Strong coupling, vibrational frequency and negatve thermophoresis

Rodrigo de Miguel
Norwegian University of Science and Technology

J. Miguel Rubí
University of Barcelona (Spain)
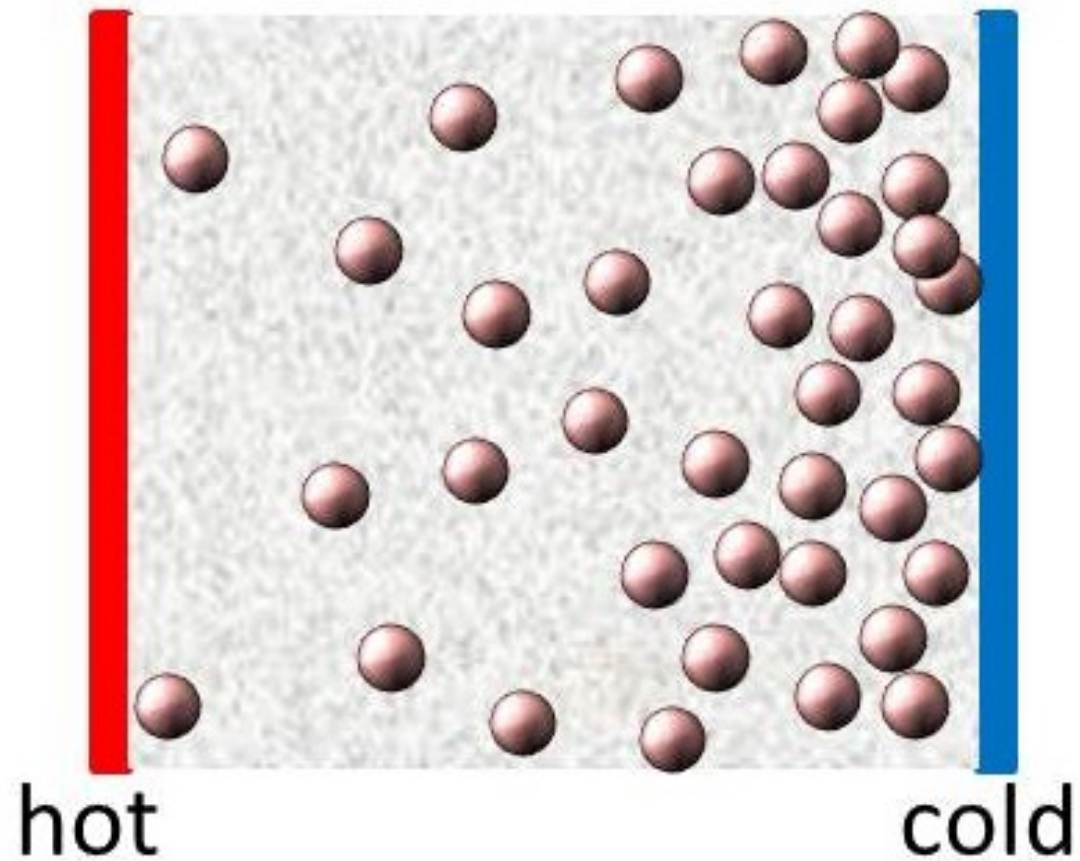
Steven Neshyba
University of Puget Sound (USA)

XXVII Sitges Conference on Statistical Mechanics
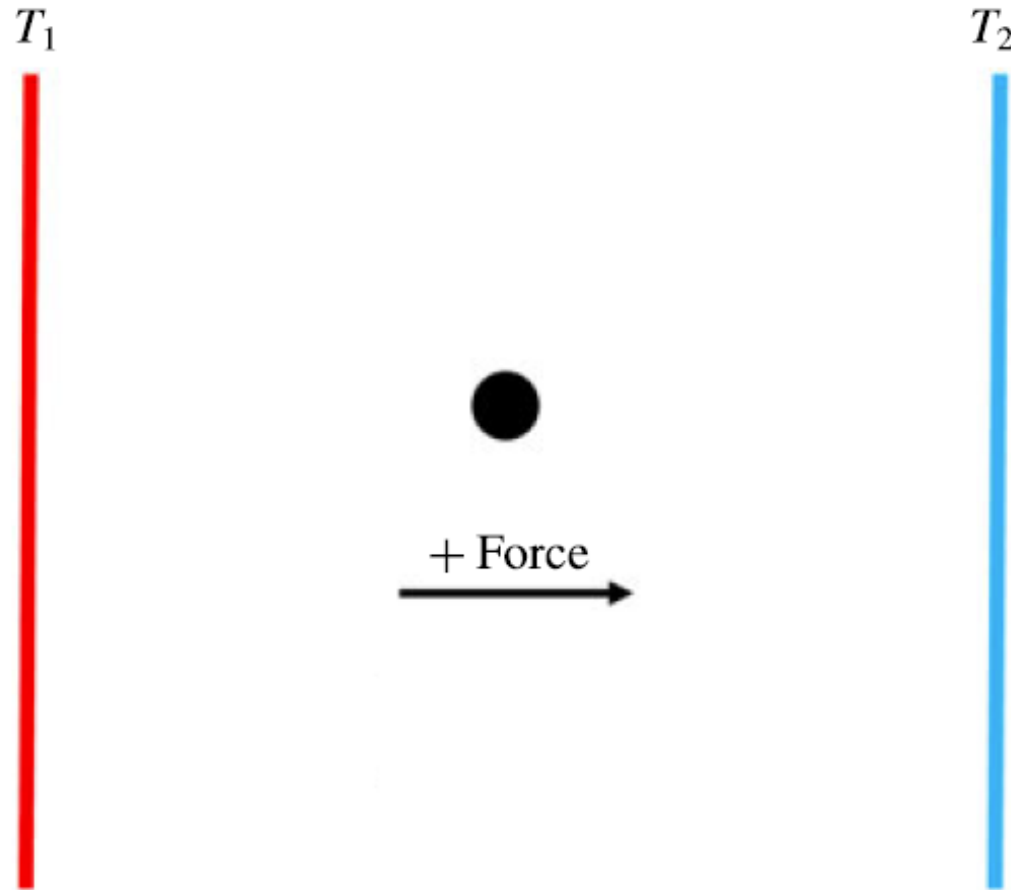**June 2023**

(rough) Outline

- Thermophoresis
    - Negative thermophoresis
- Strong coupling
- Internal vs. free energy
- Thermophoretic force
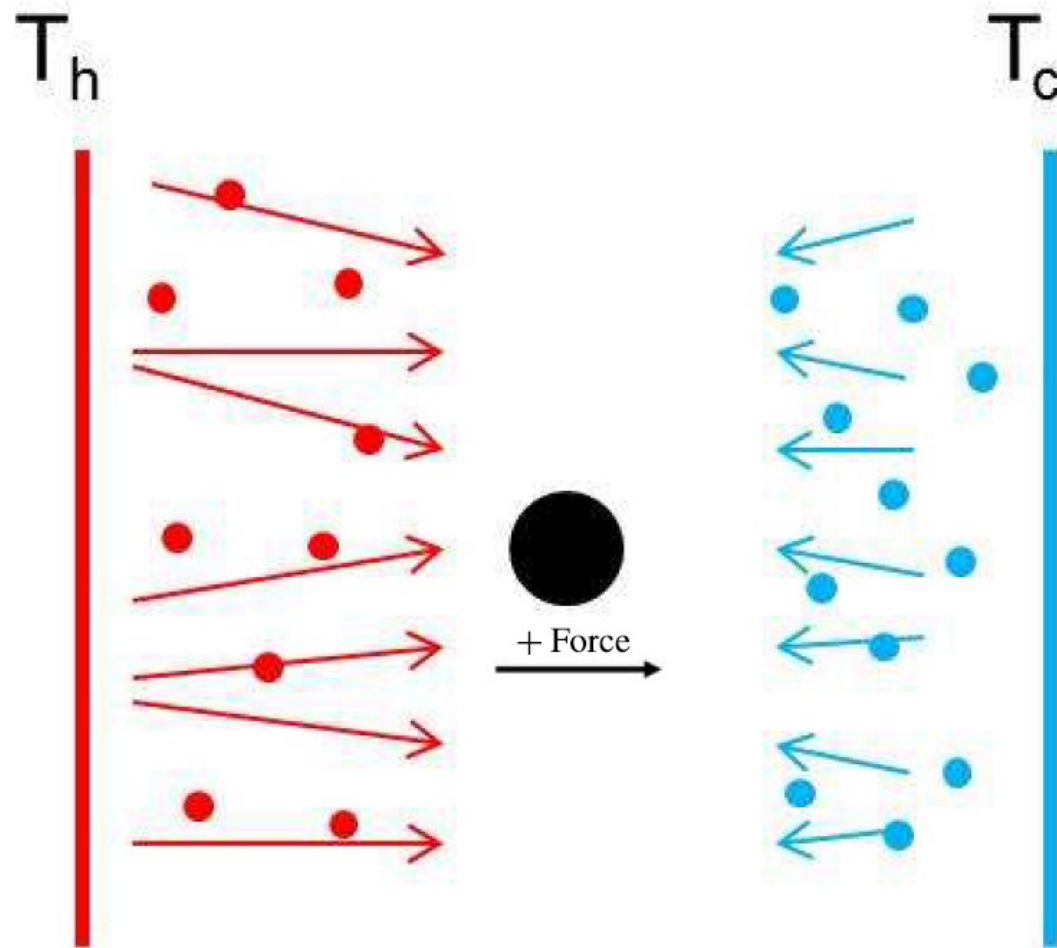- Example
- Conclusion
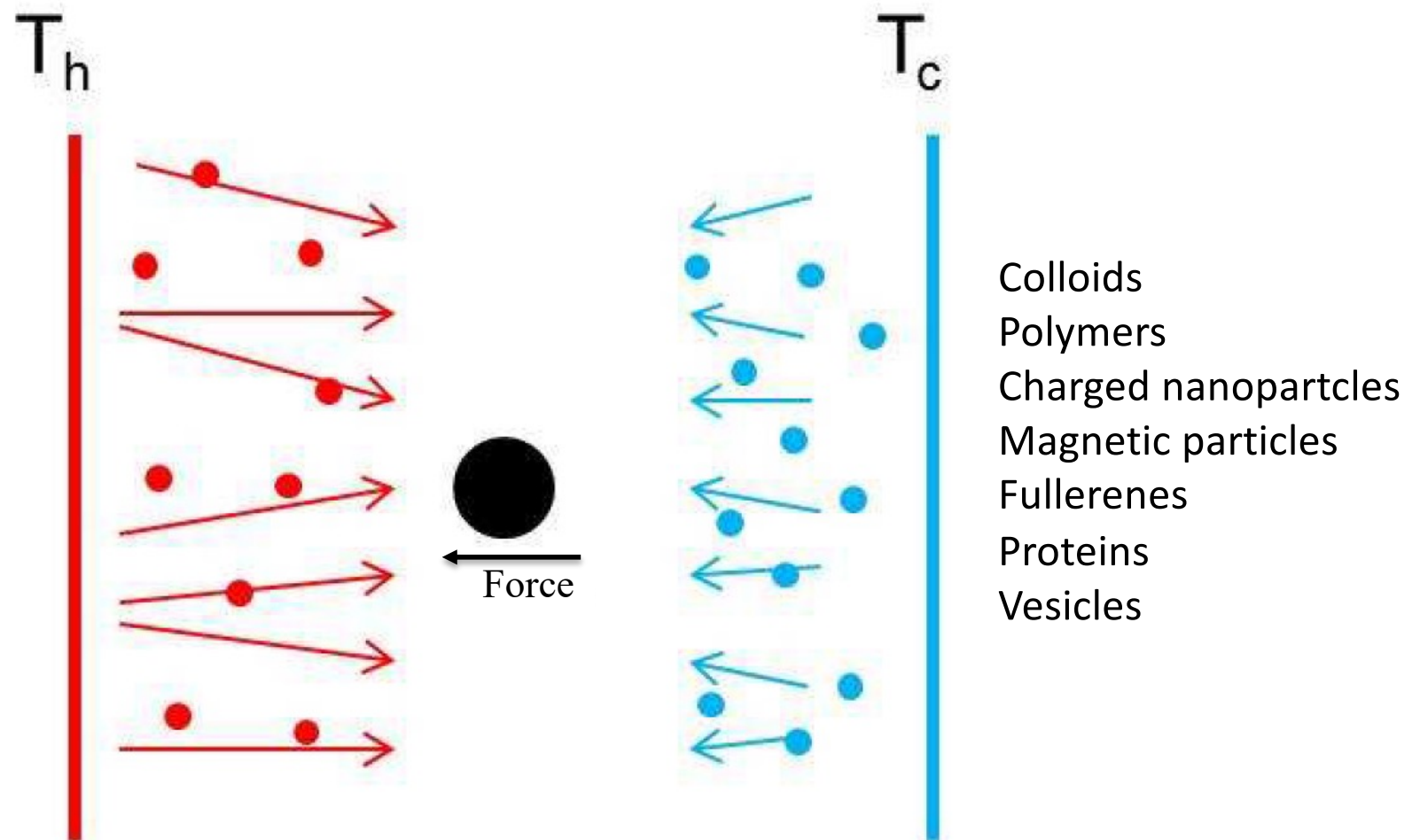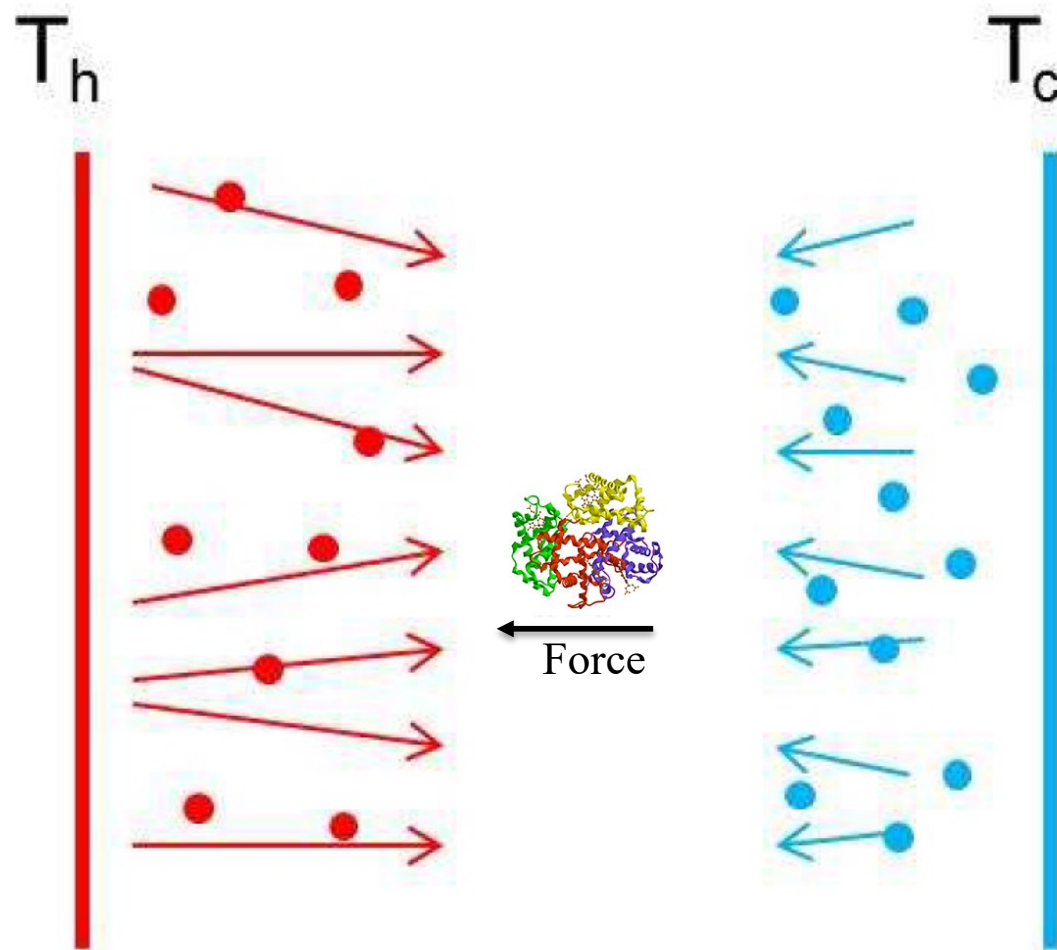- Some applications

NTNU

Thermodiffusion

hot   cold

NTNU

Thermophoresis

T_1

T_2

$+$ Force

NTNU

Thermophoresis

Negative thermophoresis

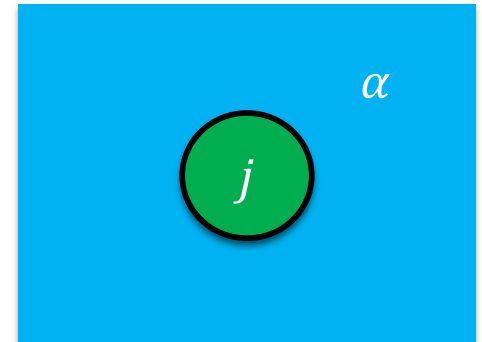NTNU

Negative thermophoresis

NTNU

Strong coupling

System's Hamiltonian in state j $\mathcal{H}_j^S$

Bath's Hamiltonian in state α $\mathcal{H}_\alpha^B$

Interaction system-bath $\mathcal{H}_{j,\alpha}^I$

Total Hamiltonian $\mathcal{H}_j^S + \mathcal{H}_\alpha^B + \mathcal{H}_{j,\alpha}^I$

Average over bath to get a temperature-dependent *Hamiltonian of mean force*, $\mathcal{E}_j$, for the system:

$$e^{-\mathcal{E}_j/k_B T} = \frac{\sum_\alpha e^{-\frac{\mathcal{H}_j^S + \mathcal{H}_{j,\alpha}^I}{k_B T}} e^{-\frac{\mathcal{H}_\alpha^B}{k_B T}}}{\sum_\alpha e^{-\frac{\mathcal{H}_\alpha^B}{k_B T}}}$$

Talkner, P.; Hanggi, P. *Phys. Rev. E* **2016**, 94, 022143.

Strong coupling

System's Hamiltonian in state j $\mathcal{H}_j^S$

Bath's Hamiltonian in state α $\mathcal{H}_\alpha^B$

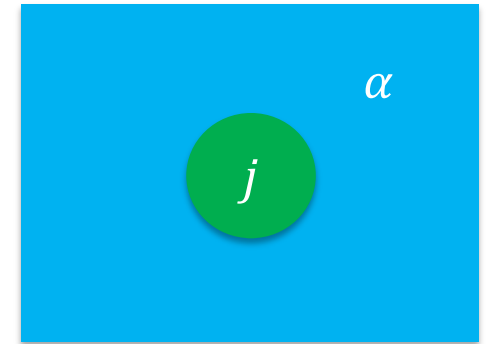Total Hamiltonian $\mathcal{H}_j^S + \mathcal{H}_\alpha^B$

Average over bath to get a temperature-dependent *Hamiltonian of mean force*, $\mathcal{E}_j$, for the system:

$$e^{-\mathcal{E}_j/k_B T} = \frac{\sum_\alpha e^{-\frac{\mathcal{H}_j^S}{k_B T}} e^{-\frac{\mathcal{H}_\alpha^B}{k_B T}}}{\sum_\alpha e^{-\frac{\mathcal{H}_\alpha^B}{k_B T}}}$$
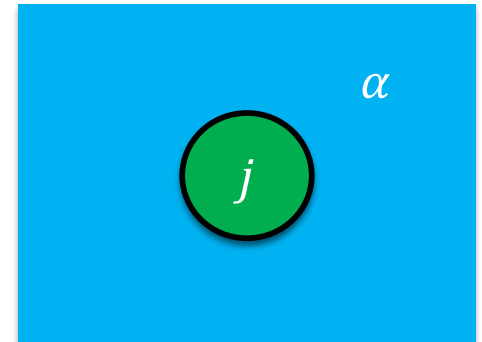
NTNU

Strong coupling

System's Hamiltonian in state j $\qquad$ $\mathcal{H}_j^S$

Bath's Hamiltonian in state α $\qquad$ $\mathcal{H}_\alpha^B$

Interaction system-bath $\qquad$ $\mathcal{H}_{j,\alpha}^I$

Total Hamiltonian $\qquad$ $\mathcal{H}_j^S + \mathcal{H}_\alpha^B + \mathcal{H}_{j,\alpha}^I$

Average over bath to get a temperature-dependent *Hamiltonian of mean force*, $\mathcal{E}_j$, for the system:

$$e^{-\mathcal{E}_j/k_BT} = \frac{\sum_\alpha e^{-\frac{\mathcal{H}_j^S + \mathcal{H}_{j,\alpha}^I}{k_BT}} e^{-\frac{\mathcal{H}_\alpha^B}{k_BT}}}{\sum_\alpha e^{-\frac{\mathcal{H}_\alpha^B}{k_BT}}}$$

NTNU

Strong coupling

Eigenenergies $\mathcal{E}_j$ are effectively dependent on the temperature T of the environment.

Partition function $\quad \mathcal{Z}(T) = \sum_j g_j\, e^{-\mathcal{E}_j(T)/k_B T}$

Energy $\quad E(T) = k_B T^2 \dfrac{\mathrm{d}}{\mathrm{d}T} \ln \mathcal{Z}(T)$

$$= \frac{1}{\mathcal{Z}(T)} \sum_j g_j\, e^{-\mathcal{E}_j(T)/k_B T} \left(\mathcal{E}_j(T) - T \frac{\mathrm{d}\mathcal{E}_j(T)}{\mathrm{d}T} \right) = \left\langle \mathcal{E}_j(T) - T \frac{\mathrm{d}\mathcal{E}_j(T)}{\mathrm{d}T} \right\rangle$$

Elcock, E. W.; Landsberg P. T. Temperature Dependent Energy Levels in Statistical Mechanics. *Proc. Phys. Soc., London, Sect B* **1957**, *70*, 161-168.

Seifert, U. First and Second Law of Thermodynamics at Strong Coupling. *Phys. Rev. Lett.* **2016**, 116, 020601.

Talkner, P.; Hanggi, P. Open system Trajectories specify fluctuating work but not heat. *Phys. Rev. E* **2016**, 94, 022143.

NTNU

Strong coupling

$$E(T) = \langle \phi_j(T) \rangle$$

where $\qquad \phi_j(T) \equiv \mathcal{E}_j(T) - T\Sigma(T)$

$$\Sigma(T) \equiv \frac{\mathrm{d}\mathcal{E}_j(T)}{\mathrm{d}T}$$

$\phi_j(T)$ is the contribution made to the internal energy by state j once it is occupied.
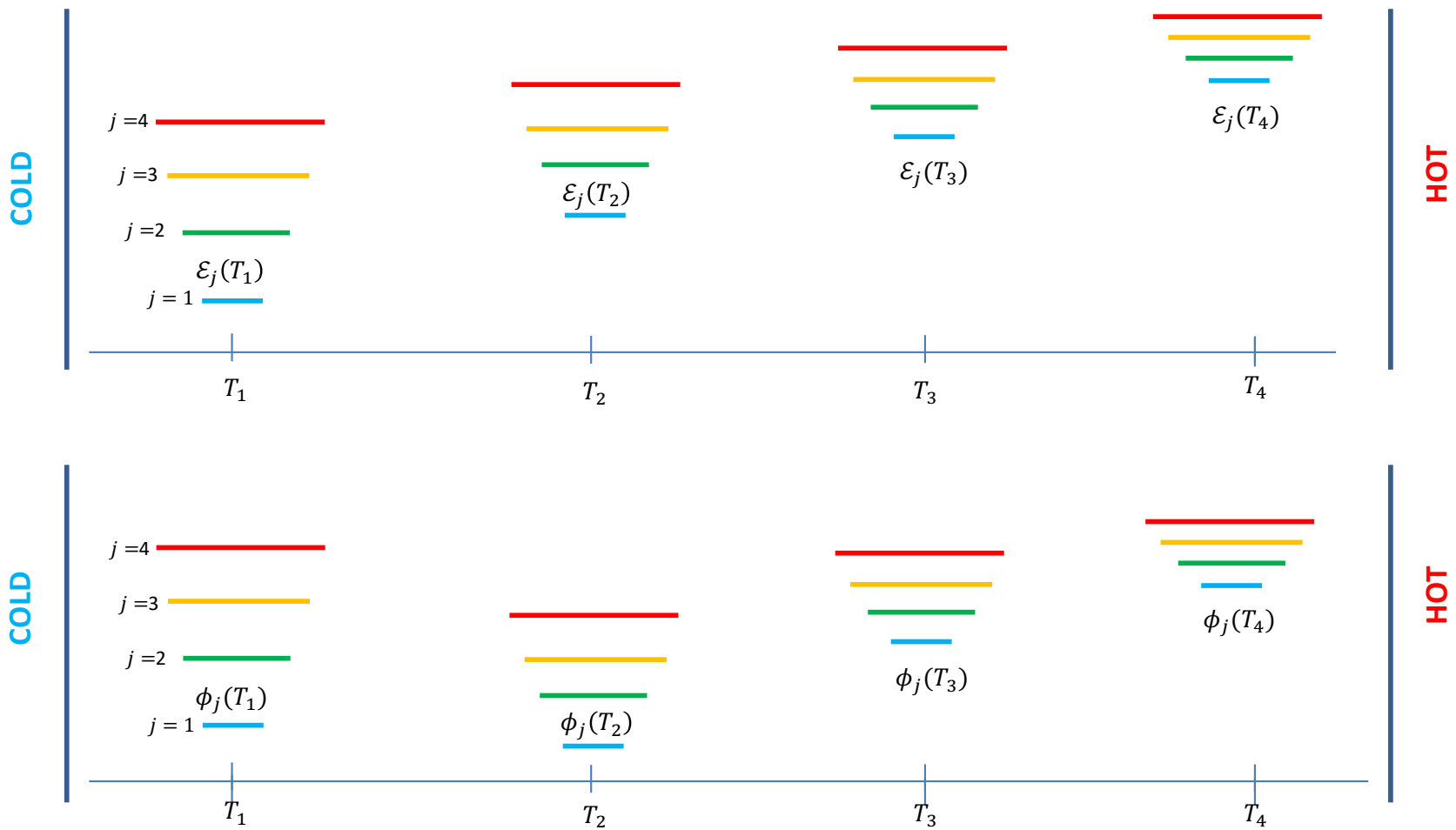
$\phi_j(T)$ decreases with T when T is low.

$\mathcal{E}_j(T)$ gives the probability that state j is occupied.

$$\mathcal{Z}(T) = \sum_j g_j \, e^{-\mathcal{E}_j(T)/k_B T}$$

$\mathcal{E}_j(T)$ is a monotonic increasing function of T.

The effective energy profile $E(T)$ is a non-monotonic function of temperature.

Whitfield, G.; Engineer, M. *Phys. Rev. B* **1975**, 12, 5472.

NTNU

NTNU

Internal energy?

The *internal* energy $\quad E(T) = \left\langle \mathcal{E}_j(T) - T \dfrac{\mathrm{d}\mathcal{E}_j(T)}{\mathrm{d}T} \right\rangle$

is a nonmonotonic function of temperature.

Negative heat capacity ?

Unstable??

Free energy

The *~~free~~ internal* energy

$$E(T) = \left\langle \mathcal{E}_j(T) - T\frac{\mathrm{d}\mathcal{E}_j(T)}{\mathrm{d}T} \right\rangle$$

is a nonmonotonic function of temperature.
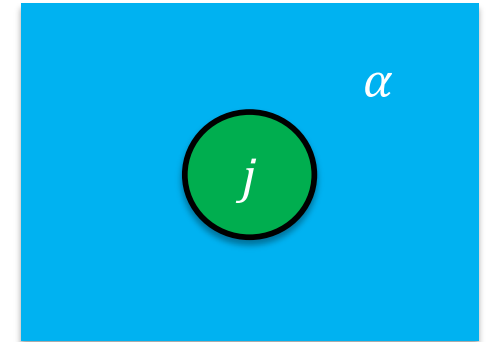
The internal energy $\langle \mathcal{E}_j(T) \rangle$ is still a monotonically increasing function of T.

Positive heat capacity. Stable.

NTNU

Thermophoretic force

Non-isothermal heat bath $T(x)$

Free energy $\quad E(x) = \left\langle \phi_j(T) \right\rangle \quad$ with $\quad \phi_j(T) \equiv \mathcal{E}_j(T) - T \dfrac{\mathrm{d}\mathcal{E}_j(T)}{\mathrm{d}T}$

Thermophoretic force $\qquad F = -\nabla E(x) = -\dfrac{\mathrm{d}\left\langle \phi_j(T) \right\rangle}{\mathrm{d}T} \nabla T$

where $\quad \left\langle \phi_j(T) \right\rangle = \dfrac{\displaystyle\sum_j \phi_j(T)\ g_j\ e^{-\mathcal{E}_j(T)/k_B T}}{\displaystyle\sum_j g_j\ e^{-\mathcal{E}_j(T)/k_B T}}$

results in $\qquad \boxed{F = \left\langle T \dfrac{\mathrm{d}^2\mathcal{E}_j}{\mathrm{d}T^2} \right\rangle \nabla T + \dfrac{\sigma_\phi^2}{k_B} \nabla \dfrac{1}{T}} \qquad$ with $\quad \sigma_\phi^2 \equiv \left\langle \phi_j^2 \right\rangle - \left\langle \phi_j \right\rangle^2$

Thermophoretic force

$$F = \left\langle T\frac{\mathrm{d}^2\mathcal{E}_j}{\mathrm{d}T^2} \right\rangle \nabla T + \frac{\sigma_\phi^2}{k_B}\nabla\frac{1}{T}$$

thermophilic   thermophobic

High temperature:

- Energy becomes a linearized function of the temperature and $\frac{\mathrm{d}^2\mathcal{E}_j}{\mathrm{d}T^2} \rightarrow 0$.

- Thermal fluctuations σ_ϕ^2 scale as $\sim c(T)\, T^2$.

- Thermophobic term dominates: *Positive thermophoresis*.

Lower temperature:

- Thermal fluctuations σ_ϕ^2 tend to vanish. Second term shrinks.

- As the populated energy levels $\mathcal{E}_j(T)$ come close to their minimum value, $\frac{\mathrm{d}^2\mathcal{E}_j}{\mathrm{d}T^2}$ becomes more and more positive.

- The first term, albeit small, may become significant.

- At sufficiently low (system specific) T, first term is largest: ***Negative thermophoresis***.

■ NTNU

Thermophoretic force

$$F = \left\langle T \frac{d^2 \mathcal{E}_j}{dT^2} \right\rangle \nabla T + \frac{\sigma_\phi^2}{k_B} \nabla \frac{1}{T}$$

thermophilic   thermophobic

NTNU
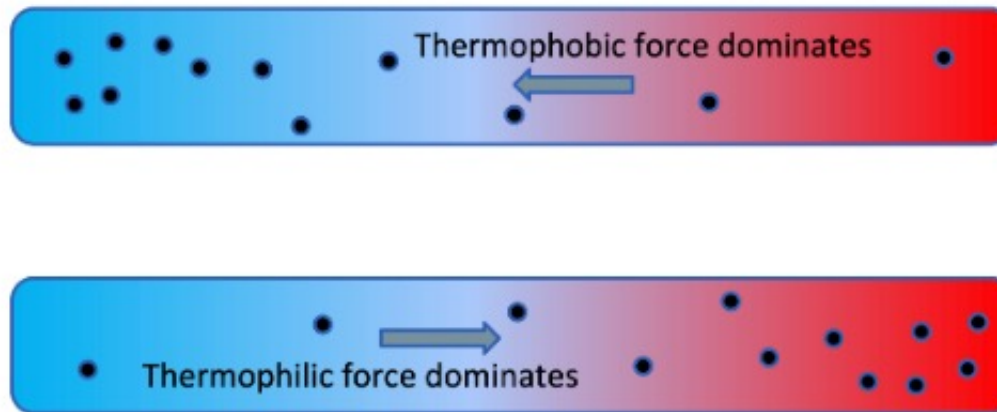
Thermophoretic force

$$F = \left\langle T\,\frac{\mathrm{d}^2\varepsilon_j}{\mathrm{d}T^2} \right\rangle \nabla T + \frac{\sigma_\phi^2}{k_B}\nabla\frac{1}{T}$$

thermophilic   thermophobic

Experiments do show thermophobic motion at high temperatures and thermophillic motion at low temperatures.

Putnam, S. A. et al. Temperature Dependence of Thermodiffusion in Aqueous Suspensions of Charged Nanoparticles. *Langmuir* **2007**, *23*, 9221.

Iacopini S.; Piazza, R. Thermophoresis in protein solutions. *Europhys. Lett.* **2003**, 63, 247.

Talbot, E. L. et al. Thermophoretic migration of vesicles depends on mean temperature and head group chemistry. *Natur. Comm.* **2017**, 8, 15351.

Rita, R. et al. Thermally induced sign change of Soret coefficient for dilute and semidilute solutions of poly(*N*-isopropylacrylamide) in ethanol. *J. Chem. Phys.* **2004**, 121, 9140.

Sugaya, R. et al. Thermal Diffusion of Dextran in Aqueous Solutions in the Absence and the Presence of Urea. *Biomacromolecules* **2006**, 7, 435.

NTNU

Reversal temperature

Polystyrene particles: 20° C
[*Langmuir* 23, 9221 (2007)]

Ionic micelles: 4°C
[*Eur. Phys. J. E* 19, 59 (2006)]

Lysozome proteins: ~20°C
[*Langmuir* 23, 9221 (2007); *Eur. Phys. J. E* 19, 59 (2006); *Europhys. Lett.* 63, 247 (2003)]
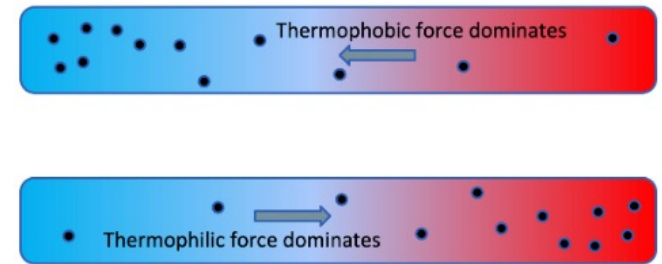
Dextran: 45°C
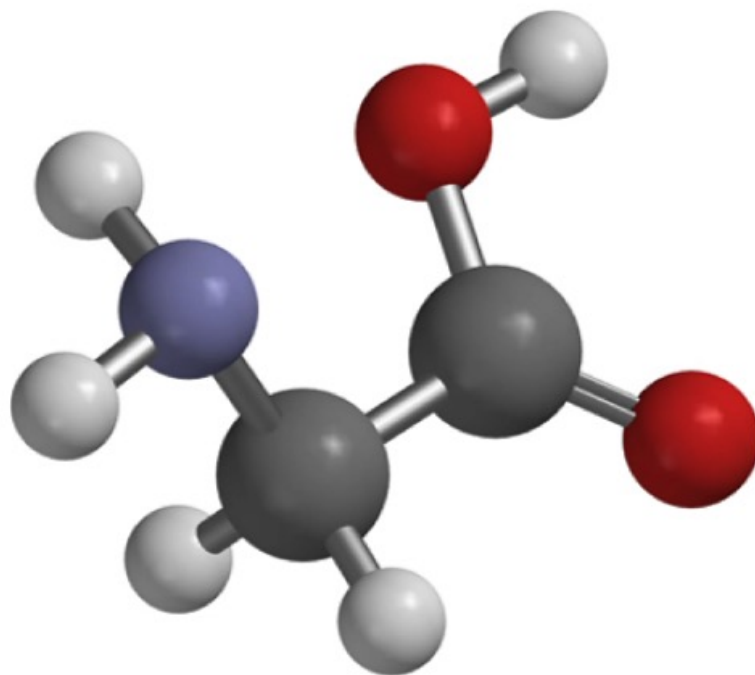[*Biomacromolecules* 7,435 (2006)]

Vesicles: 10°C - 50°C
[*Nat. Commun.* 8, 15351 (2017)]

Poly(N-isopropylacrylamide) in ethanol: 34°C
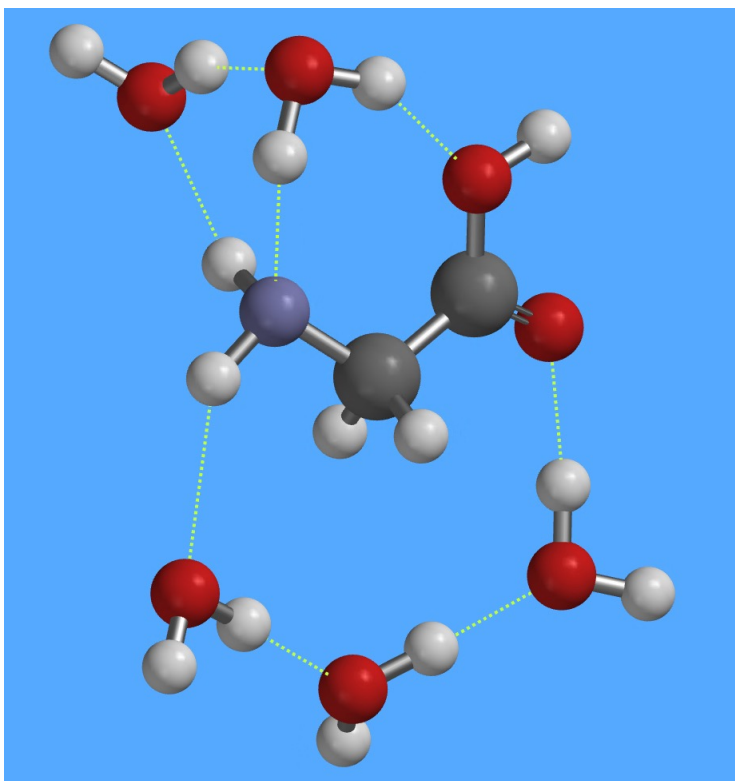[*J. Chem. Phys.* 121, 9140 (2004)]

Thermophobic force dominates

Thermophilic force dominates

NTNU
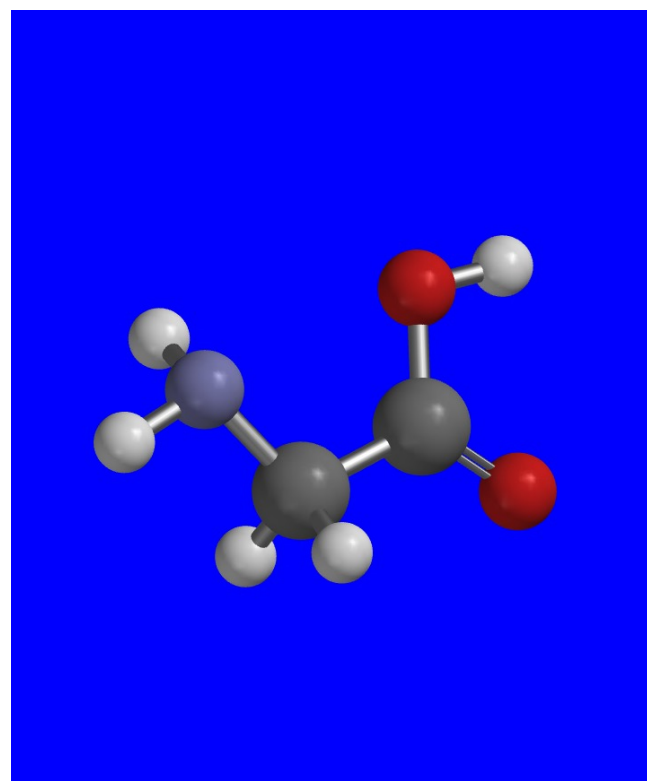
Electronic structure calculation: Glycine in water

Proteinogenic aminoacid

Electronic structure calculation: Glycine in water

Low T

Hight T

Electronic structure calculation: Glycine in water

Electronic structure calculation: Glycine
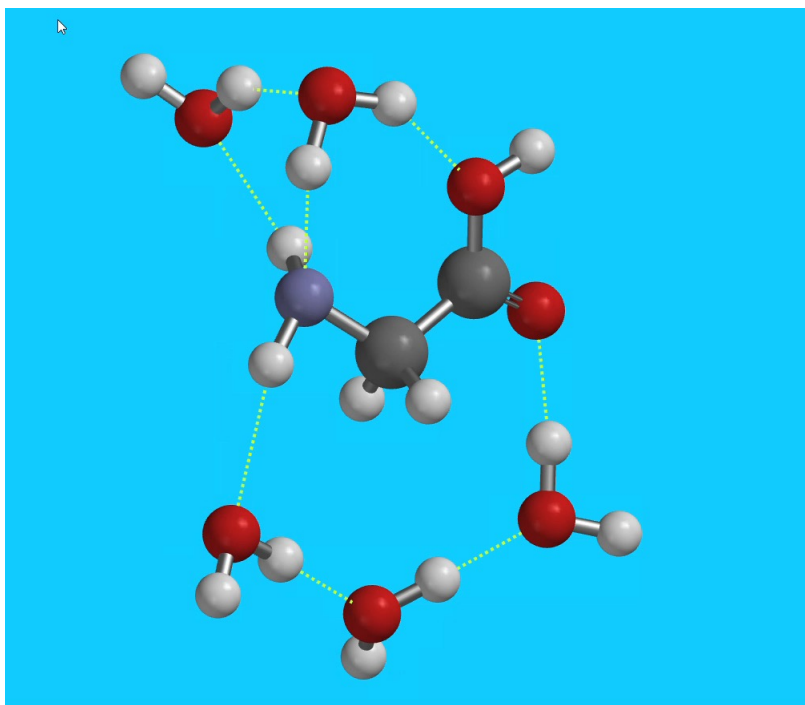
Low T: Implicit water solvent with explicit water
$$\nu = 1732\ cm^{-1}$$
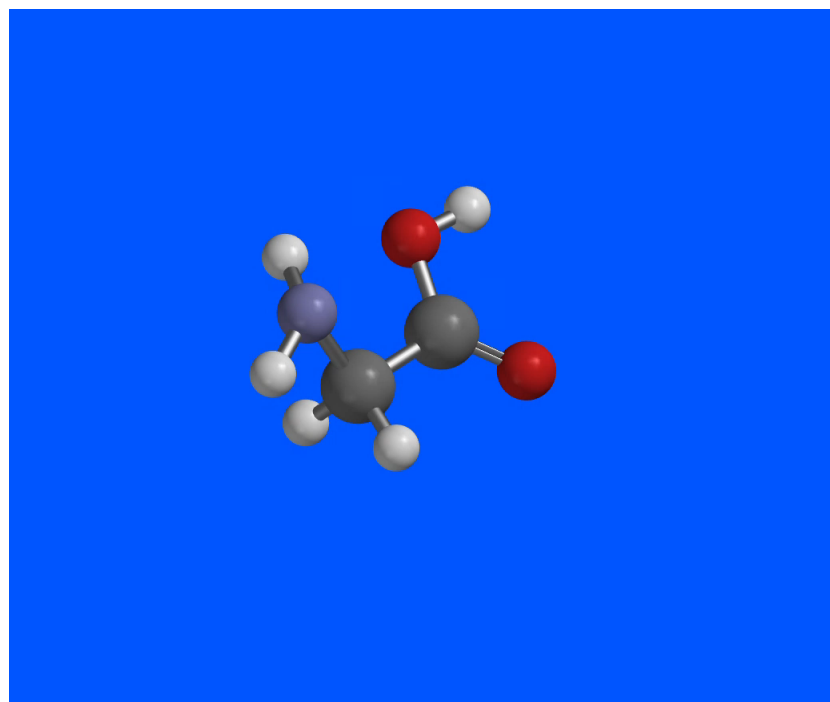
High T: Implicit water solvent
$$\nu = 1663\ cm^{-1}$$

Model:
Harmonic oscillator coupled to the heat bath

Proteins may be modelled as a set of harmonic oscillators [*Protein Sci.* 14, 633 (2005)].

Models have been proposed to treat the heat bath as a large collection of oscillators coupled to the particle in solution [*Phys. Rep.* 168, 115 (1988), *Stoch. Dyn.* 02, 533 (2002)].

Coupling between oscillators occurs when they are allowed to interact and exchange energy.
The spectrum of the system is then modified into vibrational frequencies that differ from the original oscillator modes [*Rep. Prog. Phys.* 78, 013901 (2015)].

Weak coupling: frequency modifications negligible.
Strong coupling: frequency modifications significant.

Model:
Harmonic oscillator coupled to the heat bath

Harmonic oscillator: j energy units of size $\hbar\omega$

Strongly coupled to the oscillators in the heat bath.
Energy exchange is regulated by the heat bath temperature T.

Frequency becomes temperature dependent: $\quad \mathcal{E}_j(T) = (j + 1/2)\hbar\omega(T)$

Partition function $\quad \mathcal{Z}(T) = \sum_{j=0}^{\infty} e^{-(j+1/2)\hbar\omega(T)/k_B T}$

Energy $\quad E(T) = k_B T^2 \dfrac{\mathrm{d}}{\mathrm{d}T} \ln \mathcal{Z}(T) = \dfrac{1}{2} \coth\left(\dfrac{\hbar\omega(T)}{2k_B T}\right) \hbar[\omega(T) - T\omega'(T)\,]$

NTNU

Model:
Harmonic oscillator coupled to the heat bath

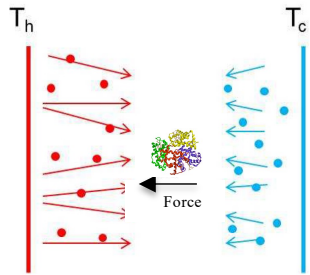Temperature-dependent frequency $\qquad \omega(T) = \omega_0\, e^{-\alpha T}$

Then, the energy function

$$E(T) = k_B T^2 \frac{\mathrm{d}}{\mathrm{d}T}\ln \mathcal{Z}(T) = \frac{1}{2}\coth\left(\frac{\hbar\omega(T)}{2k_B T}\right)\hbar[\,\omega(T) - T\omega'(T)\,]$$

has **one and only one** minimum at a positive temperature $T = T^*$.
Reversal temperature.

Nummerical example: $\omega_0 = 10^{15}\,\mathrm{Hz}, \;\; \alpha = 1/120\mathrm{K}$,
then the reversal temperature is $T^* = 24^{\mathrm{o}}\mathrm{C}$.

NTNU

Some applications of negative thermophoresis

Drug delivery
- Local heating is easier than local cooling
- Guide self-propelled particles towards locally heated targets

Baylis, J. R. et al. Halting hemorrhage with self-propelling particles and local drug delivery. *Thromb. Res.* **2016**, 141, S36.

Capture of **DNA and other biological indicators** in serum
- Detection of small quantities unachievable in thermally homogeneous samples

Yu, L.-H.; Chen, Y.-F.;. Concentration-dependent thermophoretic accumulation for the detection of DNA using DNA-functionalized nanoparticles. *Annal. Chem.* **2015**, 87, 2845.

Origin of life?
- Thermophilic accumulation of lipids and nucleic acids
- Self assembly of nucleic acids and protocells

Niether, D. et al. Accumulation of formamide in hydrothermal pores to form prebiotic nucleobases. *Proc. Natl. Acad. Sci. USA* **2016**, 113, 4272.

Budin, I. et al. Formation of Protocell-like Vesicles in a Thermal Diffusion Column. *J. Am. Chem. Soc.* **2009**, 131, 9628.

NTNU

Conclusion

Negative thermophoretic force results from strong coupling.

Effective macrostate energies $\mathcal{E}_j$ become temperature-dependent

$$E = k_B T^2 \frac{\mathrm{d}}{\mathrm{d}T} \ln \mathcal{Z} = \left\langle \mathcal{E}_j - T \frac{\mathrm{d}\mathcal{E}_j}{\mathrm{d}T} \right\rangle \quad \text{is a free energy of solvation}$$

$$\mathrm{d}E = \mathrm{d}\langle \mathcal{E}_j \rangle - \mathrm{d}\left\langle T \frac{\mathrm{d}\mathcal{E}_j}{\mathrm{d}T} \right\rangle$$

the system takes heat $+\mathrm{d}\langle \mathcal{E}_j \rangle$ from the environment
and returns work $-\mathrm{d}\langle T \mathrm{d}\mathcal{E}_j / \mathrm{d}T \rangle$ to the environment.

Potential energy surface changes.
Vibrational frequencies depend on the temparature of the solvent.

Temperature-dependence of effective energy profile $E(T)$ is nonmonotonic

The sign of the force function $\mathrm{d}E/\mathrm{d}T$ becomes temperature dependent.

Thermostatistical description of negative thermophoresis

NTNU

More info: *Physical Review Letters* **123**, 200602 (2019)

Thank you

NTNU – Trondheim
Norwegian University of
Science and Technology

www.ntnu.edu