Supplementary information: Chemical Kinetics and Mass Action in Coexisting Phases

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1. GIBBS FREE ENERGY DENSITY FOR MULTICOMPONENT MIXTURE

The Gibbs free energy density for \((M+1)\) components reads:

\[
g(\{n_i\}, p, T) = k_B T \sum_{i=0}^{M} n_i \log(n_i) + \sum_{i,j=0}^{M} \chi_{ij} n_i n_j \\
+ \sum_{i=0}^{M} \omega_i(T)n_i + p.
\]  

\(\text{(S1)}\)

The chemical potential, \(\mu_i \equiv \partial G/\partial n_i|_{T,p,N_i \neq j}\) of each component can be expressed as,

\[
\mu_i = \frac{\partial g}{\partial n_i} + \nu_i \left( g - \sum_{k=0}^{M} \frac{\partial g}{\partial n_k} n_k \right).
\]

\(\text{(S2)}\)

The above expression is obtained using the following relations, \(G = gV\) and \(V = \sum_{k=0}^{M} \nu_k N_k\). Employing Eq. (S1), the chemical potential becomes

\[
\mu_i = \nu_i p + \omega_i + k_B T (1 + \ln(n_i \nu_i)) + \sum_{k=0}^{M} \chi_{ik} n_k
\]

\[- \nu_i \left( \sum_{k,l=0; k \neq l}^{M} \chi_{kl} n_k n_l + k_B T \sum_{k=0}^{M} n_k \right) .
\]

\(\text{(S3)}\)

Using Eq. (1) and (2) in the main text, together with the chemical potential above we obtain the activity coefficients as in Eq. (3) in the main text.

2. KINETICS OF PARTICLE NUMBER AND PHASE VOLUMES

The rate of change of particle number \(N_i\) in each phase due to chemical reactions occurring with the rate \(R_i\) and the exchange rate \(J_i\) between the phases \(J_i\) is given by,

\[
\frac{d}{dt} N_i = R_i^{\text{I/II}} - J_i^{\text{I/II}} .
\]

\(\text{(S4)}\)

Due to conservation of number of particles of individual components during the exchange between phases, \(J_i^{\text{I}} = -J_i^{\text{II}}\) and

\[
R_i^{\text{I/II}} = V^{\text{I/II}} r_i^{\text{I/II}},
\]

\(\text{(S5)}\)

where \(r_i^{\text{I/II}} = \sum_{\alpha=1}^{R} \sigma_{\alpha} r_{\alpha}^{\text{I/II}}\) and \(r_{\alpha} = (r_{\alpha}^{+} - r_{\alpha}^{-})\), each with the units of particle number per time and volume. Each phase volume is defined as the total volume occupied by all
the components in each phase, \( V^{I/II} = \sum_{i=0}^{M} \nu_i N_i^{I/II} \). Therefore, the dynamic equation for the phase volume is,

\[
\frac{d}{dt} V^{I/II} = \sum_{i=0}^{M} \nu_i^{I/II} (R_i^{I/II} - J_i^{I/II}) + \sum_i N_i^{I/II} \frac{d}{dt} \nu_i^{I/II}. \tag{S6}
\]

Due to incompressibility, \( d\nu_i^{I/II}/dt = 0 \) and the molecular volumes are constant and identical in each phase. Dividing both sides of the equation above with the respective phase volumes and using Eq. (S5), we obtain Eq. (14b). We can now derive the dynamic equations Eq. (14a) for the concentrations \( n_i^{I/II} \) using Eq. (S4) and Eq. (S5).

3. PARAMETERS USED FOR NUMERICAL COMPUTATIONS

A. Unimolecular chemical reaction

Given three components and one chemical reaction, we define two conserved quantities, \( \psi_0 = \nu_S n_S \) and \( \psi_1 = (\nu_A n_A + \nu_B n_B) \). The kinetic equations for the reactive solutes in each phase are obtained using Eq. (14a). We choose the initial average volume fractions along conserved line \( \psi_1 = 0.55 \) for kinetic studies in Fig. (3).

The thermodynamic parameters used to construct Fig. (1) and Fig. (3) are listed below. The reference chemical potentials in units of \( k_B T \) are \( \mu_0^A/(k_B T) = 2 \) and \( \mu_0^B/(k_B T) = 0 \). The molecular volumes of all components, in units of solvent molecular volume \( \nu_S \) are identical \( \nu_A/\nu_S = 1 \) and \( \nu_B/\nu_S = 1 \). Therefore we use \( \nu \) for the identical molecular volumes. The mean field interaction parameters in units of \( (k_B T \nu_S) \) are \( \chi_{AS}/(k_B T \nu_S) = -1 \), \( \chi_{BS}/(k_B T \nu_S) = 3 \) and \( \chi_{AB}/(k_B T \nu_S) = 0 \). The reaction rate coefficient used for studying the reaction kinetics of the system in Fig. (3a-b) is chosen identical in each phase, \( k^{I/II} = 1 \) per unit time. In Fig. (3c-f), for different ratios of reaction rate coefficients, the value of \( k^{II} = 1 \) per unit time is kept constant and \( k^I \) is varied accordingly to maintain the ratio. The initial conditions for two cases in Fig. (3a-b) are (i) \( \nu \bar{n}_A(0) = 0.4, \nu \bar{n}_B(0) = 0.15 \) and (ii) \( \nu \bar{n}_A(0) = 0.05, \nu \bar{n}_B(0) = 0.5 \).

B. Bimolecular chemical reaction

Given four components and one chemical reaction, we have three conserved quantities as defined in Sec. (II G). The kinetic equations for the reactive solutes in each phase are obtained using Eq. (14a). We choose the initial average volume fractions corresponding
to two systems along intersection of conserved plane $\psi_1 = 0.42$ and $\psi_2 = 0.05$ and 0.1, respectively. The thermodynamic parameters used to construct Fig. (4) are listed below. The reference chemical potentials in units of $k_B T$ are $\mu_A^0/(k_B T) = 3.5$, $\mu_B^0/(k_B T) = 3.5$ and $\mu_C^0/(k_B T) = 0$. The molecular volumes in units of solvent volume fraction $\nu_S$ are $\nu_A/\nu_S = 1$, $\nu_B/\nu_S = 1.0$ and $\nu_C/\nu_S = 2$, respectively. The mean field interaction parameters in units of $(k_B T \nu_S)$ are $\chi_{AS}/(k_B T \nu_S) = 1.25$, $\chi_{BS}/(k_B T \nu_S) = 0$, $\chi_{CS}/(k_B T \nu_S) = 3.2$, $\chi_{AB}/(k_B T \nu_S) = 0$, $\chi_{AC}/(k_B T \nu_S) = -1.25$ and $\chi_{BC}/(k_B T \nu_S) = 0$.

The reaction rate coefficient is chosen identical in each phase, $k^{I/II} = 1$ per unit time.

C. Unimolecular chemical reaction maintained away from chemical equilibrium

The thermodynamic parameters used to construct Fig. (5) are the same as in Appendix (3). We choose the conserved quantity as $\psi_1 = 0.55$ (Figs. (5a-c)). The initial condition used in Fig. (5b) is $\bar{\nu}n_A(0) = 0.4$ and $\bar{\nu}n_B(0) = 0.15$, which lies in the mixed phase. We choose the value of backward external reaction free energy in the mixed phase from the sigmoidal function which depends on the product B volume fraction,

$$\tilde{\mu}^{-1}(n_B) = 0.5 \left[ \tanh \left( \frac{\nu n_B - 0.3}{0.05} \right) + 1 \right] \tilde{\mu}^{-1},$$

(S7)

where $\tilde{\mu}^{-1}$ is fixed to two different non-zero values (see legends in Fig. (5)). The choice of the external reaction free energies along with the conserved quantity uniquely defines the NESS composition in the coexisting phases.

4. MAINTAINING CHEMICAL REACTIONS AWAY FROM EQUILIBRIUM

Phase-separated systems can be maintained away from equilibrium by the supply of fuel; discussion see main text and Ref. [34,35,47]. A simple example of such non-equilibrium situations can arise when products can from from reactants with and without a fuel component. This coupling to fuel can be described explicitly or, as we proceed in this section, by an external reaction free energy $\Delta \tilde{\mu}_\alpha$, as introduced in Eq. (28). When the fuel $F$ and its product components, waste $W$, are controlled via external reservoirs, the system can be maintained away from equilibrium.

We demonstrate this for the simple unimolecular reaction occurring without fuel with a reaction rate coefficient $k$,

$$A \rightleftharpoons B.$$  

(S8)
There is a further reaction where fuel \( F \) can couple to this reaction, such that it occurs with the reaction rate coefficient \( k_F \),

\[
A + F \rightleftharpoons B + W.
\]  
(S9)

The chemical potentials of fuel and waste, \( \mu_F \) and \( \mu_W \), can be controlled externally by chemostats. The forward (+) and backward (−) reaction rates of the non-fuel driven and fuel driven reactions are \( r^+ \) and \( r^+_F \) respectively. Using Eq. (19), the ratio of the net forward and backward reaction rates, \( r^+ + r^+_F \) and \( r^- + r^-_F \), is

\[
\frac{r^+ + r^+_F}{r^- + r^-_F} = k \exp\left(\frac{\mu_A}{k_B T}\right) + k_F \exp\left(\frac{\mu_A + \mu_F}{k_B T}\right)
\]

\[
= \exp\left(-\frac{\mu_B - \mu_A}{k_B T}\right) \left(1 + \frac{k_F}{k} \exp\left(\frac{\mu_F}{k_B T}\right)\right).
\]  
(S10)

Following Eq. (28) in the main text, we define the effective reaction free energy \( \Delta \mu \) which obeys

\[
\frac{r^+ + r^+_F}{r^- + r^-_F} = \exp\left(-\frac{\Delta \mu}{k_B T}\right).
\]  
(S11)

The effective reaction free energy can be written as \( \Delta \mu = (\mu_B - \mu_A) + \Delta \tilde{\mu} \), where

\[
\Delta \tilde{\mu} = k_B T \log \left(\frac{1 + \frac{k_F}{k} \exp\left(\frac{\mu_F}{k_B T}\right)}{1 + \frac{k_F}{k} \exp\left(\frac{\mu_W}{k_B T}\right)}\right).
\]  
(S12)

plays the role of an external reaction free energy. The latter can also be written as \( \Delta \tilde{\mu} = \tilde{\mu}^- - \tilde{\mu}^+ \), with the external reactant and product free energy

\[
\tilde{\mu}^{+/−} = k_B T \log \left(1 + \frac{k_F}{k} \exp\left(\frac{\mu^{+/−}}{k_B T}\right)\right).
\]  
(S13)

Note that the reactant and product free energies \( \tilde{\mu}^{+/−} \) do not depend solely on thermodynamic quantities, such as the chemical potential of the fuel and the waste, \( \mu_F \) and \( \mu_W \), respectively. They also depend on the reaction rate coefficients \( k \) and \( k_F \). Such reaction rate coefficients \( k \) and \( k_F \) can depend on phase composition and thus create differences in the reaction pathways between the phases.

In Sect. II H, we consider the special case with \( \tilde{\mu}^{−,I/II} = 0 \) and \( \tilde{\mu}^{+,I/II} = 0 \), and \( \tilde{\mu}^{−,I} = k_B T \log \left(1 + \frac{k_F}{k} \exp\left(\frac{\mu_W}{k_B T}\right)\right) \), which we refer to as chemostat potential in Fig. 5(c) in the main text.
5. THE TIE LINE SELECTING CURVE

At thermodynamic equilibrium the composition of coexisting phases is connected by a tie line in the phase diagram. For different average concentrations along a tie line, only the volumes of the phases change (see Sec. ID). For example, in a ternary system with one chemical reaction at thermodynamic equilibrium, a unique tie line is selected. Thus, varying the conserved quantity $\psi_1$ is equivalent to moving along this tie line and therefore does not affect the composition of the coexisting phases. However, for systems maintained away from equilibrium, the composition at the non-equilibrium steady state (NESS) depends on the volumes of the coexisting phases $V^{I/II}$ (see Eq. (31)). Therefore, in our considered example of a ternary system with a non-equilibrium chemical reaction, the composition at the non-equilibrium steady state depends on the conserved quantity $\psi_1$. Thus, the tie line corresponding to the NESS also varies with $\psi_1$. We illustrate this graphically (see Fig. (S1a,b)) for the models considered in the main text (Sect. II H).

As a measure of the deviation to thermodynamic equilibrium, we determined the non-equilibrium reaction free energy (r.f.e) $\Delta \mu^{NESS}$ as a function of the conserved quantity $\psi_1$ (Fig. (S1c)). Due to the external supply of free energy via the chemostat potential in phase I, $\tilde{\mu}^{-1}$, the absolute value of the non-equilibrium reaction free energy $\Delta \mu^{NESS}$ increases for larger values of the conserved quantity $\psi_1$. Increasing $\psi_1$, the volume of phase I $V^I$ grows. The non-equilibrium reaction free energy $\Delta \mu^{NESS}$ is positive when $A$ is favored over $B$ ($\tilde{\mu}^{-1} > 0$) by the non-equilibrium reaction, and vice versa.
FIG. S1: **Selection of tie line for varying conserved quantity** $\psi_1$. For the model as used in Fig. (5), we show the influence of the conserved quantity $\psi_1$ on the non-equilibrium steady state (NESS). **(a,b)** Binodal (phase equilibrium) is shown in green. In (a) and (b), we show the two cases of the mono-nodal considered in the main text (Fig. 5), where the yellow mono-nodal in (a) corresponds to $\bar{\mu}^{-1} = -3$, while the red mono-nodal in (b) corresponds to $\bar{\mu}^{-1} = 1.3$. For each value of the conserved quantity $\psi_1$, a specific tie line is selected, which is the tie line that contains the intersection point between the conservation line $\psi_1$ (thin grey) and the line of average concentrations described by the steady state condition, $dn_{I/II}/dt = 0$ and $dV_{I/II}/dt = 0$ (thick black). In (a,b), the conservation line is shown for $\psi_1 = 0.55$. The average concentrations at steady-state (thick black line) are drawn for all values of $\psi_1$ for which a demixed NESS exists. For those, the range of $\psi_1$ is constrained between the points at which the mono-nodal crosses the binodal. **(c)** We show the non-equilibrium reaction free energy $\Delta \mu^{NESS}$ as a function of the conserved quantity $\psi_1$ for two values of the chemostat potential $\bar{\mu}^{-1}$ considered in (a) and (b), respectively. The chemostat potential values (dashed lines) are limiting the non-equilibrium reaction free energy $\Delta \mu^{NESS}$, correspondingly.