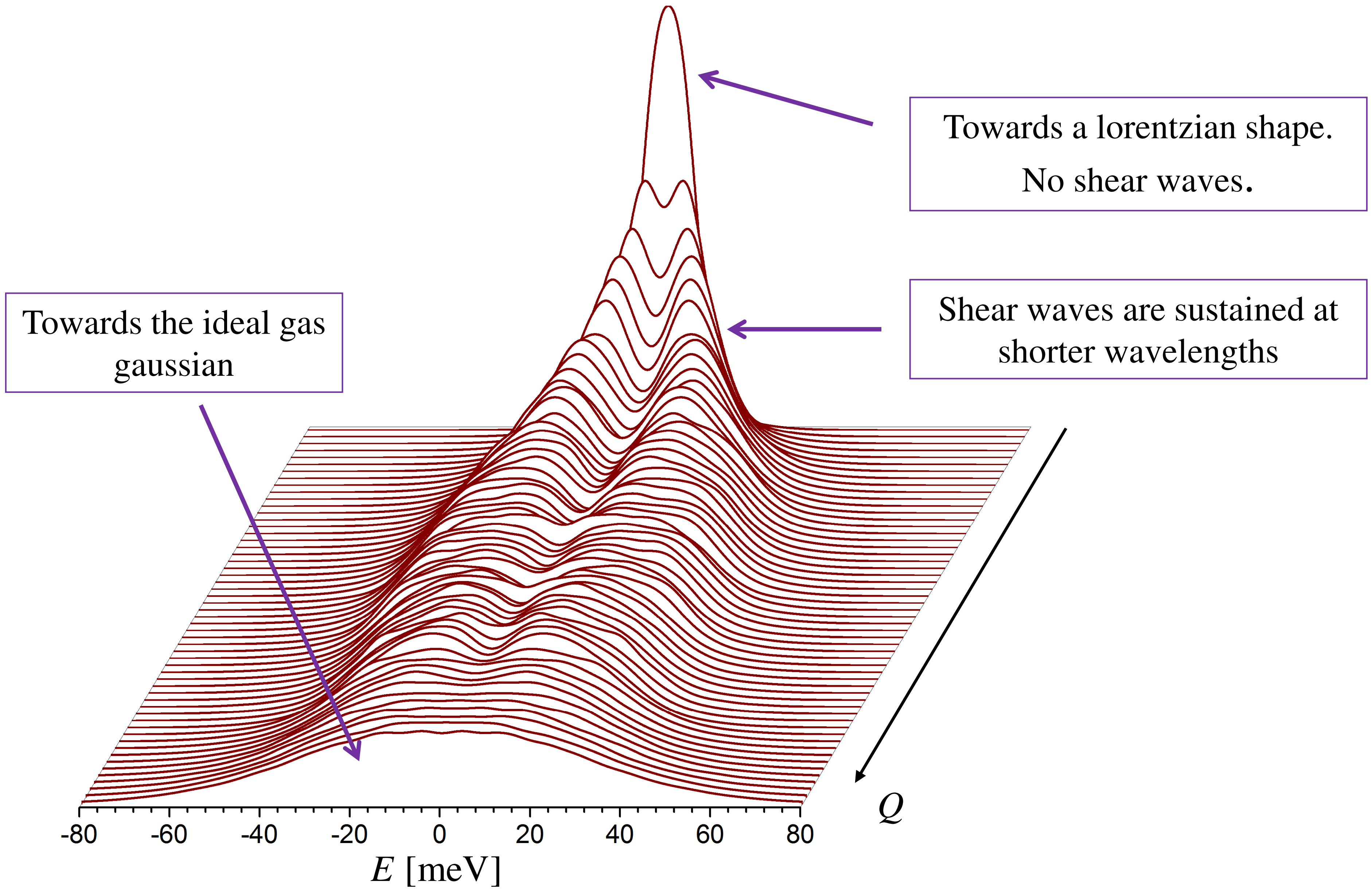
$$C_L(Q,\omega) = \frac{\omega^2}{Q^2} S(Q,\omega)$$

At low Q, the spectrum has peaks approximately in correspondence of $S(Q,\omega)$ Brillouin peaks positions

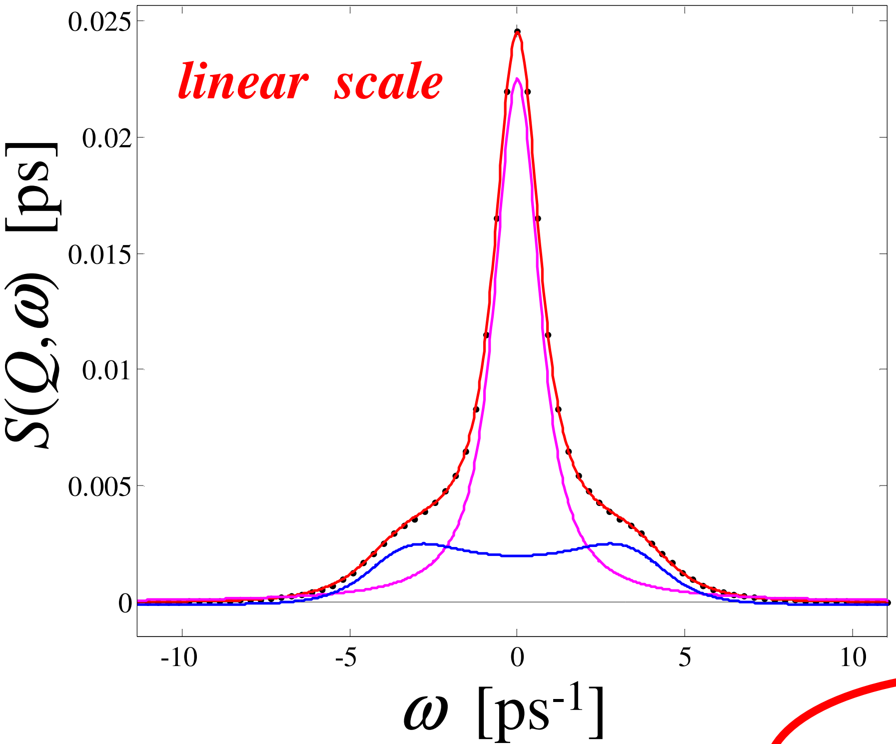


At high Q, the peaks in the spectrum do not correspond to propagating waves

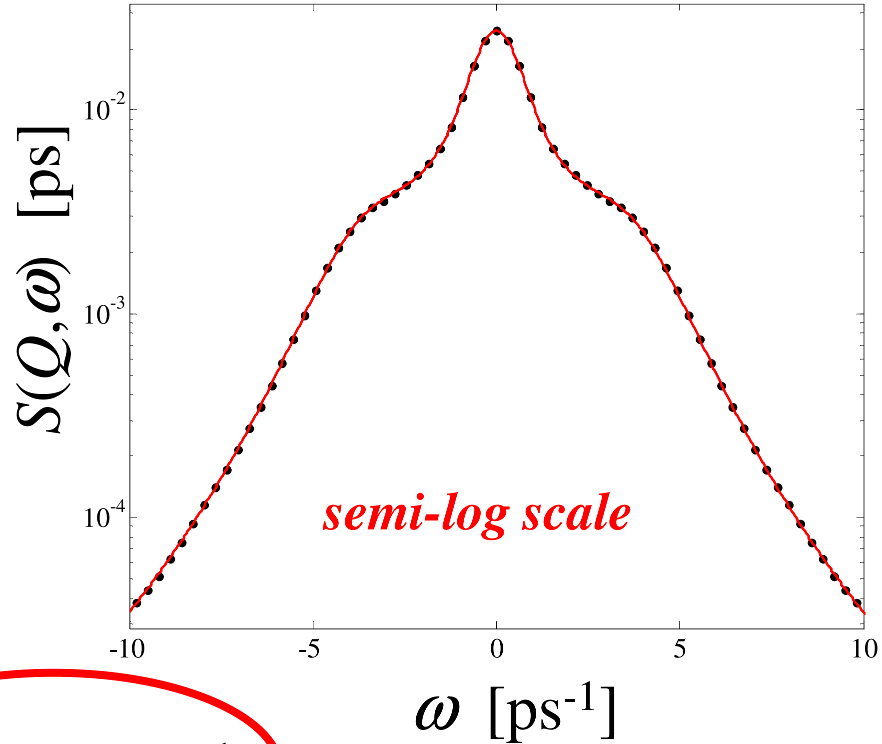
Typical $C_T(Q,\omega)$ of a liquid



Fit and its components



MD data and global fit



Q = 3 nm^{-1}

2 Real modes + 2 Complex modes (1 CC pair)

L'importanza di guardare più correlazioni