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THE DETERMINATION OF COMPLEX SHEAR MODULUS OF DEIONIZED WATER USING KRAMER-KRONIG RELATION (KKR) METHOD

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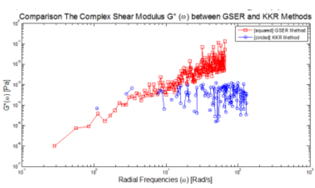
Graphical abstract



Abstract

Complex Shear Modulus (CSM) contains fruitful information about mechanical properties,especially in microrheologystudies. CSM calculation depends onComplex Response Function (CRF) of an object motion. The aim of this paper is to provide guidance on the determination of the CSM by using Kramer-Kronig Relation (KKR) method. The procedure takes advantage of Brownian Motion (BM) of a micron-sized polystyrene in water. The BM occurs when the particle were responseto the thermal force in fluids medium. We use Laplace Transform(LT) algorithm to analyze the BMand to find CRF and CSM.The result will be displayedas Radial Frequencies Function.

Keywords: Complex Shear Modulus (CSM), Kramer-Kronig Relation (KKR), Complex Response Function (CRF), Brownian Motion (BM)

Abstrak

Modulus Ricih Kompleks (CSM) mengandungi maklumat bermanfaat tentang sifat-sifatmekanik, terutama dalam kajian microrheology. Pengiraan CSM bergantung kepada Fungsi Response Kompleks (CRF) daripada gerakan objek. Tujuan kertas kerja iniadalah untuk memberi panduan mengenai penentuan CSM dengan menggunakan Kramer-Kronig Perhubungan (KKR) kaedah. Prosedur ini mengambil kesempatan daripada Brownian Motion (BM) daripada polistirenamikron bersaiz dalam air. BM berlaku apabila zarah itu adalah tindak balas kepada tenaga haba dalam medium cecair. Kami menggunakan algoritma Jelmaan Laplace (LT) untuk menganalisis BM dan untuk mencari CRF dan CSM. Hasilnya akan dipaparkan seperti Radial Kekerapan Fungsi.

Kata kunci: Modulus Ricih Kompleks (CSM), Perhubungan Kramer–Kronig(KKR), Fungsi Respons Kompleks (CRF), Gerakan Brownian (BM)

1.0 INTRODUCTION

In microrheology studies, the Complex Shear Modulus $G^*(\omega) = G'(\omega)+iG''(\omega)$ (CSM) [Pa]is the main information which contains mechanical properties of a viscoelastic material. The CSM consist of shear storage and shear loss modulus. By definition, the CSM is represented through the Equation (1) as below,

$$\sigma(t) = \gamma_o[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)] \tag{1}$$

Where $\sigma(t)$ is the shear stress [Pa] modulus and $\gamma(t)$ is shear strain [dimensionless] modulus.

Equation (1) defines $G'(\omega)$ as the storage modulus and $G''(\omega)$ as the loss modulus of the viscoelastic medium. Storage and loss moduli depend on how the material response to the shear strain, shear stress and phase between shear strain and shear stress [1].

The storage modulus G'(ω) of CSM give information how much contribution and distribution of elasticity inside the materials. Then, the loss modulus G"(ω) is depicting distribution viscosity properties of the material. These quantities were shown as Equation (2) and Equation (3) [1, 2].

$$\tan(\delta) = \frac{G''(\omega)}{G'(\omega)} \quad (2)$$

$$\frac{G''(\omega)}{\omega} \sim \eta'(\omega) \quad \text{and} \quad \frac{G'(\omega)}{\omega} \sim \eta''(\omega) \quad (3)$$

In micro-sized sample case, the displacements of the material probe represent the response from environment, such as thermal force and external force.Brownian Motion (BM) is one of the phenomenon describing random motion and depending on local information. The local information in a material is related to the thermal contribution [3]. Exploration of the thermal factor gives advantages inthe microparticlesstudies. Forces were provided by mediumitselfand it can be used to calculate viscoelasitcity properties of the materials.

There were many ways to study CSM [4]. One ofthe study is the application of Generalized Stokes-Einstein Relation (GSER). The GSER uses Mean-Squared Displacements (MSD) directly to calculate CSM. The linearity degree of the MSD discriminate between Newtonian or Non-Newtonian type of viscoelastic material.The MSD describesthe relation between inter positions and the response toward thermal force using AutoCorrelation Function (ACF). The ACF were widely applied in stationary and non-stationary signals [5]. The ACF is special case when the random motion depends on time factor butdoes notdepends on spatial/space factor.

The other than GSER isthe use of Kramer-Kronig Relation (KKR).The KKR method employedPower Spectrum Density(PSD) of MSD which is related to thermal factor contribution to get imaginary part of the Complex Response Function (CRF). The CRF representssystem stabilityin frequency domain [3]. Moreover, the CRF are widely used to study the perturbation effects in optical material, signals processings and electrochemicalstudies [6, 7]. Meanwhile, equivalent with MSD, we can apply the PSD from the position of particle. This relation is following Wiener-Khinchin Theorem. Wiener-Khinchin Theorem provides connection fluctuation dissipation and PSD to analyze distribution energy of random motion [8].

From these potentials, this paper describes the procedure of CSM determinationusing Kronig Relation (KKR) for deionized water by observing the BM of a single microparticle. This study proposes an alternative measurement of water viscosity. For possible extension, this method could be performed to characterize viscoelastic of material such as polymer, surfactant solutions and biological materials using optical tweezers where the single microparticle is confined in space [9, 10].

2.0 BASIC THEORY

2.1 Relation between Generalized Stokes-Einstein Relation(GSER) and Kramer-Kronig Relation (KKR)

The Brownian Motion has formulated using the fact that the microparticle in normal condition follows general Equation (4) [11, 12]. The motion of a probe in one dimension of freedom is represented by the particle displacement, x, which subjects to stochastic forces, F_s, on the probe due to the thermal fluctuation as described by the following relation:

$$m\ddot{x} + \gamma\dot{x} = F_s(t) \quad (4)$$

Where *m* is the mass of the probe [kg] and γ is the drag coefficient [kg/s]

The microparticle motion in deionized water is following the Generalized-Stokes Einstein (GSER). It is also known as Diffusion Equation[13]. The diffusion constantcan be obtained fromMean-Squared Displacements $\langle \Delta r^2(\Delta t) \rangle$, via Thermal Equi-Partition Theory in the form of

$$\langle \Delta r^2(\Delta t) \rangle = \frac{1}{N-n}\sum_{j=1}^{N-n}(\vec{r}_{j+n} - \vec{r}_j)^2$$

$$\langle \Delta r^2(\Delta t) \rangle = 2D\Delta t \quad (5)$$

where *j*= index data position =1,2,...,*N*;*N* is number of data frame video recorded; *n*=increment of d*t*=1,2,..., *N*-1 and Δt is lag time[14].

From the Equation (5), we can use the MSD to get Complex Shear Modulus $G^*(\omega)$ (CSM) of fluids. The solution of $G^*(\omega)$ is given by Laplace Transform (LT) of the Diffusion Equation, i.e

$$G^*(s = i\omega) = \frac{1}{6\pi R}\left[\frac{k_B T}{D}\right] - \frac{\kappa}{6\pi R} \quad (6)$$

$$= \frac{1}{6\pi R}\left[\frac{1}{\alpha^*(\omega)}\right] - \frac{\kappa}{6\pi R} \quad (7)$$

where *R* is radius of a probe particle [m], k_B is Boltzmann Constant [J/K], *T* is Temperature [K], then κ is force constant in optical trapping[N/m] and α*(ω) is Complex Response Function (CRF). When the system is absence of optical trapping, the Equation (7) become

$$G^*(\omega) = \frac{1}{6\pi R}\left[\frac{1}{\alpha^*(\omega)}\right] \quad (8)$$

The CRF [α*(ω)] consist of real and imaginary parts. The imaginary parts [α"(ω)] of the CRF depend on Power Spectrum Density (PSD) from displacement. Displacement *r*(*t*) is alternative choiser $r(\omega)$ by experimenter which have assume representing the Fourier amplide by Period equal to unlimited [8]. It can be writen as

$$S(\omega) = \lim_{T\to\infty} \frac{1}{T}\left\langle \left|r_T(\omega)\right|^2 \right\rangle \tag{9}$$

The relation between $\alpha''(\omega)$ and PSD is following [15]

$$\alpha''(\omega) = \frac{\omega}{4k_B T} S(\omega) \quad \text{[m/N or s}^2\text{/kg]} \tag{10}$$

The real part $\alpha'(\omega)$ of the CRF is [3]

$$\alpha'(\omega) = \frac{2}{\pi}\int_0^\infty \cos(\omega t)\left[\int_0^\infty \alpha''(\xi)\sin(\xi t)d\xi\right]dt \quad \text{[m/N]} \tag{11}$$

The Equations (10) and (11) were known as Kramer-Kronig Relation. Based on these equations, the CRF of fluids system were dependent to the thermal force and Power Spectrum Density (PSD) of displacements. Also, these Equation were calculated contribution of memory positions to the future positions. So, we can find the CSM in Equation (8) via CRF in the Equation (10) and Equation (11).

3.0 EXPERIMENTAL

Samples were prepared using microparticle as aprobe in deionized water. The particle is polybead® polystyrene (2.95±3%) μm. We have been diluting the polystyrene together with the deionized mediumwith ratio 1:1,000. The motion of the microparticle is observed by Inverted Microscope (Olympus GX51, Oil Immersion 100X) and video recorded at 21 frames/second using digital camera(Motic® Video 3.0 MP) at temperature (26.2±1)oC. We use Open Source Program Tracker (http://www.opensourcephysics.org/) to get the position of particle as the function of time. Equation (8) to Equation (11) is employed to analyze the BM.

4.0 RESULTS AND DISCUSSION

This procedure is starting by process to get the CRF of deionized water. We use amplitude mode FFT of Origin 9.1® to find the imaginary part of CRF. The CRF depicts response particle within changing position per applied force unit. From the Equation (10), the imaginary part is proportional to the frequency and inversely to the thermal energy. It has meant that thermal energy is contribution to resist motion of the particle.

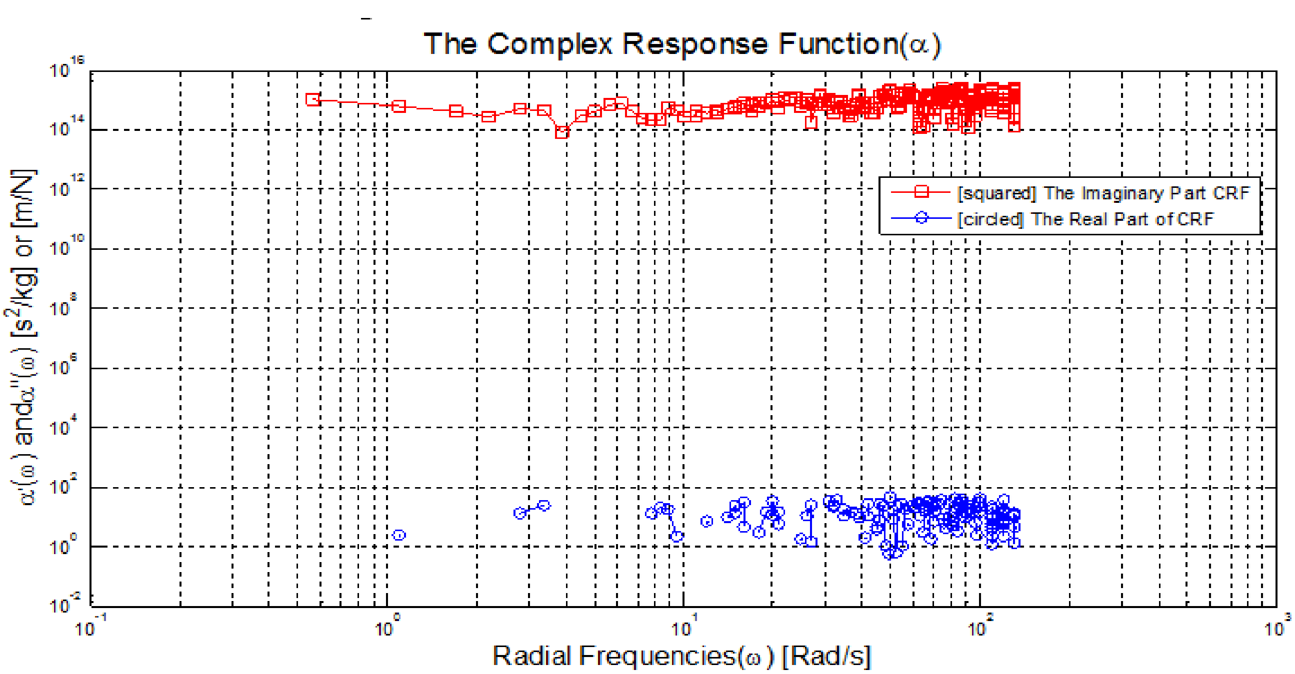


Figure 1 Pattern of CRF using KKR method. The imaginary part of CRF is dominant

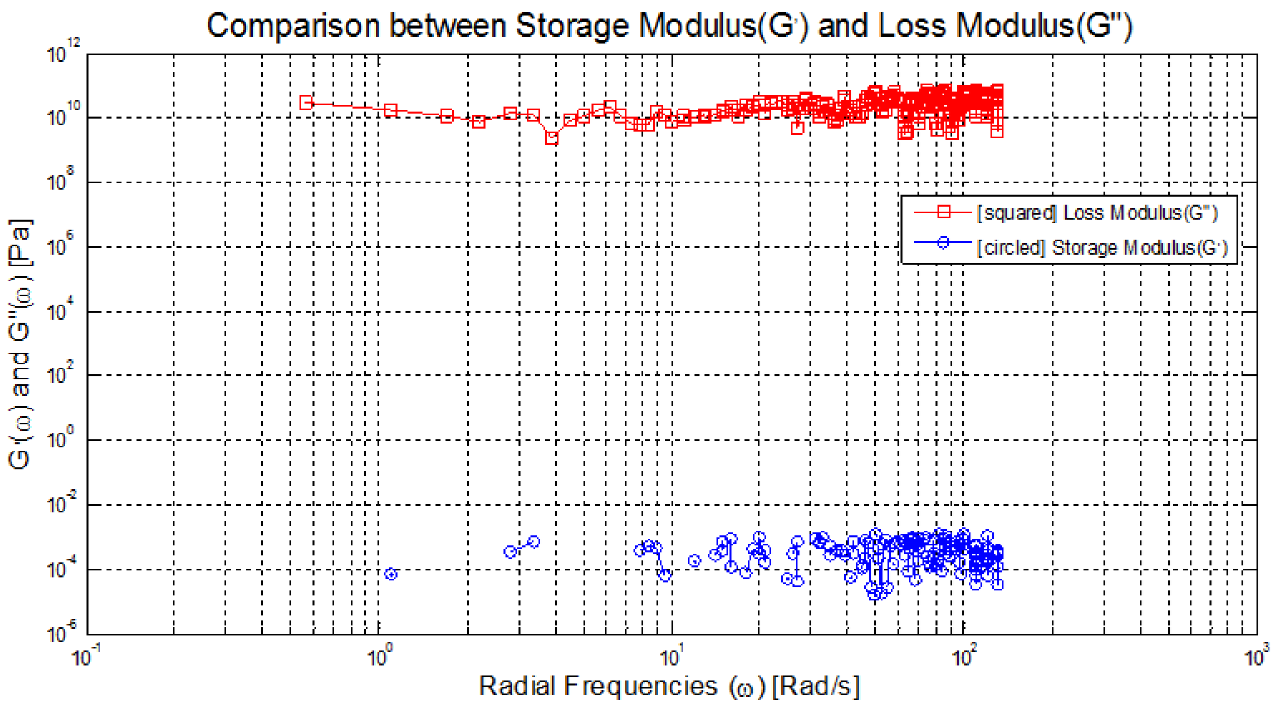


Figure 2 Comparison between storage and loss modulus using KKR method

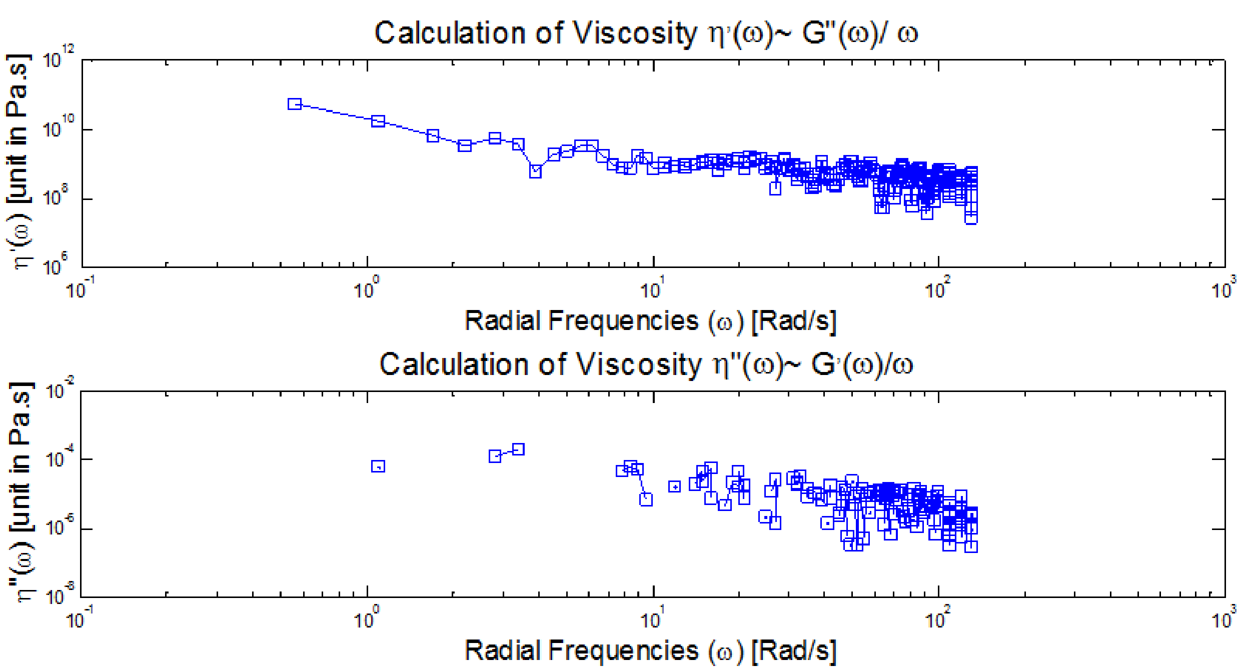


Figure 3 Calculation viscosity of water. There are real and imaginary parts of viscosity

Based on Figure 1, the Imaginary Part is 14 orders larger than Real Part. This is as expected since Real Part contributes to the elasticity while Imaginary Part contributes to the viscosity of the water. Since water is in fluidic form, its elasticity is neglibly small as compared to its viscosity. Figure 1 shows the dominan of loss response of the water. Once CRF is obtained, we can calculate CSM as shown in Figure 2.

Based on Figure 2, the distribution of the storage modulus and loss modulus can be applied to explore the complex viscosity of the medium. Pattern of the viscosity in water will be depicted in Figure 3.

The complex viscosity was calculated using Equation (3) where the Imaginary part of viscosity have order~10^{-5}Pa.s. This order is equal to the reference where the order of viscosity have order equal to ~10^{-5}Pa.s at room temperature. Mean while, Order real viscosity more larger than imaginary part. It was happen because the loss modulus of CSM have big order than storage modulus.

An alternatively, we can also find the CSM of fluids using Generalized Stokes Einstein Relation (GSER). This method apply Mean Squared Displacement (MSD) of the particle probe, then via GSER equations, we can determine CSM. The result is illustrated in Figure 4.

Based on Figure 4. KKR and GSER methods were crossing at definite range frequency. These methods give alternatively to check consistency analysis CSM.

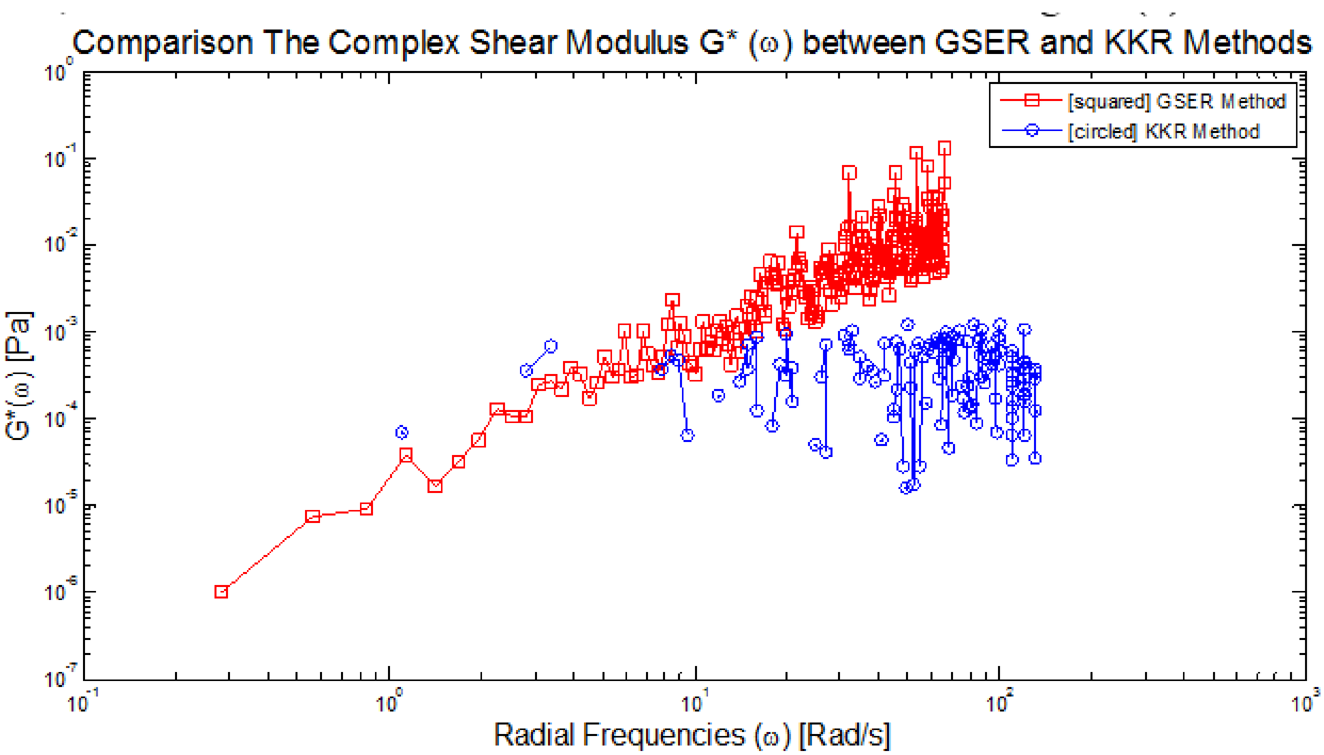


Figure 4 Determination of CSM using different method

4.0 CONCLUSION

CSM of deinozed water is calculated using KKR method. The pattern of CSM depend on distribution energy of displacements. We can explore more deeply to get other mechanical properties from CSM, such as complex viscosity, shear strain distribution and viscoelasticity of the material.

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