

Electronic Supplementary Information (ESI) for
Modeling the structure and relaxation in glycerol-silica nanocomposites

Koksal Karakus¹, Valeriy V. Ginzburg², Keith Promislow³, Leela Rakesh^{4,*}

^{1,4}Central Michigan University, Mt. Pleasant, Michigan

^{2,3}Michigan State University, East Lansing, Michigan

Derjaguin Approximation Overview

The Derjaguin approximation¹ is a widely used method in colloid and polymer science in which the force (or interaction potential) between two particles is related to the disjoining pressure between two parallel plates. Here, we illustrate it on the example of two identical spherical particles in a liquid medium (polymer melt, polymer solution, or electrolyte); the application to more complex situations where the particles have different sizes and/or non-spherical shape can be found in the literature.

Let the two spheres of radius R be immersed in a liquid medium. If the centers of the two spheres are separated by a distance r , the magnitude of the force between the two spheres is $F(r)$. Because of the symmetry, the force is “central” (directed along the line connecting the centers of the two particles) and can be either repulsive or attractive, depending on r and on the surface chemistry of the particles and the composition of the liquid medium. Regardless of what those details are, it can be shown that the magnitude of the force is related to the free energy per unit area, $W(h)$,

$$F(r) = 2\pi R_{\text{eff}} W(h) \quad (\text{S1})$$

where

$$(R_{eff})^{-1} = (R_1)^{-1} + (R_2)^{-1} = 2 / R \quad (S2)$$

and

$$h = r - 2R \quad (S3)$$

The point of this is that if we know the free energy per unit area for the planar surfaces (which is typically easier to calculate), we can easily reconstruct the interaction energies and forces for spherical particles of finite radius. This approximation generally works well if the particle radius, R , is significantly larger than molecular size, a . Typically, one can take $a \sim 1-2 \text{ nm}$ (unless the liquid medium is a polymer melt with very high molecular weight), so for $R > 10 \text{ nm}$, one can indeed disregard the curvature and use the one-dimensional flat-plate geometry.

The Analytical Solution for the Density Profile Equation

Let the free energy have a form,

$$F \equiv U_0 \int_0^H \Phi(u(x)) dx = U_0 \int_0^H dx \left[g(u) + \frac{\beta}{2} \left(\frac{du}{dx} \right)^2 + \frac{\alpha}{2} \left(\frac{d^2u}{dx^2} \right)^2 \right] \quad (S4)$$

With

$$g(u) = \frac{1}{2} [u - 1]^2 \quad (S5)$$

Here, $u(x)$ is the non-dimensionalized density profile, α and β are model parameters. The free energy minimization (Euler-Lagrange equations) is given by,

$$\frac{\partial \Phi}{\partial u} - \frac{d}{dx} \left(\frac{\partial \Phi}{\partial u'} \right) + \frac{d^2}{dx^2} \left(\frac{\partial \Phi}{\partial u''} \right) = 0 \quad (\text{S6})$$

giving rise to the following equation for the density profile,

$$\alpha u'''' - \beta u'' + (u - 1) = 0 \quad (\text{S7})$$

The solutions of eq (S4) can be sought in the form,

$$u(x) = 1 + \sum_{k=1}^4 a_k \exp(\lambda_k x) \quad (\text{S8})$$

Here, a_k are the complex coefficients (determined from boundary conditions), and λ_k are complex wavenumbers that are roots of the equation,

$$\alpha \lambda^4 - \beta \lambda^2 + 1 = 0 \quad (\text{S9})$$

The solutions can be written as,

$$(\lambda^2)_{1,2} = \frac{\beta \pm \sqrt{\beta^2 - 4\alpha}}{2\alpha} = \frac{\beta \pm i\sqrt{4\alpha - \beta^2}}{2\alpha} \quad (\text{S10})$$

The second equality in the rhs of eq (S10) specifically applies to condition $\beta^2 - 4\alpha < 0$ -- this condition ensures that the eigenvalues are complex and the solutions combine oscillations with exponential decay function.

From eq (S10) follows that there are four solutions of eq (S7), and they can be written as,

$$\lambda_{1,2,3,4} = \pm v \pm iw \quad (\text{S11})$$

Where the (real positive) coefficients v and w are solutions to the following equations,

$$v^2 - w^2 = \frac{\beta}{2\alpha}$$

$$2vw = \frac{\sqrt{\beta^2 - 4\alpha}}{2\alpha}$$

(S12)

Or

$$v = \sqrt{\frac{q + \sqrt{q^2 + p^2}}{2}}$$

$$w = \frac{p}{2v}$$

(S13)

Where $q = \frac{\beta}{2\alpha}$ and $p = \frac{\sqrt{\beta^2 - 4\alpha}}{2\alpha}$

The experimentally determined density profile is described by the function,

$$u(x) \equiv f(x) = 1 + a \exp(-bx) \cos(cx - d) \quad (S14a)$$

for $0 < x < H/2$, and

$$u(x) \equiv f(H - x) = 1 + a \exp(-b[H - x]) \cos(c[H - x] - d) \quad (S14b)$$

for $H/2 < x < H$.

It is fairly straightforward to see that $v = b$ and $w = c$. Expressing v and w via α and β (eq S13), we obtain two equations for α and β as functions of b and c . After solving them numerically, we obtain the values presented in the main text.

Justification for the Use of the “Naïve” Free-Volume Theory

Here, our goal to demonstrate that the “naïve” (Doolittle) free volume theory can be derived as a limiting case of a more complex theory like LCL-CFV (Lipson et al.²) or SL-TS2 (Ginzburg et al.³) We start by assuming that the total specific volume of the material, V_{sp} , is the sum of the “free volume”, V_f , and the “occupied volume”, V_o . Within SL-TS2, they are described by two variables, ν (the occupancy) and ψ (the solid fraction),

$$V_o = V_{0,s} \frac{r}{r_s} = V_{0,s} \left[\psi + \frac{r_L}{r_s} (1 - \psi) \right] \quad (\text{S15a})$$

$$V_f = V_{0,s} \frac{r}{r_s \nu} (1 - \nu) = V_{0,s} \left[\psi + \frac{r_L}{r_s} (1 - \psi) \right] \frac{1 - \nu}{\nu} \quad (\text{S15b})$$

The free energy is written as a function of ν and ψ , $F = F(\nu, \psi, T)$, and the logarithm of the relaxation time is written as, $\ln \left(\frac{\tau[T]}{\tau_\infty} \right) = Q[\nu, \psi, T]$. Here, F and Q are some functions whose specific forms can be found elsewhere.

The equilibrium functions $\psi_{eq}[T]$ and $\nu_{eq}[T]$ can be found by minimizing the free energy F and solving two coupled nonlinear equations for each T . The solutions are unique, i.e., for each T , there is a single $\psi_{eq}[T]$ and $\nu_{eq}[T]$. Moreover, the functions $\psi_{eq}[T]$ and $\nu_{eq}[T]$ are monotonic and decreasing with temperature. This means that if one knows ν_{eq} , one can immediately determine the corresponding temperature, T , and the corresponding solid fraction, ψ_{eq} . Thus, the relaxation time can be written as,

$$\ln \left(\frac{\tau[T]}{\tau_\infty} \right) = Q[\nu, \psi_{eq}[T[\nu]], T[\nu]] \quad (\text{S16})$$

If we define the fractional free volume $f_v = 1 - \nu$, it is then possible to re-write eq S16 in the form,

$$\ln \left(\frac{\tau[f_v]}{\tau_\infty} \right) = W \left[\frac{1}{f_v} \right] \quad (\text{S17})$$

with $W[x] = Q[x^{-1}, \psi_{eq}[T[x^{-1}]], T[x^{-1}]]$. **The “naïve” free volume theory then means simply that $W[x] = Kx$ (note that any zero-order term would be automatically absorbed into the definition of τ_∞ . Thus,**

$$\ln\left(\frac{\tau[f_v]}{\tau_\infty}\right) = \frac{K}{f_v} \quad (\text{S18})$$

The overall change in the specific volume over a 1K temperature change, measured by the coefficient of thermal expansion, α_L , consists of the change in the free volume and the change in the occupied volume. Thus,

$$\alpha_L = \alpha_o + \alpha_f \quad (\text{S19})$$

We assume that in the narrow temperature range considered in this study, one can neglect higher-order terms and assume that both α_o (the coefficient of thermal expansion for the occupied volume) and α_f (the coefficient of thermal expansion for the free volume) can be considered constant. Thus,

$$f_{tot} \equiv \ln\left[\frac{V}{V_0}\right] = \alpha_L [T - T_0] = \frac{\alpha_L}{\alpha_f} f_v \quad (\text{S20})$$

where we assumed that the free volume as a function of temperature can be expressed as a linear function,

$$f_v = \alpha_f [T - T_0] \quad (\text{S21})$$

Equation S21 is approximately valid in the vicinity of $T = T_g$, way above T_0 – we expect it to break down as $T \rightarrow T_0$, but it is not relevant for the current analysis.

Combining eqs S20 and S21, we obtain for the equilibrium relaxation time of bulk glass-formers close to T_g ,

$$\ln\left(\frac{\tau[f_v]}{\tau_\infty}\right) = \frac{K}{f_v} = \frac{K}{\alpha_f (T - T_0)} = \frac{K\alpha_L}{\alpha_f \alpha_L (T - T_0)} = \frac{A}{f_{tot}} \quad (\text{S22})$$

Here,

$$A = K \frac{\alpha_L}{\alpha_f} \quad (\text{S23})$$

Within the “naïve” free volume theory, we assume that $f_{tot} = f_v$, leading to eq 9a in the main text and all the subsequent estimates. Thus, at least for the bulk materials in the narrow temperature range near $T = T_g$, the predictions of the “naïve” free-volume theory would coincide with those of more advanced ones. The differences become pronounced only as one attempts to describe the wider temperature ranges and/or include the influence of pressure.

When generalizing to inhomogeneous systems, like films and nanocomposites, we make an additional implicit assumption – that as we force a local change in the free volume, δf_v , the change in the occupied volume, δf_o , would be given by, $\delta f_o = \left(\frac{\alpha_o}{\alpha_f} \right) \delta f_v$. Within SL-TS2, we can justify this assumption by saying that increasing the void fraction leads to the corresponding increase in the liquid fraction; similar arguments can be advanced using LCL-CFV.

Obviously, the above reasoning applies only if the material is in equilibrium (i.e., above the glass transition temperature) and probably only in a narrow temperature range (where the function Q can be linearized). We hypothesize that these conditions are satisfied for the experiments analyzed here.

The Number of Layers in a Cooperatively Rearranging Region

In the main text, we assumed that a cooperatively rearranging region (CRR) is comprised of two layers. Here, we consider scenarios where one CRR includes three or four layers. The “normalized smoothed density” profiles are plotted in Figure S1 below. It can be seen that there is little difference between the “two-layer” and “four-layer” models. The “three-layer” model is obviously different as the first element would have two maxima and one minimum, the second would have one maximum and two minima, and so on – so the resulting “smoothed density” would exaggerate, rather than smoothen, the initial layering. We will use the two-layer model, but expect the four-layer model to work equally well.

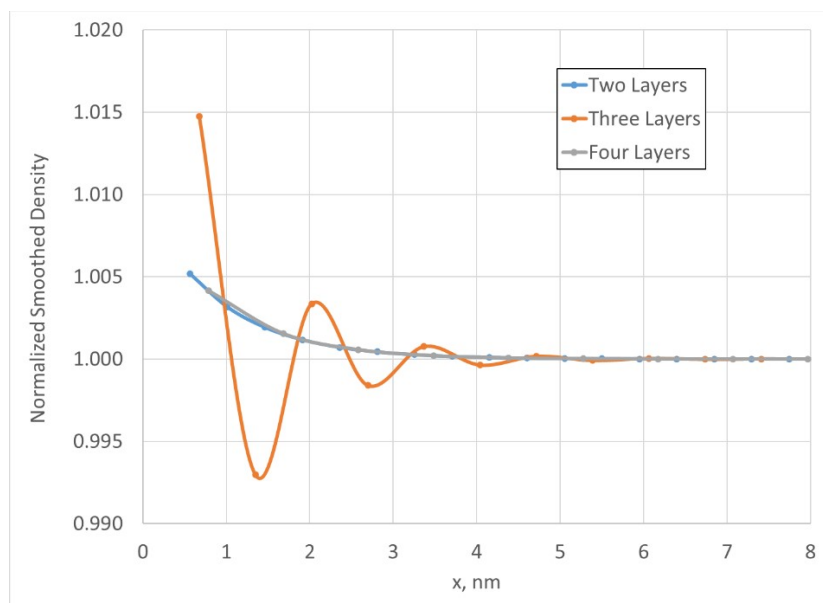


Figure S 1. Normalized smooth density profiles for the two-layer (blue), three-layer (orange), and four-layer CRRs.

References

- 1 B. Derjaguin, *Kolloid-Zeitschrift*, 1934, **69**, 155–164.
- 2 R. P. White and J. E. G. Lipson, *Macromolecules*, 2016, **49**, 3987–4007.
- 3 V. V Ginzburg, A. Zaccone and R. Casalini, *Soft Matter*, 2022, **18**, 8456–8466.