Supporting Information:
Two-dimensional Raman Spectroscopy of Lennard-Jones Liquids via Ring-Polymer Molecular Dynamics

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In this Supporting Information, we show the derivation of double Kubo transformation (DKT) formalism for 2D response function expressed in terms of the relative time intervals t_1, t_2, (different in notations from the original derivation using absolute interaction times t, t')[1].

Without loosing generality, the 2D Raman response function can be expressed in fully quantum mechanical form as below[2]

$$R(t_1,t_2) = \left(\frac{i}{\hbar}\right)^2 \mathrm{Tr}\left(\hat{C}(t_1+t_2)\left[\hat{B}(t_1),\left[\hat{A}(0),\hat{\rho}_{eq}\right]\right]\right). \quad (1)$$

Here, $\hat{A}$, $\hat{B}$, and $\hat{C}$ are the many-body polarizability $\mathbf{\Pi}$, $\hat{A}(t) = e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}$ is the operator evolved in the Heisenberg picture.

Expanding the commutators in Eq. 1, the response function is given by the standard time correlation functions (TCFs),

$$\begin{aligned} R(t_1,t_2) = -\frac{1}{\hbar^2}\big[&\langle\hat{A}(0)\hat{B}(t_1)\hat{C}(t_1+t_2)\rangle + \langle\hat{C}(t_1+t_2)\hat{B}(t_1)\hat{A}\rangle \\ &- \langle\hat{A}(0)\hat{C}(t_1+t_2)\hat{B}(t_1)\rangle - \langle\hat{B}(t_1)\hat{C}(t_1+t_2)\hat{A}(0)\rangle\big]. \end{aligned} \quad (2)$$

Performing double Fourier transform,

$$\begin{aligned} &\tilde{R}(\omega_1,\omega_2) \\ &= -\frac{1}{\hbar^2}[\langle AB(\omega_1)C(\omega_1+\omega_2)\rangle + \langle C(\omega_1+\omega_2)B(\omega_1)A\rangle \\ &\quad - \langle AC(\omega_1+\omega_2)B(\omega_1)\rangle - \langle B(\omega_1)C(\omega_1+\omega_2)A\rangle]. \end{aligned} \quad (3)$$

In the energy representation $\hat{H}|n\rangle = E_n|n\rangle$ with the eigenvalue $E_n = \hbar\omega_n$ and the eigenstate $|n\rangle$, the TCFs can be written by inserting $\sum_n |n\rangle\langle n| = \hat{\mathbf{1}}$ (with $\hat{\mathbf{1}}$ the identity operator):

$$\begin{aligned} &\langle\hat{A}\hat{B}(t_1)\hat{C}(t_1+t_2)\rangle \\ &= \frac{1}{Z}\mathrm{Tr}\left[\hat{A}e^{\frac{i}{\hbar}\hat{H}t_1}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t_1}e^{\frac{i}{\hbar}\hat{H}(t_1+t_2)}\hat{C}e^{-\frac{i}{\hbar}\hat{H}(t_1+t_2)}e^{-\beta\hat{H}}\right] \\ &= \frac{1}{Z}\mathrm{Tr}\left[e^{-\frac{i}{\hbar}\hat{H}t_1}\hat{A}e^{\frac{i}{\hbar}\hat{H}t_1}\hat{B}e^{\frac{i}{\hbar}\hat{H}t_2}\hat{C}e^{-\frac{i}{\hbar}\hat{H}t_2}e^{-\beta\hat{H}}\right] \\ &= \langle\hat{A}^*(t_1)\hat{B}\hat{C}(t_2)\rangle \\ &= \frac{1}{Z}\sum_{q,r,s}\langle q|\hat{A}|r\rangle\langle r|e^{\frac{i}{\hbar}\hat{H}t_1}\hat{B}|s\rangle\langle s|e^{-\frac{i}{\hbar}\hat{H}t_1}e^{\frac{i}{\hbar}\hat{H}(t_1+t_2)} \\ &\quad\times\hat{C}e^{-\frac{i}{\hbar}\hat{H}(t_1+t_2)}e^{-\beta\hat{H}}|q\rangle \\ &= \frac{1}{Z}\sum_{q,r,s}e^{-\beta\hbar\omega_q}e^{i\omega_{rs}t_1}e^{i\omega_{sq}(t_1+t_2)}\langle q|\hat{A}|r\rangle\langle r|\hat{B}|s\rangle\langle s|\hat{C}|q\rangle, \\ &\langle\hat{C}(t_1+t_2)\hat{B}(t_1)\hat{A}\rangle = \langle\hat{C}(t_2)\hat{B}\hat{A}^*(t_1)\rangle \\ &= \frac{1}{Z}\sum_{q,r,s}e^{-\beta\hbar\omega_q}e^{i\omega_{sr}t_1}e^{i\omega_{qs}(t_1+t_2)}\langle q|\hat{C}|s\rangle\langle s|\hat{B}|r\rangle\langle r|\hat{A}|q\rangle, \\ &\langle\hat{A}\hat{C}(t_1+t_2)\hat{B}(t_1)\rangle = \langle\hat{A}^*(t_1)\hat{C}(t_2)\hat{B}\rangle \\ &= \frac{1}{Z}\sum_{q,r,s}e^{-\beta\hbar\omega_r}e^{i\omega_{sr}t_1}e^{i\omega_{qs}(t_1+t_2)}\langle r|\hat{A}|q\rangle\langle q|\hat{C}|s\rangle\langle s|\hat{B}|r\rangle, \\ &\langle\hat{B}(t_1)\hat{C}(t_1+t_2)\hat{A}\rangle = \langle\hat{B}\hat{C}(t_2)\hat{A}^*(t_1)\rangle \\ &= \frac{1}{Z}\sum_{q,r,s}e^{-\beta\hbar\omega_r}e^{i\omega_{rs}t_1}e^{i\omega_{sq}(t_1+t_2)}\langle r|\hat{B}|s\rangle\langle s|\hat{C}|q\rangle\langle q|\hat{A}|r\rangle, \end{aligned} \quad (4)$$

where $\omega_{\alpha\beta} = \omega_\alpha - \omega_\beta$ and $Z = \mathrm{Tr}[e^{-\beta\hat{H}}]$ is the partition function. Performing double Fourier transform on the above

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TCFs, we have

$$\langle\hat{A}\hat{B}(\omega_1)\hat{C}(\omega_1+\omega_2)\rangle = \frac{1}{Z}\sum_{q,r,s} e^{-\beta\hbar\omega_q}\delta\left(\omega_1-\omega_{rs}-\omega_{sq}\right) \times\delta\left(\omega_2-\omega_{sq}\right)\langle q|\hat{A}|r\rangle\langle r|\hat{B}|s\rangle\langle s|\hat{C}|q\rangle,$$
$$\langle\hat{C}(\omega_1+\omega_2)\hat{B}(\omega_1)\hat{A}\rangle = \frac{1}{Z}\sum_{q,r,s} e^{-\beta\hbar\omega_q}\delta\left(\omega_1-\omega_{sr}-\omega_{qs}\right) \times\delta\left(\omega_2-\omega_{qs}\right)\langle q|\hat{C}|s\rangle\langle s|\hat{B}|r\rangle\langle r|\hat{A}|q\rangle,$$
$$\langle\hat{A}\hat{C}(\omega_1+\omega_2)\hat{B}(\omega_1)\rangle = \frac{1}{Z}\sum_{q,r,s} e^{-\beta\hbar\omega_r}\delta\left(\omega_1-\omega_{sr}-\omega_{qs}\right) \times\delta\left(\omega_2-\omega_{qs}\right)\langle r|\hat{A}|q\rangle\langle q|\hat{C}|s\rangle\langle s|\hat{B}|r\rangle,$$
$$\langle\hat{B}(\omega_1)\hat{C}(\omega_1+\omega_2)\hat{A}\rangle = \frac{1}{Z}\sum_{q,r,s} e^{-\beta\hbar\omega_r}\delta\left(\omega_1-\omega_{rs}-\omega_{sq}\right) \times\delta\left(\omega_2-\omega_{sq}\right)\langle r|\hat{B}|s\rangle\langle s|\hat{C}|q\rangle\langle q|\hat{A}|r\rangle. \tag{5}$$

We can then show the relationships between the frequency-domain TCFs by enforcing the Dirac's delta function,

$$\langle\hat{A}\hat{B}(\omega_1)\hat{C}(\omega_1+\omega_2)\rangle = e^{\beta\hbar\omega_1}\langle\hat{B}(t_1)\hat{C}(\omega_1+\omega_2)\hat{A}\rangle,$$
$$\langle\hat{C}(\omega_1+\omega_2)\hat{B}(\omega_1)\hat{A}\rangle = e^{-\beta\hbar\omega_1}\langle\hat{A}\hat{C}(\omega_1+\omega_2)\hat{B}(\omega_1)\rangle. \tag{6}$$

Substituting the above relationships back into Eq. 3, we can have

$$\tilde{R}(\omega_1,\omega_2) = -\frac{1}{\hbar^2}\left(1-e^{-\beta\hbar\omega_1}\right)[\langle AB(\omega_1)C(\omega_1+\omega_2)\rangle - e^{\beta\hbar\omega_1}\langle C(\omega_1+\omega_2)B(\omega_1)A\rangle]. \tag{7}$$

Assuming $\hat{A}$, $\hat{B}$, and $\hat{C}$ are Hermitian operators that only depend on positions, following the definition of single Kubo transform[3]

$$\langle A;B(t)\rangle = \frac{1}{Z\beta}\int_0^\beta \mathrm{d}\lambda\,\mathrm{Tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}\hat{B}(t)\right], \tag{8}$$

the DKT correlation function is defined as[4]

$$\langle A;B(t);C(t')\rangle = \frac{1}{Z\beta^2}\int_0^\beta \mathrm{d}\lambda\int_0^\lambda \mathrm{d}\lambda'\mathrm{Tr}[e^{-(\beta-\lambda)\hat{H}} \times\hat{A}e^{-(\lambda-\lambda')\hat{H}}\hat{B}(t)e^{-\lambda'\hat{H}}\hat{C}(t')], \tag{9}$$

Following the definition of DKT correlation and working in the energy representation, we have

$$\begin{aligned}
&\langle\hat{A};\hat{B}(t_1);\hat{C}(t_1+t_2)\rangle\\
&= \frac{1}{Z\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda'\mathrm{Tr}\Big[e^{\lambda\hat{H}}\hat{A}e^{-(\lambda-\lambda')\hat{H}}e^{\frac{i}{\hbar}\hat{H}t_1}\\
&\quad\times\hat{B}e^{-\frac{i}{\hbar}\hat{H}t_1}e^{-\lambda'\hat{H}}e^{\frac{i}{\hbar}\hat{H}(t_1+t_2)}\hat{C}e^{-\frac{i}{\hbar}\hat{H}(t_1+t_2)}e^{-\beta\hat{H}}\Big]\\
&= \frac{1}{Z\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda'\sum_{q,r,s}\langle q|e^{\lambda\hat{H}}\hat{A}|r\rangle\langle r|e^{-(\lambda-\lambda')\hat{H}}e^{\frac{i}{\hbar}\hat{H}t_1}\\
&\quad\times\hat{B}|s\rangle\langle s|e^{-\frac{i}{\hbar}\hat{H}t_1}e^{-\lambda'\hat{H}}e^{\frac{i}{\hbar}\hat{H}(t_1+t_2)}\hat{C}e^{-\frac{i}{\hbar}\hat{H}(t_1+t_2)}e^{-\beta\hat{H}}|q\rangle\\
&= \frac{1}{Z\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda'\sum_{q,r,s}e^{-\beta\hbar\omega_q}e^{i\omega_{rs}t_1}e^{i\omega_{sq}(t_1+t_2)}\\
&\quad\times\langle q|\hat{A}|r\rangle\langle r|\hat{B}|s\rangle\langle s|\hat{C}|q\rangle e^{\lambda\hbar\omega_{qr}}e^{\lambda'\hbar\omega_{rs}},
\end{aligned} \tag{10}$$

$$\begin{aligned}
&\langle\hat{C}(t_1+t_2);\hat{B}(t_1);\hat{A}\rangle\\
&= \frac{1}{Z\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda'\sum_{q,r,s}e^{-\beta\hbar\omega_q}e^{i\omega_{rs}t_1}e^{i\omega_{sq}(t_1+t_2)}\\
&\quad\times\langle q|\hat{A}|r\rangle\langle r|\hat{B}|s\rangle\langle s|\hat{C}|q\rangle e^{\lambda\hbar\omega_{qr}}e^{\lambda'\hbar\omega_{rs}},
\end{aligned} \tag{11}$$

The double Fourier transform of the DKT is defined as

$$\begin{aligned}
&\langle A;B(\omega_1);C(\omega_1+\omega_2)\rangle \equiv \mathcal{F}[\langle A;B(t_1);C(t_1+t_2)\rangle]\\
&= \int_{-\infty}^{\infty}\mathrm{d}t_1\int_{-\infty}^{\infty}\mathrm{d}t_2 e^{-i\omega_1 t_1-i\omega_2 t_2}\langle A;B(t_1);C(t_1+t_2)\rangle
\end{aligned} \tag{12}$$

Performing double Fourier transform on the above DKT correlation functions, the DKT can be shown to be related to standard correlation function $\langle AB(t_1)C(t_1+t_2)\rangle$ in the frequency domain:

$$\begin{aligned}
&\langle\hat{A};\hat{B}(\omega_1);\hat{C}(\omega_1+\omega_2)\rangle\\
&= \frac{1}{Z\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda'\sum_{q,r,s}e^{-\beta\hbar\omega_q}\delta\left(\omega_1-\omega_{rs}-\omega_{sq}\right)\\
&\quad\times\delta\left(\omega_2-\omega_{sq}\right)\langle q|\hat{A}|r\rangle\langle r|\hat{B}|s\rangle\langle s|\hat{C}|q\rangle e^{\lambda\hbar\omega_{qr}}e^{\lambda'\hbar\omega_{rs}}\\
&= \frac{1}{\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda' e^{-\lambda\hbar\omega_1}e^{\lambda'\hbar(\omega_1-\omega_2)}\mathcal{F}\left[\langle\hat{A}\hat{B}(t_1)\hat{C}(t_1+t_2)\rangle\right]\\
&= F(-\omega_1,\omega_1-\omega_2)\langle\hat{A}\hat{B}(\omega_1)\hat{C}(\omega_1+\omega_2)\rangle,
\end{aligned} \tag{13}$$

$$\begin{aligned}
&\langle\hat{C}(\omega_1+\omega_2);\hat{B}(\omega_1);\hat{A}\rangle\\
&= \frac{1}{Z\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda'\sum_{q,r,s}e^{-\beta\hbar\omega_q}\delta\left(\omega_1-\omega_{sr}-\omega_{qs}\right)\\
&\quad\times\delta\left(\omega_2-\omega_{qs}\right)\langle q|\hat{C}|s\rangle\langle s|\hat{B}|r\rangle\langle r|\hat{A}|q\rangle e^{\lambda\hbar\omega_{qs}}e^{\lambda'\hbar\omega_{sr}}\\
&= \frac{1}{\beta^2}\int_0^\beta d\lambda\int_0^\lambda d\lambda' e^{\lambda\hbar\omega_2}e^{\lambda'\hbar(\omega_1-\omega_2)}\mathcal{F}\left[\langle\hat{C}(t_1+t_2)\hat{B}(t_1)\hat{A}\rangle\right]\\
&= F(\omega_2,\omega_1-\omega_2)\langle\hat{C}(\omega_1+\omega_2)\hat{B}(\omega_1)\hat{A}\rangle.
\end{aligned} \tag{14}$$

where

$$\begin{aligned}
F(\omega,\omega') &= \frac{1}{\beta^2}\int_0^\beta \mathrm{d}\lambda\int_0^\lambda \mathrm{d}\lambda' e^{\lambda\hbar\omega}e^{\lambda'\hbar\omega'}\\
&= \frac{1}{\beta^2\hbar^2}\left[\frac{e^{\beta\hbar(\omega+\omega')}}{\omega'(\omega+\omega')}-\frac{e^{\beta\hbar\omega}}{\omega'\omega}+\frac{1}{\omega(\omega+\omega')}.\right].
\end{aligned} \tag{15}$$

Similarly, we also can get the below relations

$$\begin{aligned}\langle\hat{B}(\omega_1);\hat{C}(\omega_1+\omega_2);\hat{A}\rangle =&F(\omega_1-\omega_2,\omega_2)\\ &\times\langle\hat{B}(\omega_1)\hat{C}(\omega_1+\omega_2)\hat{A}\rangle,\\ \langle\hat{C}(\omega_1+\omega_2);\hat{A};\hat{B}(\omega_1)\rangle =&F(\omega_2,-\omega_1)\\ &\times\langle\hat{C}(\omega_1+\omega_2)\hat{A}\tilde{\hat{B}}(\omega_1)\rangle,\\ \langle\hat{B}(\omega_1);\hat{A};\hat{C}(\omega_1+\omega_2)\rangle =&F(\omega_1-\omega_2,-\omega_1)\\ &\times\langle\hat{B}(\omega_1)\hat{A}\hat{C}(\omega_1+\omega_2)\rangle,\\ \langle\hat{A};\hat{C}(\omega_1+\omega_2);\hat{B}(\omega_1)\rangle =&F(-\omega_1,\omega_2)\\ &\times\langle\hat{A}\hat{C}(\omega_1+\omega_2)\hat{B}(t_1)\rangle. \qquad (16)\end{aligned}$$

It can be verified that

$$\begin{aligned}F(-\omega_1,\omega_1-\omega_2)&=e^{-\beta\hbar\omega_1}F(\omega_1-\omega_2,\omega_2)\\ &=e^{-\beta\hbar\omega_2}F(\omega_2,-\omega_1),\\ F(\omega_2,\omega_1-\omega_2)&=e^{\beta\hbar\omega_1}F(\omega_1-\omega_2,-\omega_1)\\ &=e^{\beta\hbar\omega_2}F(-\omega_1,\omega_2). \qquad (17)\end{aligned}$$

Then, we express the response function in terms of DKT by applying Eq. 14 in Eq. 7:

$$\begin{aligned}\tilde{R}(\omega_1,\omega_2)=&Q_1(\omega_1,\omega_2)\langle A;B(\omega_1);C(\omega_1+\omega_2)\rangle\\ &+Q_2(\omega_1,\omega_2)\langle C(\omega_1+\omega_2);B(\omega_1);A\rangle,\end{aligned}$$

where

$$\begin{aligned}Q_1(\omega_1,\omega_2)=&-\frac{1}{\hbar^2}\frac{(1-e^{-\beta\hbar\omega_1})}{F(-\omega_1,\omega_1-\omega_2)}\\ =&-\frac{1}{\hbar^2}\frac{(1-e^{-\beta\hbar\omega_1})\omega_1\omega_2(\omega_1-\omega_2)}{e^{-\beta\hbar\omega_1}\omega_2-e^{-\beta\hbar\omega_2}\omega_1+\omega_1-\omega_2}, \qquad (18)\\ Q_2(\omega_1,\omega_2)=&\frac{1}{\hbar^2}\frac{(1-e^{-\beta\hbar\omega_1})e^{\beta\hbar\omega_1}}{F(\omega_2,\omega_1-\omega_2)}\\ =&\frac{1}{\hbar^2}\frac{(e^{\beta\hbar\omega_1}-1)\omega_1\omega_2(\omega_1-\omega_2)}{e^{\beta\hbar\omega_1}\omega_2-e^{\beta\hbar\omega_2}\omega_1+\omega_1-\omega_2}. \qquad (19)\end{aligned}$$

It can be verified that $Q_1(\omega_1,\omega_2)=Q_2(-\omega_1,-\omega_2)$.

Introducing

$$Q_+(\omega_1,\omega_2)=[Q_1(\omega_1,\omega_2)+Q_1(-\omega_1,-\omega_2)]/2, \qquad (20)$$
$$Q_-(\omega_1,\omega_2)=[Q_1(\omega_1,\omega_2)-Q_1(-\omega_1,-\omega_2)]/2, \qquad (21)$$

the frequency domain response function $\tilde{R}(\omega_1,\omega_2)$ can be rewritten in terms of symmetric and asymmetric parts, which is quantum mechanically exact:[1]

$$\begin{aligned}\tilde{R}(\omega_1,\omega_2)=&Q_+(\omega_1,\omega_2)\tilde{K}^{sym}_{ABC}(\omega_1,\omega_2)\\ &+Q_-(\omega_1,\omega_2)\tilde{K}^{asym}_{ABC}(\omega_1,\omega_2).\end{aligned}$$

where $\tilde{K}^{\mathrm{sym}}(\omega_1,\omega_2)$ and $\tilde{K}^{\mathrm{asym}}(\omega_1,\omega_2)$ are the double Fourier transforms of symmetric and asymmetric DKT correlation functions

$$\begin{aligned}K^{\mathrm{sym}}(t_1,t_2)&=\langle A;B(t_1);C(t_1+t_2)\rangle+\langle C(t_1+t_2);B(t_1);A\rangle\\ &=2\,\mathrm{Re}\left[\langle A;B(t_1);C(t_1+t_2)\rangle\right], \qquad (22)\\ K^{\mathrm{asym}}(t_1,t_2)&=\langle A;B(t_1);C(t_1+t_2)\rangle-\langle C(t_1+t_2);B(t_1);A\rangle\\ &=2i\,\mathrm{Im}\left[\langle A;B(t_1);C(t_1+t_2)\rangle\right]. \qquad (23)\end{aligned}$$

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