

Kim, Scheffold and Mason [1] developed a free energy model to describe the behavior of concentrated monodisperse emulsions, specifically focusing on systems with uniform droplet sizes that exhibit isotropic, disordered structures. This assumption of identical droplet sizes allows for a simplified and consistent analysis across different volume fractions, providing a clearer understanding of the emulsion properties. The model describes two key thermodynamic parameters: the osmotic pressure (Π) and the plateau storage modulus (G'_p), which reflects the linear elastic shear response. In such emulsions, based on the droplet volume fraction ϕ , three main contributions to the total free energy emerge: entropic, electrostatic, and interfacial forces. Each of these contributions dominates at different concentration ranges, leading to different responses in the behavior of the emulsion.

1 Free Energy

The model consists of three core contributions to the total free energy:

- **Entropic term** F_{ent} : Represents the contribution of the entropy to the free energy of the emulsion system. Dominates at low volume fractions, where droplet interactions are minimal. Expressed as:

$$F_{\text{ent}}/N = -3k_B T \ln(\phi_c + \phi_d - \phi) \quad (1)$$

where N is the number of droplets in the emulsion, T is the absolute temperature of the system, ϕ_c is the critical packing fraction, ϕ_d is the deformation volume fraction and k_B is the Boltzmann constant.

- **Electrostatic term** F_{elec} : Represents the electrostatic interaction between charged droplet interfaces. Becomes prominent as the droplets approach closer to the jamming point $\phi_c \approx 0.646$, where screened electrostatic repulsions prevent further compression. Expressed as:

$$F_{\text{elec}}/N = \frac{2\pi a^2 \epsilon_r \epsilon_0 \psi_0^2 \exp(-h/\lambda_D)}{h} \quad (2)$$

where a is the droplet radius, ψ_0 is the surface potential, ϵ_r is the relative permittivity, λ_D is the Debye screening length and h is the separation at the closest approach between the droplets, and is given by:

$$h = 2\phi_c^{1/3} a \left[\phi^{-1/3} - (\phi_c + \phi_d - \alpha\gamma^2)^{-1/3} \right], \quad (3)$$

where γ is the applied shear strain.

- **Interfacial term**: Governs the system at higher volume fractions beyond ϕ_c , where increased droplet deformation is observed. Expressed as:

$$F_{\text{int}}/N = 4\pi\xi\sigma a^2 \phi_d^2 \quad (4)$$

where ξ is a numerical factor.

These three energy terms are incorporated into a total free energy expression as follows:

$$F_{\text{tot}} = F_{\text{ent}} + F_{\text{elec}} + F_{\text{int}},$$

To satisfy the near-equilibrium condition in free energy minimization, consistent with the second law of thermodynamics, the parameter ϕ_d must be chosen to minimize the total free energy F_{tot} . This ensures that the system naturally evolves towards a state of minimum free energy.

The following parameters are used for the free energy model:

- $k_B = 1.38 \times 10^{-23} \text{ J/K}$ — Boltzmann constant
- $T = 298 \text{ K}$ — Temperature in Kelvin
- $\sigma = 0.0098 \text{ J/m}^2$ — Surface tension (converted from dyne/cm)
- $a = 270 \times 10^{-9} \text{ m}$ — Droplet radius in meters
- $\xi = 0.15$ — Dimensionless parameter
- $\epsilon_r = 78.5$ — Relative permittivity of water
- $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ — Permittivity of vacuum
- $\psi_0 = 270 \times 10^{-3} \text{ V}$ — Surface potential in volts
- $\lambda_D = 3.4 \times 10^{-9} \text{ m}$ — Debye length in meters
- $\phi_c = 0.646$ — Critical volume fraction
- $\alpha = 0.85$ — Shear effect parameter

Refer to the original paper, in order to obtain the ϕ_d that could minimize the total free energy, the droplet volume fraction ϕ ranges from 0.45 to 0.85 and set the initial shear strain $\gamma = 0$ in the simulations.

To find the optimal value of ϕ_d , we define a function `find_min_phi_d` in Python. This function minimizes the total free energy F_{tot} with respect to ϕ_d for a given volume fraction ϕ and shear strain γ . We use the `minimize_scalar` function from the `scipy.optimize` module to find the value of ϕ_d that minimizes F_{tot} . The graph of ϕ_d as a function of ϕ when $\gamma = 0$ under the log scale is as follows:

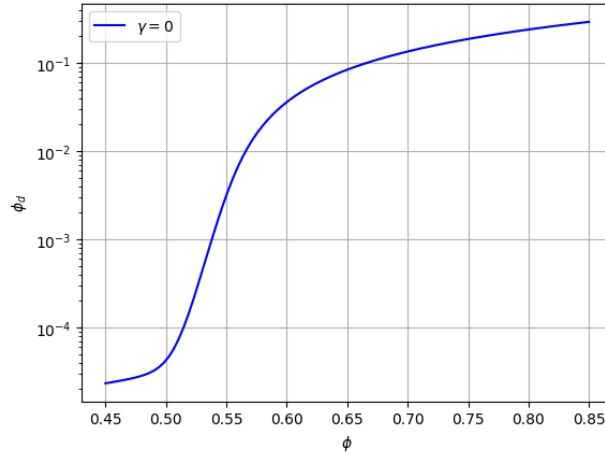


Figure 1: ϕ_d vs ϕ for $\gamma = 0$

In our approach, we chose to find ϕ_d by directly minimizing the total free energy F_{tot} with respect to ϕ_d , rather than following the method shown in the original paper, where ϕ_d is determined by solving the derivative equation:

$$\left. \frac{\partial F_{\text{tot}}}{\partial \phi_d} \right|_{\phi_d=\phi_d^*} = 0$$

Our decision is based on practical experiments in Python and Julia using different programming languages and optimization functions. We found that when ϕ is relatively small, solving for ϕ_d using the derivative method hardly leads to a change in ϕ_d , resulting in almost the same value. This lack of change in ϕ_d creates problems in later calculations of G'_p or Π due to the minimization of the dependence on ϕ_d . By choosing to minimize F_{tot} directly, we obtain a more stable and variable value of ϕ_d , resulting in more accurate and consistent results for follow-up calculations.

After obtaining the optimal value of ϕ_d through direct minimization, we substitute this ϕ_d back into the original equations (1), (2), and (4) for the respective terms F_{tot} , F_{int} , F_{ent} , and F_{elec} . This allows us to compute each component of the free energy based on the optimized ϕ_d .

The resulting plots for each term per droplet are shown in comparison with the corresponding figures from the original paper. Below, we present a side-by-side comparison of our computed results (left) and the original results from the paper (right).

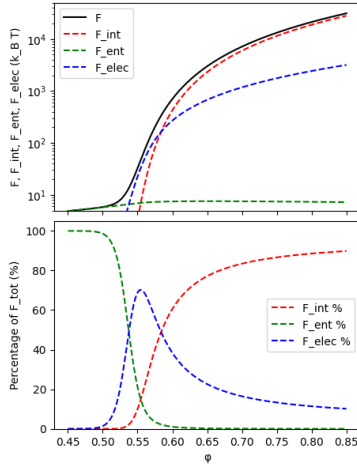


Figure 2: Our results

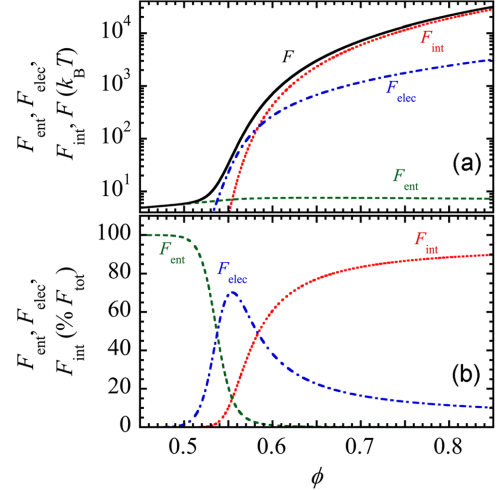


Figure 3: Original results from the paper

2 The Osmotic Pressure

To calculate the osmotic pressure Π , we use the formula in the paper:

$$\Pi = \left[\frac{\phi^2}{NV_{\text{drop}}} \right] \left[\frac{\partial F_{\text{tot}}}{\partial \phi} \right]_{\phi_d=\phi_d^*, \gamma=0} = \left[\frac{\phi^2}{V_{\text{drop}}} \right] \left[\frac{\partial (F_{\text{tot}}/N)}{\partial \phi} \right]_{\phi_d=\phi_d^*, \gamma=0} \quad (5)$$

Here, V_{drop} represents the volume of a single droplet. The osmotic pressure Π is thus dependent on the derivative of the total free energy per droplet F_{tot}/N with respect to ϕ , evaluated at the optimal deformation volume fraction ϕ_d^* and $\gamma = 0$.

To compute each component of Π (including the total and individual contributions from F_{int} , F_{ent} , and F_{elec}), we use the optimal value ϕ_d^* obtained as before, and calculate the first-order derivatives of each energy component with respect to ϕ by `np.gradient` function from NumPy library, under the values of ϕ vary between 0.45 and 0.85, and γ values range from 0 to 0.01. This function is used to compute the numerical gradient (approximate derivative) of an array and it is particularly useful for estimating the rate of change in a dataset when an analytical derivative is not available. Using these derivatives, we can then calculate the osmotic pressures for each component according to the formula (5). The resulting plots for each term per droplet are shown in comparison with the corresponding figures from the original paper. Below, we present a side-by-side comparison of our computed results (left) and the original results from the paper (right).

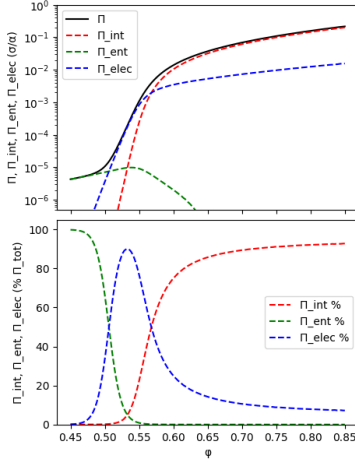


Figure 4: Our results

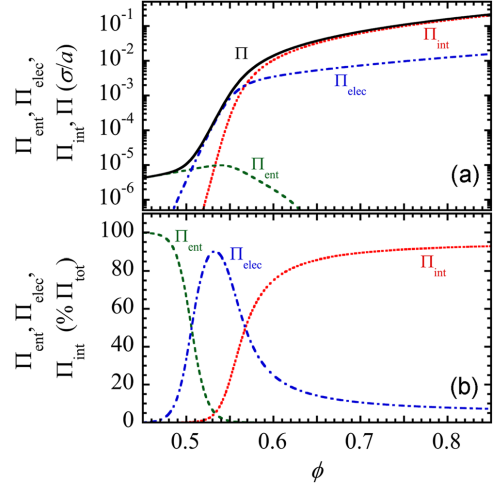


Figure 5: Original results from the paper

3 The Plateau Elastic Shear Moduli

To calculate the osmotic pressure G'_p , we use the formula in the paper:

$$\begin{aligned}
 G'_p &= \left[\frac{\phi}{NV_{\text{drop}}} \right] \left[\frac{\partial^2 F_{\text{tot}}}{\partial \gamma^2} \right]_{\phi_d=\phi_d^*, \gamma=0} \\
 &= \left(\frac{\phi}{V_{\text{drop}}} \right) \cdot \left(\frac{\partial^2 \left(\frac{F_{\text{tot}}}{N} \right)}{\partial \gamma^2} \right)_{\phi_d=\phi_d^*, \gamma=0}.
 \end{aligned} \tag{6}$$

Using the values of ϕ vary between 0.45 and 0.85, and γ values range from 0 to 0.01, we could get the optimal deformation volume fraction ϕ_d^* for each combination. After obtaining F_{tot} and its components for different γ values at each ϕ , we use cubic spline interpolation to smooth these values. This interpolation creates a continuous function, allowing us to compute second derivatives with respect to γ . Using the cubic splines, we calculate the second derivative of F_{tot} and each component (F_{int} , F_{ent} , F_{elec}) with respect to γ . We use `spline_tot.derivative(2)` to obtain the second derivative of each spline function. The second derivative is evaluated at $\gamma = 0$ by selecting the value at the 10th index of the γ array as a close approximation. Using the formula (6) we calculate G'_p for the total free energy and each component.

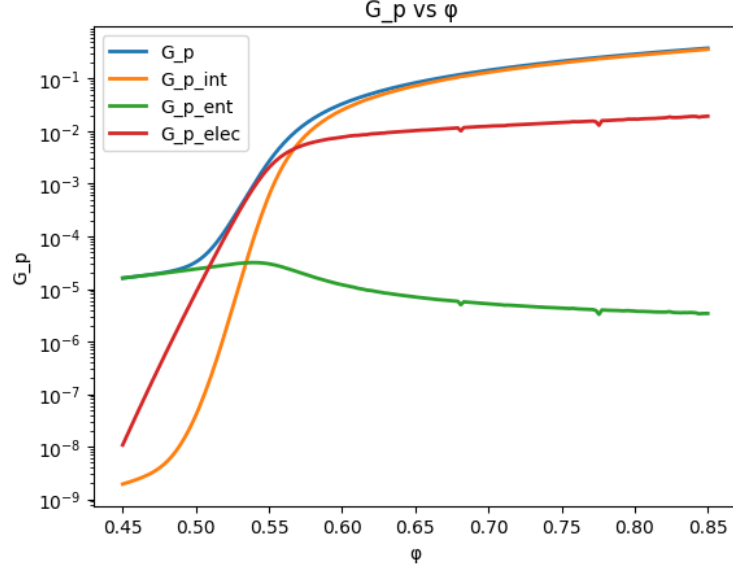


Figure 6: Our results of G'_p

The results are shown in Figure 6. We divide the range of ϕ into 200 values, and upon inspection, we observe two noticeable singularities at $\phi = 0.6811$ (corresponding to `phi_vals[115]`) and $\phi = 0.7756$ (corresponding to `phi_vals[162]`) for $G'_{p,elec}$ and $G'_{p,ent}$.

Upon analyzing the cubic spline interpolation of F , we find that it appears quite smooth. However, the first and second derivatives show two distinct singularities. The exact cause of these singularities remains unclear, and as such, we have not yet determined an approach to address them.

To enhance the visual smoothness of the plots, we apply a Gaussian filter with $\sigma = 3$ using `gaussian_filter1d` to smooth the function. The resulting plots for each term are shown in comparison with the corresponding figures from the original paper. Below, we present a side-by-side comparison of our computed results (left) and the original results from the paper (right).

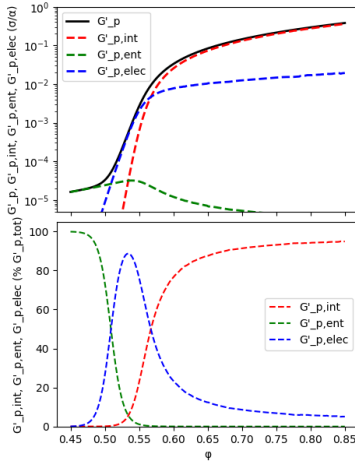


Figure 7: Our results (after smoothed)

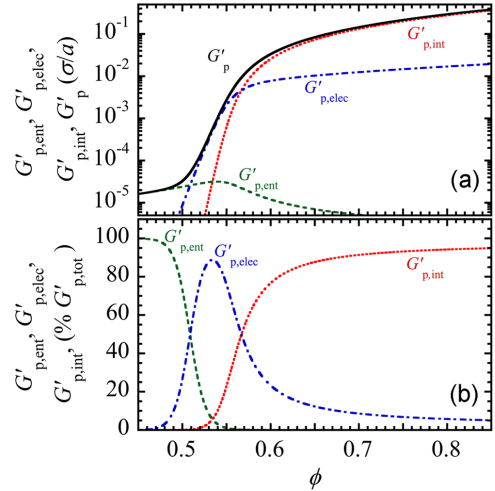


Figure 8: Original results from the paper

References

- [1] Ha Seong Kim, Frank Scheffold, and Thomas G Mason. Entropic, electrostatic, and interfacial regimes in concentrated disordered ionic emulsions. *Rheologica Acta*, 55:683–697, 2016.