Franck-Condon picture of incoherent neutron scattering

Supplementary information appendix

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**Quantum oscillator**

**Wave functions in momentum space.** We consider the stationary Schrödinger equation

\[
\left\{ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + \frac{M\Omega^2 x^2}{2} \right\} \psi(x) = E\psi(x). \tag{1}
\]

for a particle in a quadratic potential of the form \( V(x) = M\Omega^2 x^2/2 \). The eigenfunctions in momentum space, which are defined through the symmetric Fourier transform pair,

\[
\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dx \, e^{-ipx/\hbar} \psi(x),
\]

\[
\phi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dp \, e^{ipx/\hbar} \phi(x),
\]

are solutions of the differential equation

\[
\left\{ \frac{p^2}{2M} - \frac{M\Omega^2}{2} \frac{\partial^2}{\partial p^2} \right\} \phi(p) = E\phi(p). \tag{2}
\]

Defining \( z = \sqrt{2f/(MH)}p \), the solutions of the dimensionless version of (2),

\[
\phi''(z) + \left( \epsilon - \frac{z^2}{4} \right) \phi(z) = 0,
\]

are given by

\[
\phi_m(z) = e^{-\frac{z^2}{4}} H_m(z), \tag{4}
\]

where \( m = 0, 1, 2, \ldots \) and \( \epsilon = \frac{m}{m/2} \), with \( \epsilon = E/(\hbar\Omega) \).

Here \( H_m(z) \) is the \( m \)-th Hermite polynomial. The normalization of the eigenfunctions \( \phi_m(z) \) is chosen such that

\[
\int_{-\infty}^{+\infty} dz \, \phi_m^*(z)\phi_m(z) = \delta_{mn}. \tag{5}
\]

**Overlap integrals and transition probabilities.** Defining the dimensionless momentum transfer

\[
y = \sqrt{\frac{2\Omega}{M\hbar}}p,
\]

we consider overlap integrals of the form

\[
a_{m\to n}(y) = \int_{-\infty}^{+\infty} dz \, \phi_m^*(z + y)\phi_m(z)
\]

\[
= \int_{-\infty}^{+\infty} dz \, \phi_m^*(z + y/2)\phi_m(z - y/2). \tag{7}
\]

Using that [1]

\[
H_m(z + y) = \sum_{k=0}^{m} \frac{m!}{k!(m-k)!} H_k(z)y^{m-k} \tag{8}
\]

one finds that

\[
\phi_m(z \pm y/2) = e^{-\frac{3}{4}(\pm \frac{y}{2})^2} \sum_{k=0}^{m} \frac{m!}{k!(m-k)!} \frac{(\pm \frac{y}{2})^{m-k}}{\sqrt{2\pi\hbar}} H_k(z)
\]

such that

\[
a_{m\to n}(y) = \frac{e^{-\frac{3}{4}y^2} \sum_{k=0}^{m} \binom{m}{k} (-\frac{y}{2})^{m-k}}{\sqrt{2\pi\hbar\sqrt{m!/n!}}}
\]

\[
\times \int_{-\infty}^{+\infty} dz \, e^{-\frac{z^2}{4}} H_k(z)H_m(z)
\]

\[
\times \frac{\sum_{k=0}^{\min(m,n)} k!(\frac{m-n}{2})!}{\sqrt{\pi\hbar\sqrt{m!/n!}}} \left( \frac{y}{2} \right)^{2k-m-n-2k+m+n}.
\]

The polynomial in the last line can be expressed in terms of the confluent hypergeometric function \( U(a, b, z) \) [2],

\[
a_{m\to n}(y) = \frac{(-1)^m e^{-\frac{3}{4}y^2} 2^{m-n} y^{n-m} U(-m, -m+n+1, \frac{y^2}{4})}{\sqrt{\pi\hbar\sqrt{m!/n!}}} \tag{9}
\]

and using the relation [1, 3]

\[
U(-k, a+1, z) = (-1)^k L_k^{(a)}(z), \quad k = 0, 1, 2, \ldots , \tag{10}
\]

where \( L_k^{(a)}(z) \) are the generalized Laguerre Polynomials, one obtains

\[
a_{m\to n}(y) = e^{-\frac{3}{4}y^2} 2^{m-n} \frac{\sqrt{m!/n!}}{\sqrt{\pi\hbar\sqrt{m!/n!}}} L_k^{(m-n)}(z) \left( \frac{y}{2} \right)^{2k-m-n} \tag{11}
\]

The transition probabilities being defined through \( w_{m\to n}(y) = |a_{m\to n}(y)|^2 \) it follows from \( a_{m\to n}(y) = a_{m\to n}(-y) \) that \( w_{m\to n}(y) = w_{m\to n}(y)a_{m\to n}(-y) \). Using here the identity

\[
L_k^{(m-n)}(z) = L_k^{(m-n)}(z) \frac{(-1)^n m!}{n!} \tag{12}
\]

and that \((-1)^n = (-1)^m \) one obtains the compact form

\[
w_{m\to n}(y) = e^{-\frac{3}{4}y^2} (-1)^{m-n} \frac{m!}{n!} L_k^{(m-n)} \left( \frac{y^2}{4} \right)^k \left( \frac{y}{2} \right)^{2k-m-n} \tag{13}
\]

The identity (12) can be derived from Relation (10) and the Kummer transform (Ref. [3]):

\[
U(a, b, z) = z^{1-a} U(1 + a - b, 2 - b, z). \tag{14}
\]
Intermediate scattering function. An explicit analytical expression for the intermediate scattering function

$$F_s(q,t) = \frac{1}{Z} \sum_{m,n} e^{-\beta R t(m+1/2)} e^{i(n-m)\Omega t} w_{m-n}(y(q))$$  \hspace{1cm} (15)$$
can be obtained if a closed form can be found for the expression

$$g(z; u, v) = \sum_{m,n=0}^{\infty} u^m v^n L_n^{(m-n)}(z) L_m^{(n-m)}(z).$$  \hspace{1cm} (16)$$

Defining

$$u = -e^{-i\Omega (t-i\beta)},$$  \hspace{1cm} (17)$$

$$v = -e^{i\Omega},$$  \hspace{1cm} (18)$$

it follows then from (13) that

$$F_s(q,t) = \frac{C}{Z} \frac{\sin}{\sin - 1} \frac{\beta}{\gamma} \left( \frac{y(q)^2}{4} ; u, v \right),$$  \hspace{1cm} (19)$$

where $C$ is a normalization constant and the partition function is given by

$$Z = \frac{e^{\beta \sin}}{e^{\beta \sin} - 1}.$$  \hspace{1cm} (20)$$

A closed form for $g(z; u, v)$ is obtained by solving the differential equation

$$(1 - u v) \frac{\partial g(z; u, v)}{\partial z} = -g(z; u, v)(2uv + u + v),$$  \hspace{1cm} (21)$$

which is established by using that [1]

$$d \frac{d}{dz} L_n^{(\alpha)}(z) = -L_n^{(\alpha+1)}(z).$$  \hspace{1cm} (22)$$

The solution of (21) is an exponential function of the form

$$g(z; u, v) = C e^{i \left( \frac{\beta}{\sin} + \frac{1}{\sin} \right) (2uv + u + v)},$$  \hspace{1cm} (23)$$

with $C$ being a constant. Choosing the normalization $F_1(q,0) = 1$ it then follows from (19) the desired closed form for the intermediate scattering function,

$$F_s(q,t) = e^{i \left( \frac{\beta}{2} \left( \frac{(u + 1)}{\sin} + i(1 - \cos(\Omega t)) \cot(\frac{\beta t}{\sin}) \right) \right)}.$$  \hspace{1cm} (24)$$

which can be found in the literature [4].

Ideal gas – proof of formula (39) in the main text

Starting with a square-normalized Gaussian wave packet which is sharply peaked around $p = p_0$,

$$\phi(p; p_0) = \frac{1}{(2\pi e^{1/4})^{1/4}} e^{-\frac{(p - p_0)^2}{4e^{1/4}}},$$  \hspace{1cm} (25)$$
one finds

$$\langle \phi(p_1)|\phi(p_0) \rangle = \int \frac{d^3p}{(2\pi e^{1/4})^{1/4}} \phi(p_0) e^{-\frac{(p_0 - p_1)^2}{4e^{1/4}}}.$$  \hspace{1cm} (26)$$
The orthogonality relation

$$\langle \phi(p_1)|\phi(p_0) \rangle = \begin{cases} 1 & \text{if } p_1 = p_0, \\ 0 & \text{otherwise}. \end{cases}$$  \hspace{1cm} (27)$$
is thus fulfilled in the limit $\epsilon \to 0$. For the transition amplitude one obtains

$$a(p_1|p_0; q) = e^{-\frac{(p_0 + \alpha q - p_1)^2}{4\epsilon}}$$  \hspace{1cm} (28)$$
and setting for the density of final states

$$\rho(p_1) = 1/(2\sqrt{\pi} \epsilon),$$  \hspace{1cm} (29)$$
it follows that

$$W(p_1|p_0; q) = \frac{\rho(p_1)}{|a(p_1|p_0; q)|^2} = e^{-\frac{(p_0 + \alpha q - p_1)^2}{4\epsilon}}.$$  \hspace{1cm} (30)$$

QENS – proof of Eq. (55) in the main text

We consider an intermediate scattering function of the form

$$F_s(t) = EISF + (1 - EISF)R(t),$$  \hspace{1cm} (31)$$
where $0 < EISF < 1$, and $R(t)$ is a relaxation function fulfilling $R(0) = 1$ and $\lim_{t \to \infty} R(t) = 0$. Due to this property $F_s(t)$ belongs to the class of “slowly growing functions” $L(t)$ in asymptotic analysis, which fulfill $\lim_{t \to \infty} L(\lambda t)/L(\lambda t) = 1$ for any $\lambda > 0$. Therefore one can use a theorem by Karamata [5] which establishes the equivalence

$$h(t) \stackrel{t \to \infty}{\sim} L(t)^\beta \Rightarrow \lim_{\epsilon \to 0+} \frac{1}{\pi} \text{Re} \left\{ \frac{F_s(1/(i\omega + \epsilon))}{1\omega + \epsilon} \right\} = 1.$$  \hspace{1cm} (32)$$

between the asymptotic form of a function, $f(t)$, and its Laplace transform, $\tilde{f}(s) = \int_0^\infty dt \exp(-st)f(t)$ ($\Re\{s\} > 0$), for large and small arguments, respectively. The parameter $\beta$ must here fulfill the condition $\beta > -1$. Given that $F_s(t) \stackrel{t \to \infty}{\sim} L(t)$, where $L(t)$ is given by the r.h.s. of Eq. (31), we thus find that

$$F_s(s) \stackrel{s \to 0}{\sim} F_1(1/s)/s,$$  \hspace{1cm} (33)$$
such that

$$S_s(\omega) \stackrel{\omega \to \infty}{\sim} \lim_{\epsilon \to 0+} \frac{1}{\pi} \text{Re} \left\{ \frac{F_s(1/(i\omega + \epsilon))}{1\omega + \epsilon} \right\}.$$  \hspace{1cm} (34)$$

We use here that $S_s(\omega) = \lim_{\epsilon \to 0+} \text{Re} \{ F(\omega + \epsilon) \}$ since the real and imaginary part of $F(t)$ are, respectively, even and odd in time.