Supplementary Information (SI) for RSC Mechanochemistry.

Supplementary Information: Scaling theory for the kinetics of mechanochemical reactions with convective flow

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S1 Mass conservation

We here summarize the consistency condition of the jump of the volume fraction of reactants at the interface between the product-rich phase and the reactant-rich phase.[1] The volume fraction $\psi_{\rm B}$ of reactant B follows the diffusion equation

$$\frac{\partial}{\partial t}\psi_{\rm B} = D_{\rm B}\frac{\partial^2}{\partial z^2}\left(\frac{\Pi(\psi_{\rm B})v_{\rm B}}{k_{\rm B}T}\right), \tag{S1}$$

where z is the position in the system and t is the time. $D_{\rm B}$ is the diffusion constant. $\Pi(\psi_{\rm B})$ is the osmotic pressure. $v_{\rm B}$ is the volume per molecule. $k_{\rm B}$ is the Boltzmann constant and T is the absolute temperature. Integrating both sides of Eq. S1 with respect to z around $z = h(t)$, where the volume fraction $\psi_{\rm B}$ jumps between $\psi_{\rm B1}$ and $\psi_{\rm B2}$, leads to

$$\int_{h(t)-\Delta z}^{h(t)+\Delta z} dz\,\frac{\partial}{\partial t}\psi_{\rm B} \quad = \quad D_{\rm B}\frac{\partial^2}{\partial z^2}\left(\frac{\Pi(\psi_{\rm B})v_{\rm B}}{k_{\rm B}T}\right). \tag{S2}$$

The right side of Eq. S2 is evaluated as

$$\begin{aligned} D_{\rm B}\frac{\partial^2}{\partial z^2}\left(\frac{\Pi(\psi_{\rm B})v_{\rm B}}{k_{\rm B}T}\right) &= D_{\rm B}\,\frac{\partial}{\partial z}\left(\frac{\Pi(\psi_{\rm B})v_{\rm B}}{k_{\rm B}T}\right)\bigg|_{h(t)+\Delta z} - D_{\rm B}\,\frac{\partial}{\partial z}\left(\frac{\Pi(\psi_{\rm B})v_{\rm B}}{k_{\rm B}T}\right)\bigg|_{h(t)-\Delta z} \\ &= -J_{\rm B}(z = h(t) + \Delta z) + J_{\rm B}(z = h(t) - \Delta z). \end{aligned} \tag{S3}$$

The last form of Eq. S5 is derived by using the fact that the flux has the form

$$J_{\rm B}(z) = -D_{\rm B}\frac{\partial}{\partial z}\left(\frac{\Pi(\psi_{\rm B})v_{\rm B}}{k_{\rm B}T}\right). \tag{S4}$$

The left side of Eq. S2 is evaluated as

$$\begin{aligned} \int_{h(t)-\Delta z}^{h(t)+\Delta z} dz\,\frac{\partial}{\partial t}\psi_{\rm B} &= \frac{d}{dt}\left(\int_{h(t)-\Delta z}^{h(t)+\Delta z} dz\psi_{\rm B}\right) - \frac{dh(t)}{dt}(\psi_{\rm B}(z = h(t) + \Delta z) - \psi_{\rm B}(z = h(t) - \Delta z)) \\ &= -\frac{dh(t)}{dt}(\psi_{\rm B}(z = h(t) + \Delta z) - \psi_{\rm B}(z = h(t) - \Delta z)). \end{aligned} \tag{S5}$$

The last form of eq. (S5) is derived by using the fact that

$$\int_{h(t)-\Delta z}^{h(t)+\Delta z} dz \psi_{\mathrm{B}} = \psi_{\mathrm{B1}} \Delta z + \psi_{\mathrm{B2}} \Delta z \tag{S6}$$

for $\Delta z \to 0$ and this integral thus does not depend on time. Eqs. S3 and S5 lead to the form

$$(\psi_{\mathrm{B}}(z = h(t) + \Delta z) - \psi_{\mathrm{B}}(z = h(t) - \Delta z)) \frac{dh(t)}{dt} = J_{\mathrm{B}}(z = h(t) + \Delta z) - J_{\mathrm{B}}(z = h(t) - \Delta z). \tag{S7}$$

Taking the limit $\Delta z \to 0$ to both sides of Eq. S7 leads to the form

$$(\psi_{\mathrm{B2}} - \psi_{\mathrm{B1}}) \frac{dh(t)}{dt} = J_{\mathrm{B2}} - J_{\mathrm{B1}}, \tag{S8}$$

with $J_{\mathrm{B1}} = \lim_{\Delta z \to 0} J_{\mathrm{B}}(z = h(t) - \Delta z)$ and $J_{\mathrm{B2}} = \lim_{\Delta z \to 0} J_{\mathrm{B}}(z = h(t) + \Delta z)$. Eq. S8 indeed represents the mass conservation at $z = h(t)$. The jump of the volume fraction ψ_{B} at $z = h(t)$ is consistent with Eq. S1 as long as the time evolution of the interface is given by Eq. S8 and the condition $\Pi(\psi_{\mathrm{B1}}) = \Pi(\psi_{\mathrm{B2}})$ is satisfied.

S2 Lubrication approximation

We here summarize the simplification of Stokes equation by using the lubrication approximation.[2,3] The Stokes equation represents the balance of the forces arising from the gradient of hydrostatic pressure p and the forces due to the mechanical stress σ,

$$-\nabla p(\mathbf{r}) + \nabla \cdot \sigma(\mathbf{r}) = 0. \tag{S9}$$

The gradient ∇ is represented as

$$\nabla = \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\phi \frac{1}{r} \frac{\partial}{\partial \phi} + \mathbf{e}_z \frac{\partial}{\partial z} \tag{S10}$$

in the cylindrical coordinate system, where $\mathbf{e}_r$ is the unit vector to the radial direction, $\mathbf{e}_\phi$ is the unit vector the azimuthal direction, and $\mathbf{e}_z$ is the unit vector to the z-direction, see Fig. 4 in the main article.

The mechanical stress is represented by the components in the cylindrical coordinate system,

$$\begin{aligned}\sigma &= \sigma_{rr}\mathbf{e}_r\mathbf{e}_r + \sigma_{r\phi}\mathbf{e}_r\mathbf{e}_\phi + \sigma_{rz}\mathbf{e}_r\mathbf{e}_z \\ &\quad +\sigma_{\phi r}\mathbf{e}_\phi\mathbf{e}_r + \sigma_{\phi\phi}\mathbf{e}_\phi\mathbf{e}_\phi + \sigma_{\phi z}\mathbf{e}_z\mathbf{e}_\phi \\ &\quad +\sigma_{zr}\mathbf{e}_z\mathbf{e}_r + \sigma_{z\phi}\mathbf{e}_z\mathbf{e}_\phi + \sigma_{zz}\mathbf{e}_z\mathbf{e}_z \end{aligned} \tag{S11}$$

The force $\mathbf{f}$ applied by mechanical stress σ

$$\mathbf{f} = \nabla \cdot \sigma. \tag{S12}$$

have the form

$$\mathbf{f} = f_r\mathbf{e}_r + f_\phi\mathbf{e}_\phi + f_z\mathbf{e}_z \tag{S13}$$

with

$$f_r = \frac{1}{r}\frac{\partial}{\partial r}(r\sigma_{rr}) - \frac{\sigma_{\phi\phi}}{r} + \frac{\partial\sigma_{rz}}{\partial z} + \frac{1}{r}\frac{\partial\sigma_{r\phi}}{\partial\phi} \tag{S14}$$

$$f_\phi = \frac{1}{r}\frac{\partial}{\partial r}(r\sigma_{\phi r}) + \frac{1}{r}\frac{\partial\sigma_{\phi\phi}}{\partial\phi} + \frac{\sigma_{r\phi}}{r} + \frac{\partial\sigma_{\phi z}}{\partial z} \tag{S15}$$

$$f_z = \frac{1}{r}\frac{\partial}{\partial r}(r\sigma_{zr}) + \frac{1}{r}\frac{\partial\sigma_{z\phi}}{\partial\phi} + \frac{\partial\sigma_{zz}}{\partial z}. \tag{S16}$$

Because of the cylindrical symmetry, $\frac{\partial}{\partial\phi} = 0$ and $\sigma_{r\phi} = \sigma_{\phi r} = \sigma_{z\phi} = \sigma_{\phi z} = 0$, Eqs. S14 - S16 are reduced to

$$f_r = \frac{1}{r}\frac{\partial}{\partial r}(r\sigma_{rr}) - \frac{\sigma_{\phi\phi}}{r} + \frac{\partial \sigma_{rz}}{\partial z} \tag{S17}$$

$$f_\phi = 0 \tag{S18}$$

$$f_z = \frac{1}{r}\frac{\partial}{\partial r}(r\sigma_{zr}) + \frac{\partial \sigma_{zz}}{\partial z}. \tag{S19}$$

Now we treat the dynamics of a fluid between cylindrical surfaces of radius r_0, see Fig. 4 in the main article. The cylindrical surfaces are rigid bodies and their radius is fixed, while the thickness $h(t)$ of the fluid depends on time. The first and second terms of Eq. S17 are in the order of σ_{rr}/r_0 and $\sigma_{\phi\phi}/r_0$, while the third term of Eq. S17 is in the order of $\sigma_{rz}/h(t)$ by using the estimate $\frac{\partial}{\partial r} \approx \frac{1}{r_0}$ and $\frac{\partial}{\partial z} \approx \frac{1}{h(t)}$. In the limit of $h(t) \ll r_0$, the third term of Eq. S17 dominates the first and second terms of this equation. Similarly, the first term of Eq. S19 is in the order of σ_{zr}/r_0, while the second term of Eq. S19 is in the order of $\sigma_{zz}/h(t)$. In the limit of $h(t) \ll r_0$, the second term of Eq. S19 dominates the first term of this equation. This order of magnitude argument leads to the approximate forms of Eqs. S17 - S19,

$$f_r = \frac{\partial \sigma_{rz}}{\partial z} \tag{S20}$$

$$f_\phi = 0 \tag{S21}$$

$$f_z = \frac{\partial \sigma_{zz}}{\partial z}.. \tag{S22}$$

Eq. S9 is decomposed to components

$$-\frac{\partial}{\partial r}p(r) + \frac{\partial \sigma_{rz}}{\partial z} = 0 \tag{S23}$$

$$-\frac{\partial}{\partial z}p(r) + \frac{\partial \sigma_{zz}}{\partial z} = 0. \tag{S24}$$

Eq. S23 is equal to Eq. 8 in the main article. Integrating Eq. S24 with respect to z leads to

$$-p(r) + \sigma_{zz}(r) = -\sigma_\perp(r) \tag{S25}$$

Eq. S25 represents the fact that the applied normal stress $\sigma_{zz}(r)$ is balanced with hydrostatic pressure $p(r)$.

In the above argument, one might wonder the dependence of the stress components, σ_{rr}, $\sigma_{\phi\phi}$, σ_{zz}, and σ_{rz}, on the radius r_0 and the thickness $h(t)$. We here estimate the order of these stress components for viscous fluids. The viscous stress has the form

$$\sigma = 2\eta\dot{\epsilon}, \tag{S26}$$

where $\dot{\epsilon}$ is the strain rate tensor. The strain rate tensor has the form

$$\dot{\epsilon} = \frac{1}{2}((\nabla \mathbf{v}) + {}^{\mathrm{T}}(\nabla \mathbf{v})), \tag{S27}$$

where $\mathbf{v} = v_r \mathbf{e}_r + v_\phi \mathbf{e}_\phi + v_z \mathbf{e}_z$ is the velocity field in the fluid and $^{\mathrm{T}}$ is the transpose. This tensor is represented with the components of the cylindrical coordinate system

$$\begin{aligned} \dot{\epsilon} = {} & \dot{\epsilon}_{rr}\mathbf{e}_r\mathbf{e}_r + \dot{\epsilon}_{r\phi}\mathbf{e}_r\mathbf{e}_\phi + \dot{\epsilon}_{rz}\mathbf{e}_r\mathbf{e}_z \\ & + \dot{\epsilon}_{\phi r}\mathbf{e}_\phi\mathbf{e}_r + \dot{\epsilon}_{\phi\phi}\mathbf{e}_\phi\mathbf{e}_\phi + \dot{\epsilon}_{\phi z}\mathbf{e}_z\mathbf{e}_\phi \\ & + \dot{\epsilon}_{zr}\mathbf{e}_z\mathbf{e}_r + \dot{\epsilon}_{z\phi}\mathbf{e}_z\mathbf{e}_\phi + \dot{\epsilon}_{zz}\mathbf{e}_z\mathbf{e}_z \end{aligned} \tag{S28}$$

with

$$\dot{\epsilon}_{rr} = \frac{\partial v_r}{\partial r} \tag{S29}$$

$$\dot{\epsilon}_{\phi\phi} = \frac{1}{r}\frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r} \tag{S30}$$

$$\dot{\epsilon}_{zz} = \frac{\partial v_z}{\partial z} \tag{S31}$$

$$\dot{\epsilon}_{r\phi} = \dot{\epsilon}_{\phi r} = \frac{1}{2}\left(\frac{\partial v_\phi}{\partial r} + \frac{1}{r}\frac{\partial v_r}{\partial \phi} - \frac{v_\phi}{r}\right) \tag{S32}$$

$$\dot{\epsilon}_{\phi z} = \dot{\epsilon}_{z\phi} = \frac{1}{2}\left(\frac{1}{r}\frac{\partial v_z}{\partial \phi} + \frac{\partial v_\phi}{\partial z}\right) \tag{S33}$$

$$\dot{\epsilon}_{zr} = \dot{\epsilon}_{rz} = \frac{1}{2}\left(\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial z}\right). \tag{S34}$$

Because of the cylindrical symmetry of the system, $\frac{\partial}{\partial \phi} = 0$ and $v_\phi = 0$, the components of the stress tensor has the form

$$\sigma_{rr} = 2\eta\frac{\partial v_r}{\partial r} \tag{S35}$$

$$\sigma_{\phi\phi} = 2\eta\frac{v_r}{r} \tag{S36}$$

$$\sigma_{zz} = 2\eta\frac{\partial v_z}{\partial z} \tag{S37}$$

$$\sigma_{rz} = \sigma_{zr} = \eta\left(\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r}\right) \tag{S38}$$

and $\sigma_{r\phi} = \sigma_{\phi r} = \sigma_{\phi z} = \sigma_{z\phi} = 0$.

Eqs. S35 - S38 suggest that σ_{rr} and $\sigma_{\phi\phi}$ are in the order of $\eta v_r/r_0$, while σ_{rz} is in the order of $\eta v_r/h(t)$. This ensures that the third term of Eq. S17 dominates the first and second terms of Eq. S17 in the limit of $h(t) \ll r_0$. We note that the first term Eq. S38 dominates the second term of Eq. S38 in this limit. These estimates and Eq. S23 lead to the fact that the hydrostatic pressure p is in the order of $\eta r_0 v_r/h(t)$. σ_{rz} is in the order of $\eta v_r/h(t)$, see Eq. S38 and the discussion above, while σ_{zz} is in the order of $\eta v_z/h(t)$, see Eq. S37. The first term of Eq. S24 is estimated as $\eta r_0 v_r/h^2(t)$ by using the above estimate of the hydrostatic pressure and thus dominates the contribution of σ_{rz} to the second term of Eq. S24, where this contribution is estimated as $\eta v_r/(r_0 h(t))$, see the first term of Eq. S19 and the above estimate of σ_{rz}. The first term of Eq. S19 is thus negligible and this treatment leads to Eq. S24.

In Eq. S24, we have tentatively left the contribution of σ_{zz} to the second term of Eq. S24 because σ_{zz} is in the order of $\eta v_z/h(t)$ and the order estimate v_z relative to v_r is not specified. Eq. S24 leads to Eq. S25. We solve Eq. S23 with the incompressibility condition

$$\frac{1}{r}\frac{\partial}{\partial r}(r v_r) + \frac{\partial v_z}{\partial z} = 0. \tag{S39}$$

Eq. S39 implies that v_z is in the order of $h(t)v_r/r_0$. σ_{zz} is thus estimated as $\eta v_r/r_0$ and is much smaller than the hydrostatic pressure, which is in the order of $\eta r_0 v_r/h(t)$, see the above discussion. Therefore, Eq. S25 is further reduced to

$$-p(r) = -\sigma_{\perp}(r). \tag{S40}$$

We note that Eq. S40 is valid only for incompressible fluids; if not, one should use Eq. S25s.

References

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