Supporting information for: Dynamics and morphological outcomes in thin-film spherical crystallization of glycine from microfluidic emulsions – experimental studies and modeling

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I. Schematic of the experimental setup

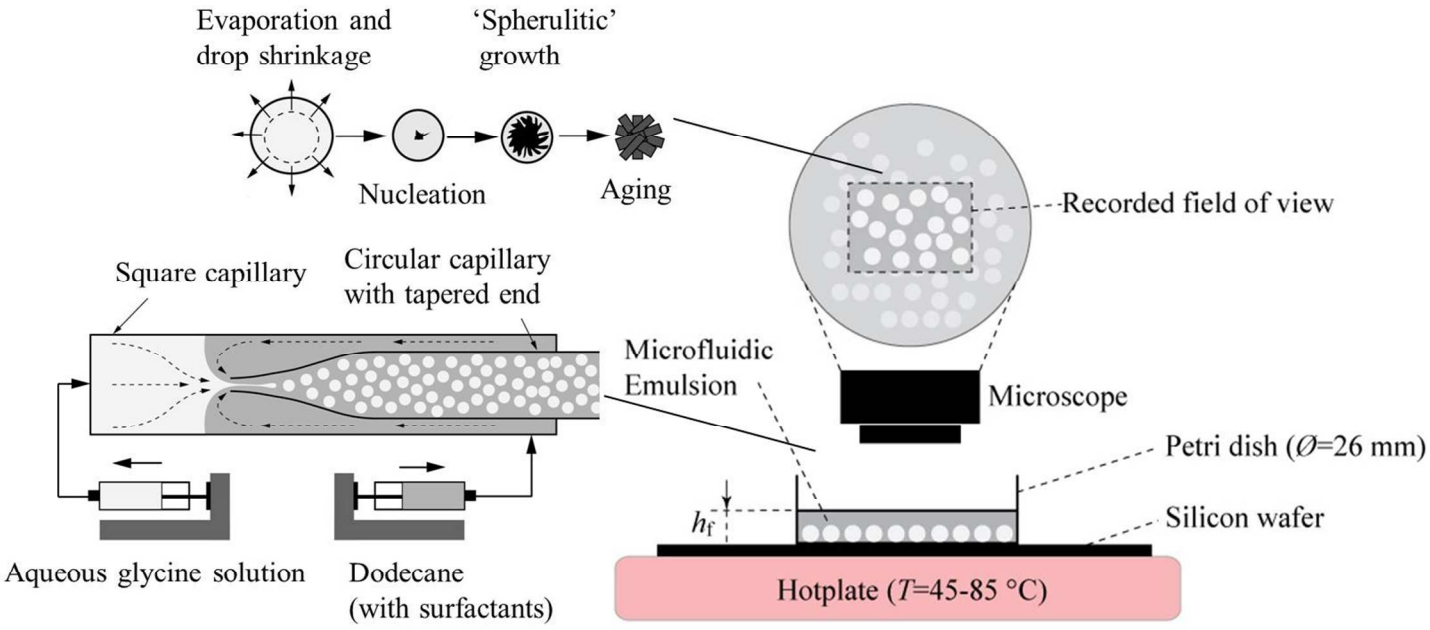

Figure S1: Schematic of experimental setup. Emulsion generation is performed in a concentric microfluidic glass capillary setup, where a square capillary (ID=1 mm) houses a tapered round capillary (OD= 1 mm). The two ends of the square capillary function as inlets and the round capillary functions as a collection tube and outlet. The continuous phase (CP) of dodecane (with dissolved surfactants) and a dispersed phase (DP) of aqueous glycine are infused by syringe

pumps into the square capillary. The emulsions are collected in a heated glass petri dish where evaporative crystallization occurs.

II. The relationship between film thickness and shrinkage at a constant temperature – an example

Figure S2 presents an empirical relationship between the effective film thickness h_e, (defined as h_f - d_0, where h_f is the dispensed film thickness, and d_0 is the initial droplet diameter) and the linear shrinkage rate d' at T=65 °C for all nine experiments at this temperature. It can be seen that as the film thickness increases, the shrinkage rate decreases with the cube of the film thickness. In a purely diffusive case, we could expect a linear decrease, which suggests the presence of a convective enhancement (possibly due to natural convection) in this system.

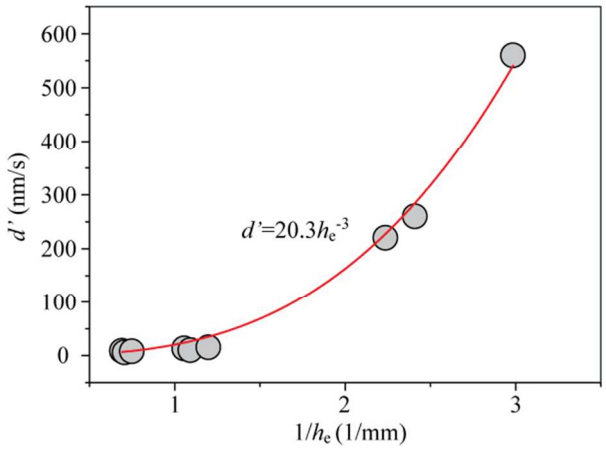

Figure S2: An empirical relationship between the effective film thickness h_e, (defined as h_f-d_0, where h_f is the dispensed film thickness, and d_0 is the initial droplet diameter) and the linear shrinkage rate d' at T=65 °C for all nine experiments at this temperature.

III. The calculated values of classical nucleation theory parameters

Table S1 presents the calculated values of CNT parameters at the temperatures used in this study, while Figure S3 shows the parameter *B* as a function of continuous phase temperature. Fitted *B* values were used for modeling.

#	T (°C)	T_{CP} (°C)	σ (mJ/m^2)	B
10	45	39	12.8	2.69
V3	50	45	12.4	2.28
11, V1	55	48	12.2	2.13
V4	60	52	11.9	1.89
1-9, V5	65	59	12.1	1.59
V6	70	63	11.2	1.44
12, V2	75	68	11.0	1.27
13	85	78	10.5	1.03

Table S1: the calculated value of classical nucleation parameters under the temperatures used in this study. #: experiment label (as seen in Table 1 and Table 4); T: heating temperature; T_{CP}: measured continuous phase temperature; σ: interfacial tension between the nucleus and the crystallizing solution; B: dimensionless exponent B.

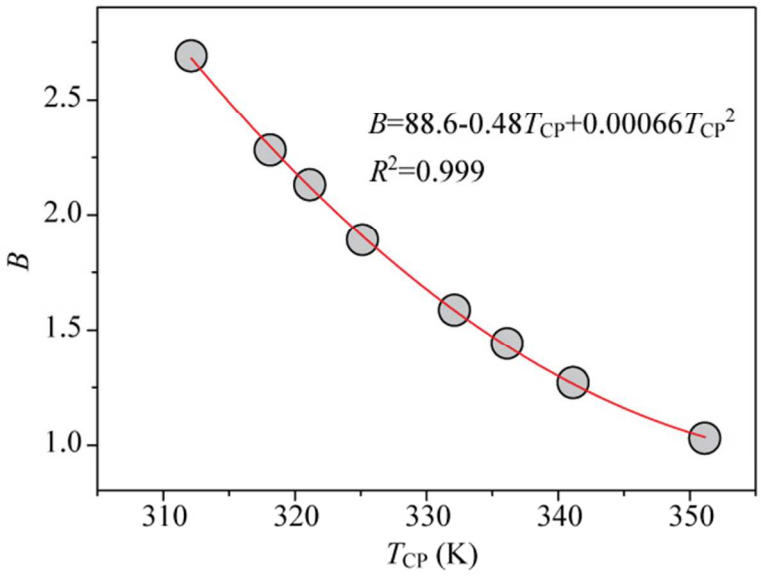

Figure S3: parameter *B* as a function of continuous phase temperature along with the polynomial fit used for modeling.

IV. Fitting of the CNT parameter *A*

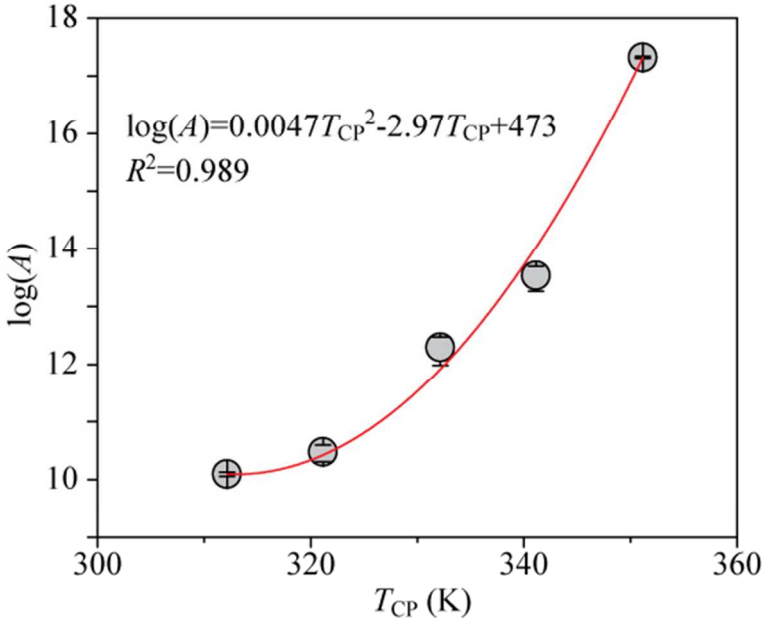

Figure S4: Experimentally derived log(*A*) values as a function of continuous phase temperature along with the fitted quadratic curve that was used in the modeling. This fit implies that the relationship is of the form $A=A_0\exp(f(T))$, which is consistent with previous reports.[1]

V. Shrinkage Rate and Temperature

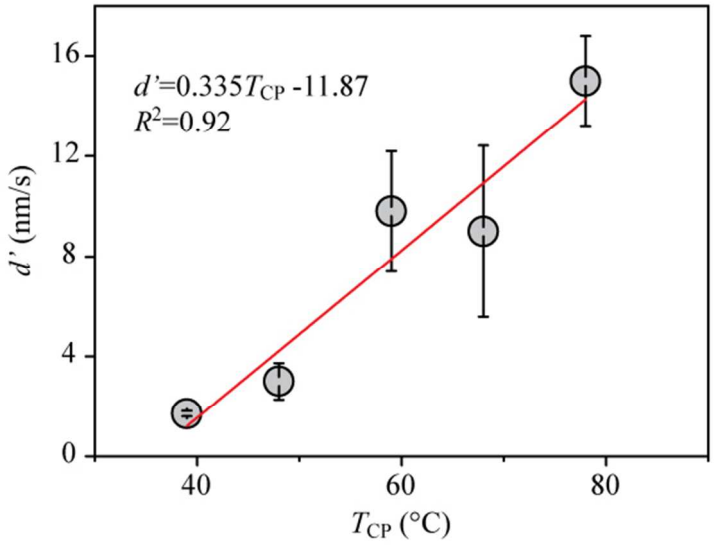

Figure S5: Experimentally measured shrinkage rates at various continuous phase temperature along with the linear fit used in the simulations for Figure 6d.

References:

(1) Pina, C. M.; Putnis, A., The kinetics of nucleation of solid solutions from aqueous solutions: a new model for calculating non-equilibrium distribution coefficients. *Geochimica et Cosmochimica Acta* **2002,** 66, (2), 185-192.