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

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

Defining $z=\sqrt{2/(M\hbar\Omega)}p$, the solutions of the dimensionless version of (2),

$$\phi''(z)+\left(\epsilon-\frac{z^2}{4}\right)\phi(z)=0, \tag{3}$$

are given by

$$\phi_m(z)=\frac{e^{-\frac{z^2}{4}}\mathrm{He}_m(z)}{\sqrt[4]{2\pi}\sqrt{m!}}, \tag{4}$$

where $m = 0, 1, 2, \ldots$ and $\epsilon = m + 1/2$, with $\epsilon = E/(\hbar\Omega)$. Here $\mathrm{He}_m(z) = \mathrm{H}_m\left(\frac{z}{\sqrt{2}}\right)/\sqrt{2^m}$ and $\mathrm{H}_m(z)$ are the Hermite polynomials. The normalization of the eigenfunctions $\phi_m(z)$ is chosen such that

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

Overlap integrals and transition probabilities. Defining the dimensionless momentum transfer

$$y=\sqrt{\frac{2\hbar}{M\Omega}}q, \tag{6}$$

we consider overlap integrals of the form

$$\begin{aligned}a_{m\to n}(y)&=\int_{-\infty}^{+\infty}dz\,\phi_n^*(z+y)\phi_m(z)\\&=\int_{-\infty}^{+\infty}dz\,\phi_n^*(z+y/2)\phi_m(z-y/2).\end{aligned} \tag{7}$$

Using that [1]

$$\mathrm{He}_m(z+y)=\sum_{k=0}^{m}\binom{m}{k}\mathrm{He}_k(z)y^{m-k} \tag{8}$$

one finds that

$$\phi_m(z\pm y/2)=\frac{e^{-\frac{1}{4}\left(z\pm\frac{y}{2}\right)^2}\sum_{k=0}^{m}\binom{m}{k}\left(\pm\frac{y}{2}\right)^{m-k}\mathrm{He}_k(z)}{\sqrt[4]{2\pi}\sqrt{m!}}$$

such that

$$\begin{aligned}a_{m\to n}(y)&=\frac{e^{-\frac{y^2}{8}}\left(\sum_{k=0}^{m}\binom{m}{k}\left(-\frac{y}{2}\right)^{m-k}\right)\left(\sum_{l=0}^{n}\binom{n}{l}\left(\frac{y}{2}\right)^{n-l}\right)}{\sqrt{2\pi}\sqrt{m!}\sqrt{n!}}\\&\quad\times\underbrace{\int_{-\infty}^{+\infty}dz\,e^{-\frac{z^2}{2}}\mathrm{He}_k(z)\mathrm{He}_l(z)}_{=\sqrt{2\pi}\sqrt{k!l!}\delta_{kl}}\\&=\frac{e^{-\frac{y^2}{8}}}{\sqrt{m!}\sqrt{n!}}\sum_{k=0}^{\min(m,n)}k!(-1)^{m-k}\binom{m}{k}\binom{n}{k}2^{2k-m-n}y^{-2k+m+n}.\end{aligned}$$

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

$$a_{m\to n}(y)=\frac{(-1)^m e^{-\frac{y^2}{8}}2^{m-n}y^{n-m}U\left(-m,-m+n+1,\frac{y^2}{4}\right)}{\sqrt{m!n!}}, \tag{9}$$

and using the relation [1, 3]

$$U(-k,\alpha+1,z)=(-1)^k k!L_k^{(\alpha)}(z),\quad k=0,1,2,\ldots, \tag{10}$$

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

$$a_{m\to n}(y)=e^{-\frac{y^2}{8}}2^{m-n}\sqrt{\frac{m!}{n!}}y^{n-m}L_m^{(n-m)}\left(\frac{y^2}{4}\right). \tag{11}$$

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

$$L_m^{(n-m)}(z)=L_n^{(m-n)}(z)(-z)^{m-n}\frac{n!}{m!} \tag{12}$$

and that $(-1)^{-n} = (-1)^n$ one obtains the compact form

$$w_{m\to n}(y)=e^{-\frac{y^2}{4}}(-1)^{m+n}L_m^{(n-m)}\left(\frac{y^2}{4}\right)L_n^{(m-n)}\left(\frac{y^2}{4}\right). \tag{13}$$

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

$$U(a,b,z)=z^{1-b}U(1+a-b,2-b,z). \tag{14}$$

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Intermediate scattering function. An explicit analytical expression for the intermediate scattering function

$$F_s(q,t) = \frac{1}{Z}\sum_{m,n} e^{-\beta\hbar\Omega(m+1/2)} e^{i(n-m)\Omega t} w_{m\to n}(y(q)) \quad (15)$$

can be obtained if a closed form can be found for the expression

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

Defining

$$u = -e^{-i\Omega(t-i\beta\hbar)}, \quad (17)$$

$$v = -e^{it\Omega}, \quad (18)$$

it follows then from (13) that

$$F_s(q,t) = \frac{C}{Z} e^{-\frac{\beta\Omega\hbar}{2} - \frac{1}{4}y(q)^2} g\left(\frac{y(q)^2}{4}; u, v\right), \quad (19)$$

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

$$Z = \frac{e^{\frac{\beta\Omega\hbar}{2}}}{e^{\beta\Omega\hbar} - 1}. \quad (20)$$

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

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

which is established by using that [1]

$$\frac{d}{dz} L_n^{(\alpha)}(z) = -L_{n-1}^{(\alpha+1)}(z). \quad (22)$$

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

$$g(z;u,v) = C e^{\frac{z(2uv+u+v)}{uv-1}}, \quad (23)$$

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,

$$F_s(q,t) = e^{i\frac{y(q)^2}{4}\left(\sin(\Omega t) + i(1-\cos(\Omega t))\coth\left(\frac{\beta\Omega\hbar}{2}\right)\right)}, \quad (24)$$

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 $\mathbf{p} = \mathbf{p}_0$,

$$\tilde{\phi}(\mathbf{p};\mathbf{p}_0) = \frac{1}{(2\pi\epsilon^2)^{3/4}} e^{-\frac{(\mathbf{p}-\mathbf{p}_0)^2}{4\epsilon^2}}, \quad (25)$$

one finds

$$\langle\phi(\mathbf{p}_1)|\phi(\mathbf{p}_0)\rangle = \int d^3p\, \tilde{\phi}(\mathbf{p};\mathbf{p}_1)^* \tilde{\phi}(\mathbf{p};\mathbf{p}_0) = e^{-\frac{(\mathbf{p}_0-\mathbf{p}_1)^2}{4\epsilon^2}}. \quad (26)$$

The orthogonality relation

$$\langle\phi(\mathbf{p}_1)|\phi(\mathbf{p}_0)\rangle = \begin{cases} 1 & \text{if } \mathbf{p}_1 = \mathbf{p}_0, \\ 0 & \text{otherwise.} \end{cases} \quad (27)$$

is thus fulfilled in the limit $\epsilon \to 0$. For the transition amplitude one obtains

$$a(\mathbf{p}_1|\mathbf{p}_0;\mathbf{q}) = e^{-\frac{(\mathbf{p}_0+\hbar\mathbf{q}-\mathbf{p}_1)^2}{8\epsilon^2}} \quad (28)$$

and setting for the density of final states

$$\rho(\mathbf{p}_1) = 1/(2\sqrt{\pi}\epsilon)^3, \quad (29)$$

it follows that

$$W(\mathbf{p}_1|\mathbf{p}_0;\mathbf{q}) = \rho(\mathbf{p}_1)|a(\mathbf{p}_1|\mathbf{p}_0;\mathbf{q})|^2 = \frac{e^{-\frac{(\mathbf{p}_0-\mathbf{p}_1+\hbar\mathbf{q})^2}{4\epsilon^2}}}{(2\sqrt{\pi}\epsilon)^3} \stackrel{\epsilon\to 0}{=} \delta(\mathbf{p}_0 + \hbar\mathbf{q} - \mathbf{p}_1). \quad (30)$$

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

We consider an intermediate scattering function of the form

$$F_s(t) = EISF + (1-EISF)R(t), \quad (31)$$

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 fulfil $\lim_{t\to\infty} L(\lambda t)/L(\lambda t) = 1$ for any $\lambda > 0$. Therefore one can use a theorem by Karamata [5] which establishes the equivalence

$$h(t) \stackrel{t\to\infty}{\sim} L(t)t^\beta \Leftrightarrow \hat{h}(s) \stackrel{s\to 0}{\sim} L(1/s)\frac{\Gamma(1+\beta)}{s^{1+\beta}} \quad (32)$$

between the asymptotic form of a function, $f(t)$, and its Laplace transform, $\hat{f}(s) = \int_0^\infty dt, \exp(-st) f(t)$ ($\Re\{s\} > 0$), for large and small arguments, respectively. The parameter β must here fulfil 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

$$\hat{F}_s(s) \stackrel{s\to 0}{\sim} F_s(1/s)/s \quad (33)$$

such that

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

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

1. Olver, F. W. J, Lozier, D. W, Boisvert, R. F, & Clark, C. W, eds. (2010) NIST Handbook of Mathematical Functions. (Cambridge University Press).
2. Wolfram Research Inc. (2017) Mathematica, Version 11.1. (Wolfram Research Inc., Champaign, Illinois, USA).
3. Abramowitz, M & Stegun, I. (1972) Handbook of Mathematical Functions. (Dover Publications, New York).
4. Lovesey, S. (1984) Theory of Neutron Scattering from Condensed Matter. (Clarendon Press, Oxford) Vol. I.
5. Karamata, J. (1931) Neuer Beweis und Verallgemeinerung der Tauberschen Sätze, welche die Laplacesche und Stieltjessche Transformation betreffen. Journal für die reine und angewandte Mathematik (Crelle's Journal) 1931, 27–39.