

# Emergent thermophoretic behavior in chemical reaction systems

Shiling Liang<sup>1</sup>, Daniel Maria Busiello<sup>1,2</sup> and Paolo De Los Rios<sup>1,3</sup>

1. Institute of Physics, School of Basic Sciences, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

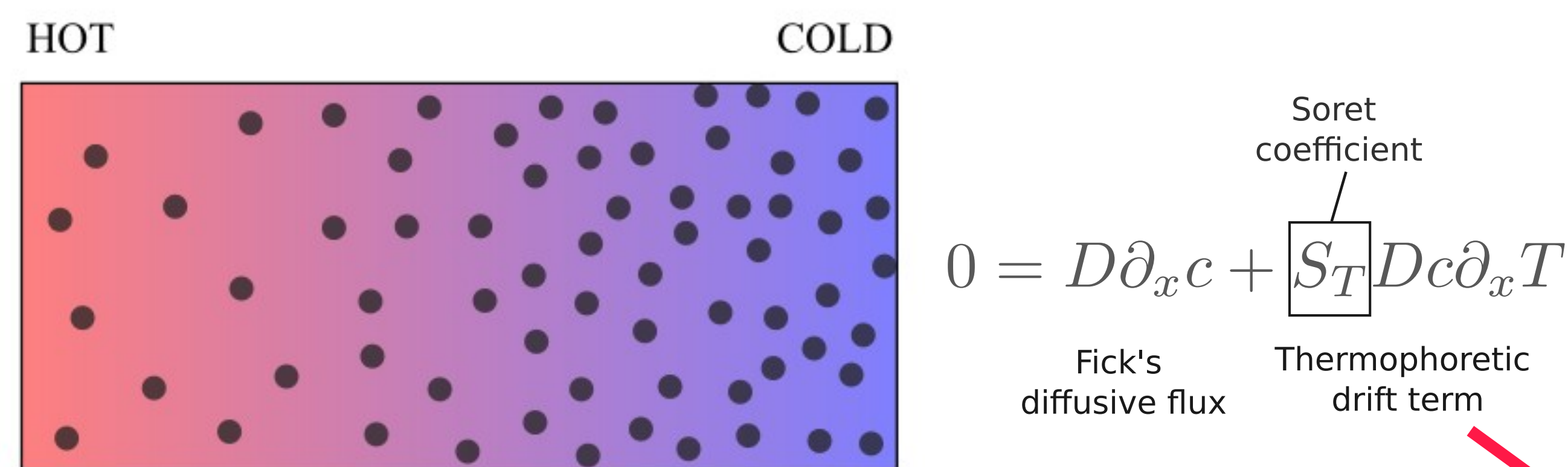
2. Max Planck Institute for the Physics of Complex Systems, 01187 Dresden, Germany

3. Institute of Bioengineering, School of Life Sciences, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland



## 1. Introduction

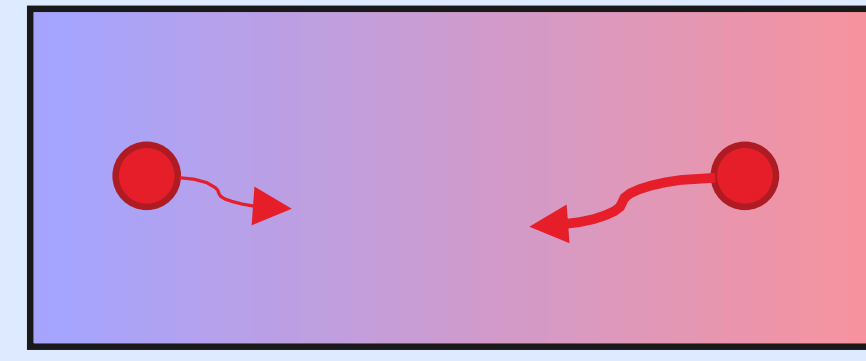
Exposing a solution to a temperature gradient can lead to the accumulation of particles on either the cold or warm side. This phenomenon is known as **thermophoresis**, and its microscopic origin is still debated. Here, we show that **thermophoresis can be observed in any system having internal states with different transport properties**, and temperature-modulated rates of transitions between the states.



## 2. Basics

a. Einstein relation of diffusion

$$D \propto T R^{-1}$$



Particles tend to **stay in the slow-diffusion region for a longer time**



$$J_D = \partial_x (Dc) = c \partial_x D + D \partial_x c$$

Drift term from inhomogeneous diffusion      Fick's diffusive flux

b. Reaction-diffusion equation (at stationary)

$$0 = \partial_x (D_i \partial_x c_i + c_i \partial_x D_i) + \sum_{j \neq i} (k_{ij} c_j - k_{ji} c_i)$$

Transition between different chemical states

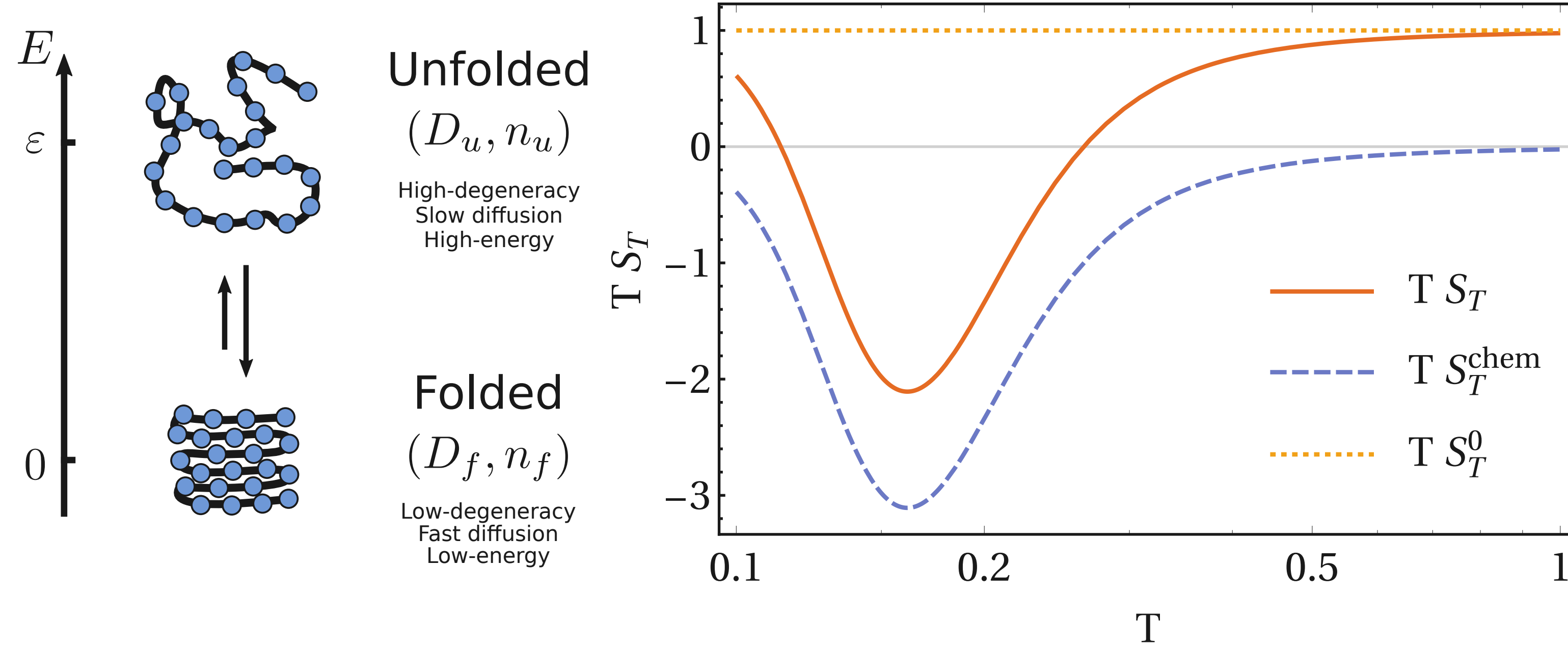
c. Thermophoresis of total concentration  $P_{\text{tot}} = \sum_i P_i$

$$0 = \partial_x (\langle D \rangle P_{\text{tot}}) \Rightarrow S_T = \frac{\partial_T \langle D \rangle}{\langle D \rangle}$$

All reaction terms cancel out during summation. We obtain an effective diffusion coefficient averaged over all states

$$S_T = \frac{\partial_T D}{D}$$

## 3. Thermophoresis of polymer and sign inversion



$$S_T = S_T^0 + S_T^{\text{ch}}$$

The standard contribution  $S_T^0$  comes from the temperature dependence of Einstein relation:  $D \propto T R^{-1}$

$$R^{-1} = \langle R^{-1} \rangle_T$$

The chemical term  $S_T^{\text{ch}}$  comes from the switching between different states with different diffusivities:  $D \propto T R^{-1}$

Averaging between two states, depends on local temperature

## 4. The Covariance form of Soret coefficient

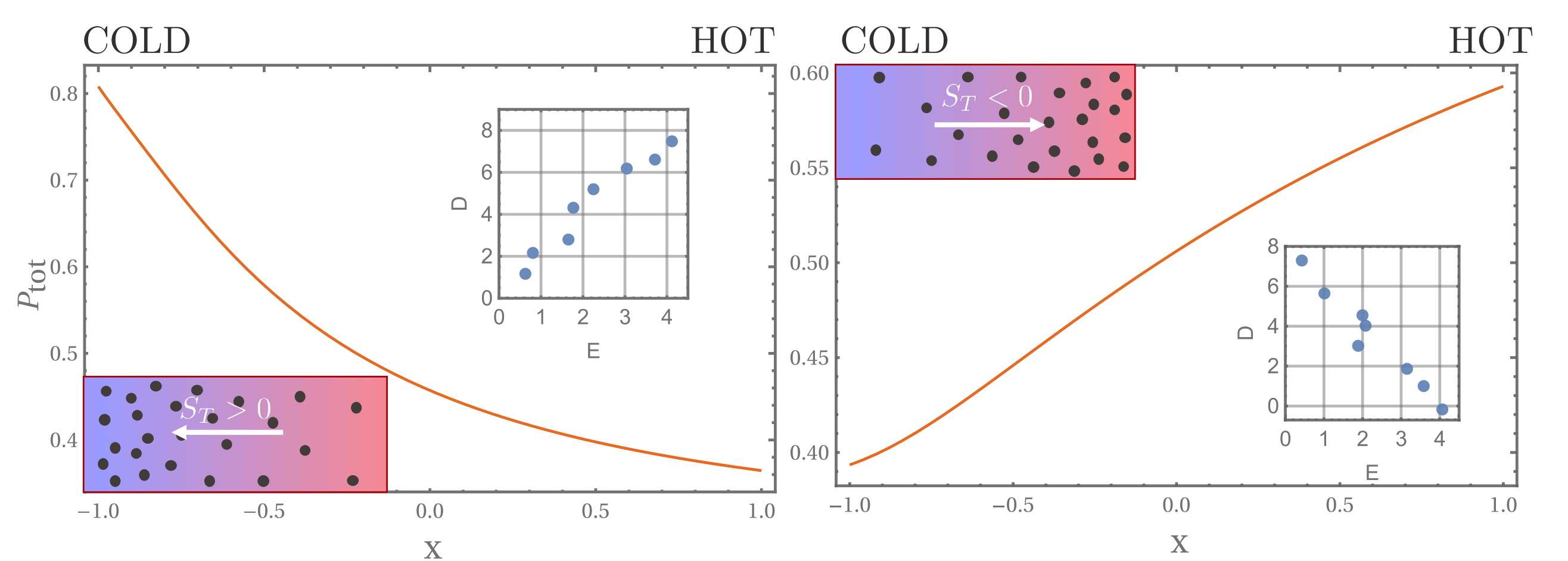
When chemical reaction kinetics is much faster than diffusion in space, we can take the local-equilibrium limit and find the effective diffusion coefficient as the local average:

$$\langle D \rangle_{\text{eq}} = \frac{\sum_i D_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)}$$

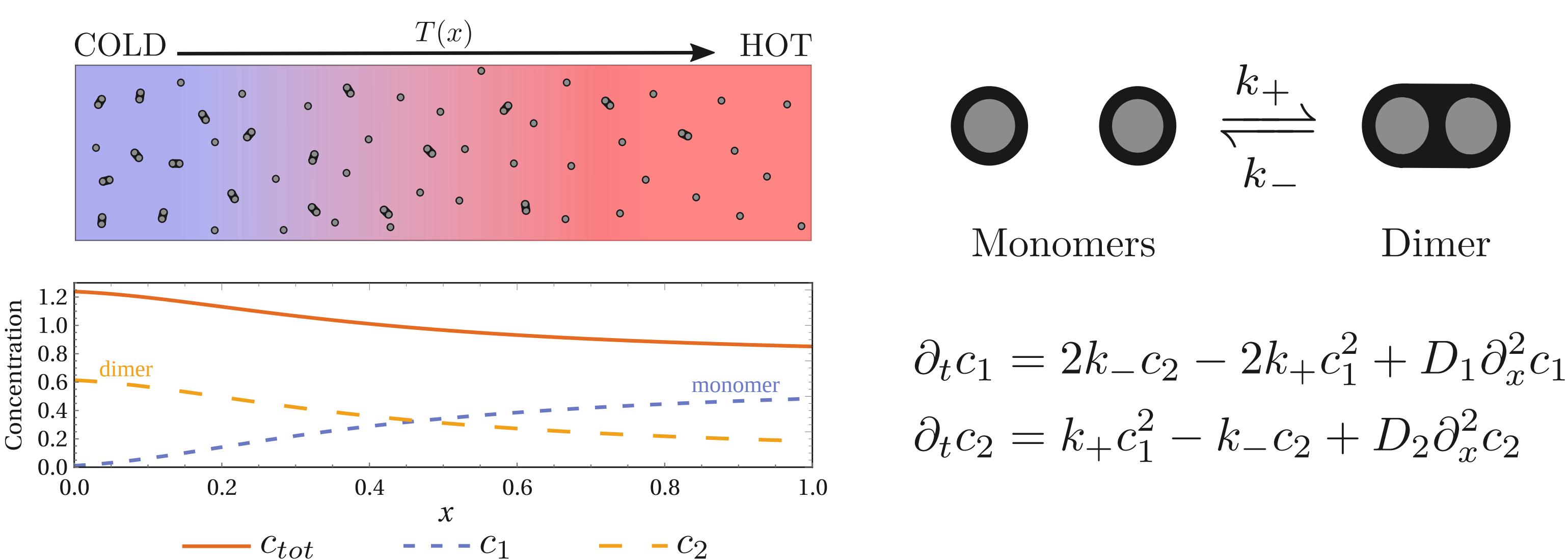
which leads to the covariance form of Soret coefficient

$$S_T^{\text{ch}} = \frac{\partial_T \langle D \rangle_{\text{eq}}}{\langle D \rangle_{\text{eq}}} = \frac{\langle ED \rangle_{\text{eq}} - \langle E \rangle \langle D \rangle_{\text{eq}}}{\langle D \rangle_{\text{eq}} k_B T^2} = \frac{\text{Cov}_{\text{eq}}(E, D)}{\langle D \rangle_{\text{eq}} k_B T^2}$$

The correlation between diffusion coefficients and energies determines the sign of the Soret coefficient from the chemical contribution:



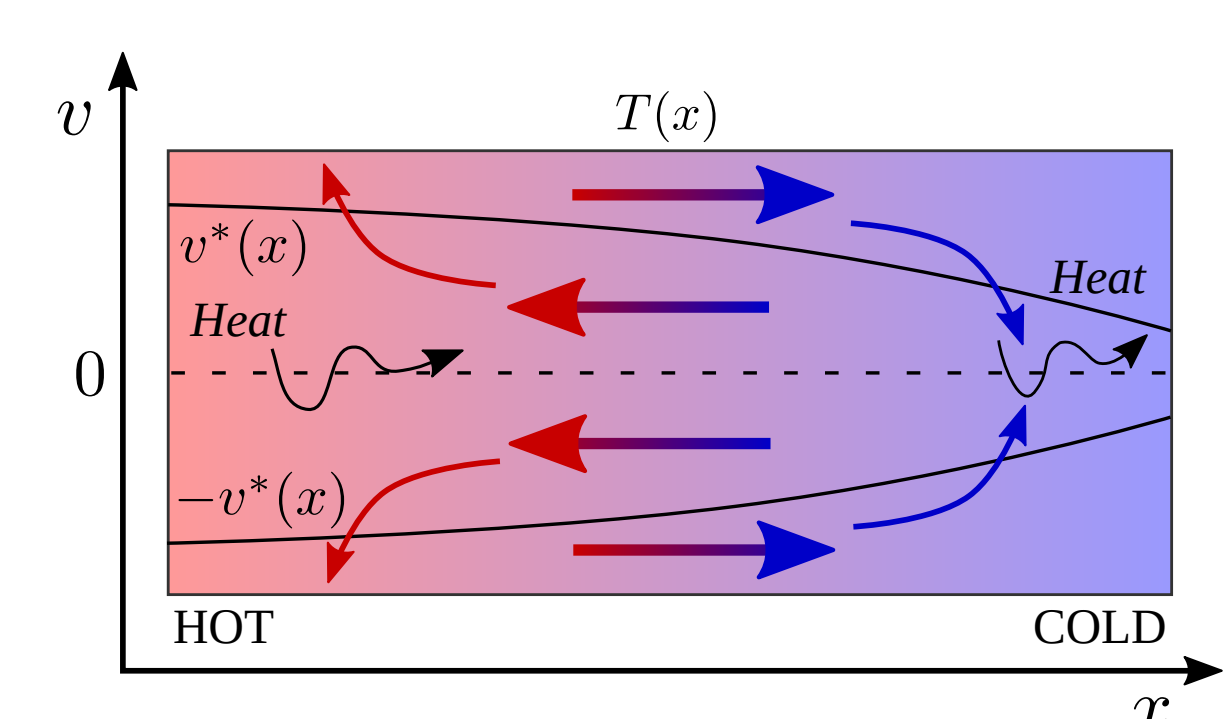
## 5. Thermophoresis of Dimerization



$$\partial_t c_1 = 2k_- c_2 - 2k_+ c_1^2 + D_1 \partial_x^2 c_1$$

$$\partial_t c_2 = k_+ c_1^2 - k_- c_2 + D_2 \partial_x^2 c_2$$

## 6. Thermophoresis in from phase space



The standard Soret coefficient  $S_T^0$  can be directly obtained from the velocity phase space:

$$S_T^0 = \frac{\partial_T (\langle v^2 \rangle_{\text{eq}})}{\langle v^2 \rangle_{\text{eq}}} = \frac{1}{T(x)}$$

## 7. Conclusion

- Thermophoresis emerges through the **interplay between transport in real space and temperature-modulated transitions in some internal space**, which can be a chemical, conformational, or velocity space

- The Soret coefficient is related to the microscopic features of the system through the **correlation between transport properties of each internal state and their energy**.

- We expect that the contributions from internal states, captured by the presented theory, might be relevant when internal (e.g., structural) modifications induce **abrupt changes in the diffusion coefficient** as a function of the temperature.

Ref: Liang et al 2022 New J. Phys.  
Doi: 10.1088/1367-2630/aca556