Comment on "A symmetrical method to obtain shear moduli from microrheology" by Kengo Nishi, Maria L. Kilfoil, Christoph F. Schmidt, and F. C. MacKintosh, Soft Matter, DOI: 10.1039/C7SM02499A

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Abstract

Nishi *et al.* have presented a new analytical method for transforming the time-dependent materials' compliance into their frequency-dependent complex shear modulus, without the need of preconceived fitting function *nor* the use of Kramers-Kronig transformations. They claim that their method significantly improves the accuracy of the outcomes, especially at high frequencies, up to "*almost*" the Nyquist frequency. Here, I corroborate that their method is actually able to provide a close estimation of the materials' complex shear modulus over the 'entire' range of explored frequencies (i.e. beyond the Nyquist frequency), as long as the compliance values are linearly spaced in the time-domain and its value at time zero is included as first data point in the input

file. Moreover, as a mean of comparison, I employ the analytical method introduced by Tassieri *et al.* [*New J. Phys.*, 2012, **14**, 115032] for performing the Fourier transform of any generic time-dependent function that vanishes for negative times, is sampled at a finite rate, *need not* be equally spaced and extends over a finite time window. This existing method does not need preconceived fitting functions *nor* the use of Kramers-Kronig transformations; yet it shows a higher degree of accuracy than the one proposed by Nishi *et al.*

Before to comment on the effectiveness of the analytical method introduced by Nishi *et al.*,[1] let us retrieve a straightforward relationship between the thermally driven mean-square-displacement (MSD) of a probe particle and the time-dependent shear compliance $J(t)$ of the suspending fluid. The latter (in conventional bulk-rheology) is defined as the ratio of the time-dependent shear strain $\gamma(t)$ to the magnitude σ_0 of the constant shear stress that is switched on at time $t = 0$: $J(t) = \gamma(t)/\sigma_0$. The compliance is related to the materials' shear relaxation modulus $G(t)$ by means of a convolution integral:[2]

$$\int_0^t G(\tau)\, J(t-\tau)\, d\tau = t. \tag{1}$$

Moreover, given that the complex shear modulus $G^*(\omega)$ is defined as the Fourier transform of the time derivative of $G(t)$, by taking the Fourier transform of Eq. (1) one obtaines:

$$G^*(\omega) = i\omega\hat{G}(\omega) = \frac{1}{i\omega\hat{J}(\omega)} \tag{2}$$

where $\hat{G}(\omega)$ and $\hat{J}(\omega)$ are the Fourier transforms of $G(t)$ and $J(t)$, respectively. Let us also remind that for a thermally excited probe particle suspended into a viscoelastic fluid at thermal equilibrium, the particles' MSD is simply related to $G^*(\omega)$ by means of the generalised Stokes-Einstein equation:[3]

$$G^*(\omega) = \frac{k_B T}{a\pi i\omega \left\langle \Delta\widehat{r^2}(\omega) \right\rangle} \tag{3}$$

where a is the beads radius, k_B is Boltzmann's constant, T is absolute temperature and $\left\langle \Delta\widehat{r^2}(\omega) \right\rangle$ is the Fourier transform of the MSD ($\langle \Delta r^2(\tau) \rangle \equiv \left\langle [\vec{r}(t+\tau) - \vec{r}(t)]^2 \right\rangle$, where $\vec{r}(t)$ is the particle position and τ the lag-time). The average $\langle \ldots \rangle$ is taken over all initial times t and all particles, if more than one is observed. In addition, given that the Fourier transform is a linear operator, by equating Equations (2) and (3) one obtains:

$$\left\langle \Delta\widehat{r^2}(\omega) \right\rangle = \frac{k_B T}{\pi a}\hat{J}(\omega) \quad \Longleftrightarrow \quad \left\langle \Delta r^2(\tau) \right\rangle = \frac{k_B T}{\pi a} J(t) \tag{4}$$

where it has been assumed that for micron sized particles the inertial term $m\omega^2$ (otherwise present on the right side of Equation (3)) is negligible for frequencies $\ll$ MHz and that $J(0) = 0$ for viscoelastic fluids. Equation (4) expresses the linear relationship between the MSD of suspended spherical particles and the macroscopic creep compliance of the suspending fluid.[4] Therefore, it allows the evaluation of the fluid's complex shear modulus (*via* Equation (3)) without the need of any preconceived model once an effective analytical method for performing the Fourier transform of a discrete set of experimental data is adopted, like either of the two methods discussed in this comment.

Despite the elementary appearance of Equations (2) and (3), it has been shown[5] that the evaluation of the above mentioned Fourier transforms, given only a finite set of data points over a finite time domain, is non-trivial[3,6–10] since interpolation and extrapolation from those data can yield artefacts that lie within the bandwidth of interest.

An analytical procedure for the evaluation of the Fourier transform of any generic function sampled over a finite time window was proposed by Evans *et al.*,[8,9] to convert $J(t)$ into $G^*(\omega)$ directly (i.e., via Equations (2)), without the use of Laplace transforms or fitting functions. This method is based on the interpolation of the finite data set by means of a piecewise-linear function. In particular, the general validity of the proposed procedure makes it equally applicable to find the Fourier transform $\hat{g}(\omega)$ of any time-dependent function $g(t)$ that vanishes for negative t, sampled at a finite set of data points (t_k, g_k), where $k = 1 \ldots N$, which extend over a finite range, and *need not* be equally spaced:[8]

$$
\begin{aligned}
-\omega^2 \hat{g}\left(\omega\right) = i\omega g(0) + \left(1 - e^{-i\omega t_1}\right) \frac{\left(g_1 - g(0)\right)}{t_1} + \\
+ \dot{g}_\infty e^{-i\omega t_N} + \sum_{k=2}^{N} \left(\frac{g_k - g_{k-1}}{t_k - t_{k-1}}\right) \left(e^{-i\omega t_{k-1}} - e^{-i\omega t_k}\right) \qquad (5)
\end{aligned}
$$

where $\dot{g}_\infty$ is the gradient of $g(t)$ extrapolated to infinite time and $g(0)$ is the value of $g(t)$ extrapolated to $t = 0$ from above.

The above method was improved by Tassieri *et al.*[5] while analysing microrheology measurements performed with optical tweezers and its effectiveness has been corroborated by direct comparison with conventional bulk-rheology measurements of a variety of complex fluids.[11] The authors[5] found that a substantial reduction in the size of the high-frequency artefacts, from which some high-frequency noise tends to spill over into the top of the experimental frequency range, can be achieved by an *over-sampling* technique. The technique involves first numerically interpolating between data points using a standard non-overshooting cubic spline, and then generating a new, over-sampled data set, by sampling the interpolating function not only at the exact data points but also at a number of equally-spaced points in between. Notice that, over-sampling is a common procedure in signal processing and it consists of sampling a signal with a sampling frequency f_s much higher than the Nyquist rate $2B$, where B is the highest frequency contained in the original signal. A signal is said to be oversampled by a factor of $\beta \equiv f_s/(2B)$.[12]

Driven by the same aim, Nishi *et al.*[1] have developed an analytical method for transforming the time-dependent materials' compliance into their frequency-dependent complex shear modulus, without the need of preconceived fitting function *nor* the use of Kramers-Kronig transformations. In order to validate their method, they have applied it to '*synthetic*' data

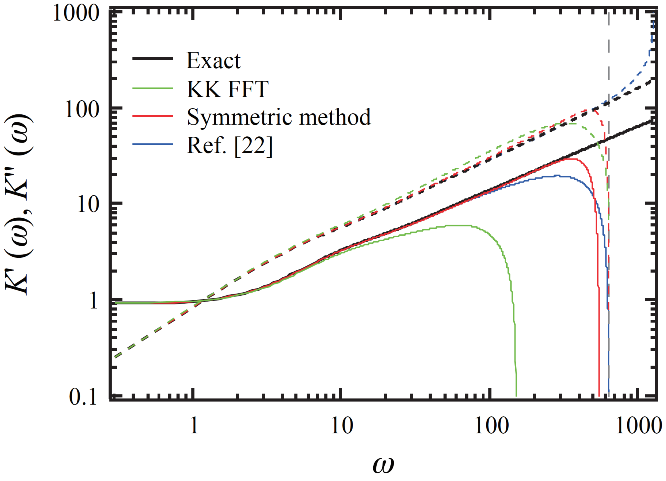

Figure 1: This figure has been reproduced from Nishi *et al.*[1] for convenience of the reader. It represents the real (K', dashed lines) and imaginary (K'', continuous lines) parts of the micromechanical stiffness $K = 1/\chi$ (in units of $2kT$). Exact results (from Equation (7)) are shown for comparison with three different methods based on (i) a Kramers Kronig integral (KK FFT), (ii) the symmetric method described by Nishi *et al.*[1] and (iii) the method described by Evans *et al.*[8,9] (labelled as Ref. [22]). The vertical dashed line indicates the Nyquist frequency.

resembling the mean-square-displacement of a weakly trapped probe particle suspended into a non-Newtonian fluid (similar to those often seen in optical tweezers experiments[5,13–17]):

$$MSD(n,t) \propto \sum_{n=1}^{\infty} \frac{1}{n^4}\left(1 - e^{-n^4 t}\right), \quad t \geqslant 0, \tag{6}$$

where n is the mode number and time is measured in units of the longest relaxation time for $n = 1$. As explained by Nishi *et al.*,[1] Equation (6) converges rapidly as $n \geqslant 11$. Therefore, also here its evaluation has been terminated at $n = 11$ with a sampling frequency of $f = 160 = \omega/(2\pi)$ in units of the inverse of the longest relaxation time (see inset in the top-left quadrant of Figure 2). Interestingly, the Fourier transform of the time derivative of Equation (6) can be calculated analytically and therefore an exact expression of the complex modulus can be derived *via* Equation (3):

$$G^*(\omega) \propto \left[\sum_{n=1}^{\infty} \frac{(n^4 - i\omega)}{(n^8 + \omega^2)}\right]^{-1} \tag{7}$$

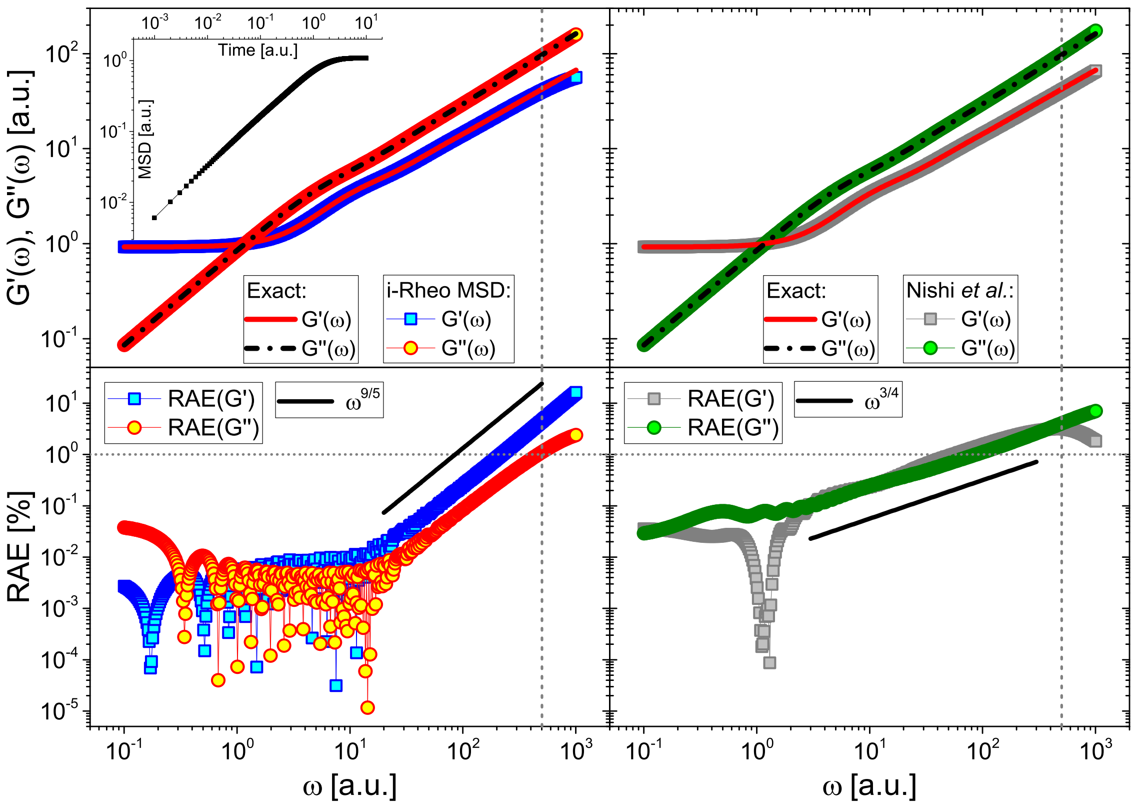

Figure 2: (Top) Comparisons between the viscoelastic moduli determined by means of Equation (7) (lines) and those evaluated via either i-Rheo-MSD (top-left quadrant, symbols) or the algorithm developed by Nishi *et al.*[1] (top-right quadrant, symbols), both applied to the synthetic MSD data generated by means of Equation (6), which are shown in the inset of the top-left quadrant. (Bottom) The frequency-dependent Relative-Absolute-Error (RAE) of the viscoelastic moduli determined by means of the two methods cited above. The vertical dash-line indicates the Nyquist frequency. The horizontal dot-line indicates a RAE of 1%. The solid lines are guides for the power laws.

The real (elastic, $G'(\omega)$) and imaginary (viscous, $G''(\omega)$) parts of Equation (7) are drawn in both Figures 1 and 2(top). They are used here as a reference to calculate the frequency-dependent Relative-Absolute-Error (RAE) of the viscoelastic moduli evaluated by means of both the analytical method introduced by Nishi *et al.*[1] and the one previously introduced by Tassieri *et al.*,[5] for comparison. In order to compare these methods, I have implemented both of them in LabVIEW and the one introduced by Nishi *et al.*[1] in Python too, for a further validation of the findings discussed below. The latter code is reported in the appendix; whereas, a LabVIEW executable named i-Rheo-MSD that implements the analytical method introduced by Tassieri *et al.*[5] is free to download (together with the instructions) from the following link: `https://sites.google.com/site/manliotassieri/labview-codes`.

In Figure 2(top) are reported the viscoelastic moduli evaluated by means of both i-Rheo-MSD (top-left quadrant) and the algorithm developed by Nishi *et al.*[1] (top-right quadrant), both applied to the synthetic MSD data generated via Equation (6). From the results shown in the top-right quadrant of Figure 2, it is possible to corroborate that, in contrast to the original results (here reproduced in Figure 1), the analytical method introduced by Nishi *et al.*[1] is actually able to evaluate both the materials' viscoelastic moduli over the '*entire*' range of explored frequencies, to a high degree of accuracy, even beyond the Nyquist frequency. It is believed that the discrepancy between the two outputs is due to two factors: (i) possible coding/indexing issues related to the specific programming tool used by Nishi *et al.*[1] and (ii) the input data has to include the value of the compliance at time equal zero, which is often equal to $[0, 0]$ for complex fluids. Nonetheless, when the analytical method introduced by Nishi *et al.*[1] is accurately implemented in any programming tool (such as the two used in this comment, i.e. LabVIEW and Python) and condition (ii) mentioned above is satisfied, the proposed method reveals to be a valuable substitute to the existing ones, as discussed below.

From Figure 2 it is clear that *none* of the two moduli diverges from the exact solution over the entire range of explored frequencies; but actually they show a good adherence up to the highest frequency contained in the original signal (here $\omega = 1005.31$), with RAE values of the moduli of RAE(G') = 1.8% and RAE(G'') = 7%. Interestingly, these values are lower than those obtained from the moduli evaluated by means of i-Rheo-MSD, which returns RAE(G') = 16.2% and RAE(G'') = 2.4%. However, it must be noted that, at relatively high frequencies, the RAE show different scaling laws for the two methods, with power laws of circa RAE $\propto \omega^{3/4}$ and RAE $\propto \omega^{9/5}$, respectively. Moreover, at relatively low frequencies (i.e., for $\omega < 10$), the RAEs of the viscoelastic moduli derived by means of i-Rheo-MSD are on average an order of magnitude lower than those calculated from the method introduced by Nishi *et al.*[1] Finally, it is important to highlight that, the latter method only works for experimental data that are equally spaced in time (as also stated by the authors[1]). This is not the case for the analytical method introduced by Tassieri *et al.*,[5] which is of general validity.[11,18]

Appendix

In this section I report the Python code implementing the analytical method developed by Nishi *et al.*[1] that has been adopted here for the evaluation of the viscoelastic moduli shown in Figure 2. The input data are in the form of regular tab-separated text files (.txt) named 'MSDtime' and 'omega'. The first contains the time and the 'synthetic' MSD evaluated via Equation 6 plus the point $[0, 0]$. The second file contains the frequency values at which the moduli are evaluated; here $\omega \in [1/t_{max}, 1/t_{min}]$, where $[t_{min}, t_{max}]$ is the time window in which Equation 6 is evaluated. The Python code is:

```
import numpy as np
def chiw_cal(data, w0):
# m and k are the number of data points
# in the frequency- and time-domain, respectively
    m = len(w0)        # frequency-domain
    k = len(data)       # time-domain
    tau = data[:,0]     # tau
    MSD = data[:,1]  # MSD

    chit = np.zeros(k)

    dt=tau[1]-tau[0]
    kBT=0.5

#// numerical derivative
    for i in range(2):
        chit[i]=1/12*(-25*MSD[i]+48*MSD[i+1]-36*MSD[i+2]+
        +16*MSD[i+3]-3*MSD[i+4])/kBT/2/dt
    for i in range(2,k-2):
        chit[i]=1/12*(MSD[i-2]-8*MSD[i-1]+
        +8*MSD[i+1]-MSD[i+2])/kBT/2/dt

    for i in range(k-2,k):
        chit[i]=1/2*(MSD[i-2]-4*MSD[i-1]+3*MSD[i])/kBT/2/dt

 # defining the real and the imaginary parts
 # of the response function
    chi1 = np.zeros(m) # the real part
    chi2 = np.zeros(m) # the imaginary part
    l=int((k-3)/2)

#// Fourier transform
for i in range(m):
  if (i%10==0):
    print(’%d/%d’%(i,m))
  for j in range(1):
    chi2[i] += chit[j]*np.sin(w0[i]*tau[j])/3*dt
    chi1[i] += chit[j]*np.cos(w0[i]*tau[j])/3*dt

  for j in range(1, l+1):
    chi2[i] += chit[2*j-1]*np.sin(w0[i]*tau[2*j-1])*4/3*dt+
    +chit[2*j]*np.sin(w0[i]*tau[2*j])*2/3*dt
    chi1[i] += chit[2*j-1]*np.cos(w0[i]*tau[2*j-1])*4/3*dt+
    +chit[2*j]*np.cos(w0[i]*tau[2*j])*2/3*dt

  for j in range(l+1, l+2):
    chi2[i] += chit[2*j-1]*np.sin(w0[i]*tau[2*j-1])*4/3*dt+
    +chit[2*j]*np.sin(w0[i]*tau[2*j])/3*dt
    chi1[i] += chit[2*j-1]*np.cos(w0[i]*tau[2*j-1])*4/3*dt+
    +chit[2*j]*np.cos(w0[i]*tau[2*j])/3*dt
```

```
return chi1, chi2


w0 = np.loadtxt(’omega’) # print(w0)

data = np.loadtxt(’MSDtime’) # print(data)

chi1, chi2 = chiw_cal(data, w0)


chi = chi1+1j*(chi2)


G1 = np.zeros(len(w0))  # G1=0

G2 = np.zeros(len(w0))  # G2=0

for i in range(len(w0)):

     G1[i]=chi1[i]/(chi1[i]*chi1[i]+chi2[i]*chi2[i])

     G2[i]=chi2[i]/(chi1[i]*chi1[i]+chi2[i]*chi2[i])


X = np.zeros((len(w0),3))

X[:,0]=w0

X[:,1]=chi1

X[:,2]=chi2

np.savetxt(’results’,X)


G = np.zeros((len(w0),3))

G[:,0]=w0

G[:,1]=G1

G[:,2]=G2

np.savetxt(’Gstar’,G)
```

Acknowledgements

In memory of Pierpaolo Tassieri. I thank Mike Evans for helpful conversations and Jorge Ramírez for the help with Python.

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