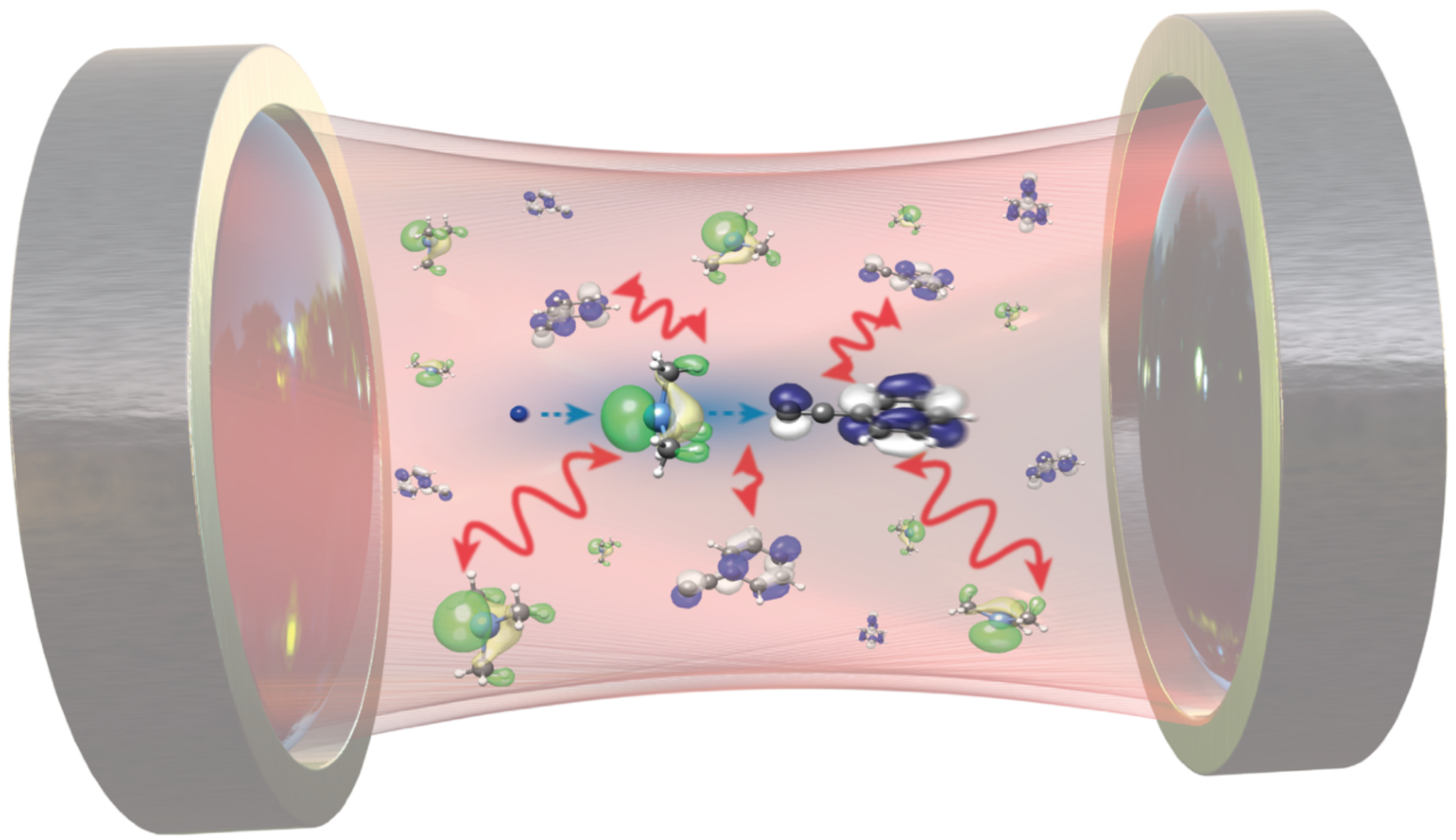
Dominik Sidler, 2025

Polaritonic / QED Chemistry

Lecture 8: Spin Glass Hypothesis
(Thermal on / off Equilibrium)



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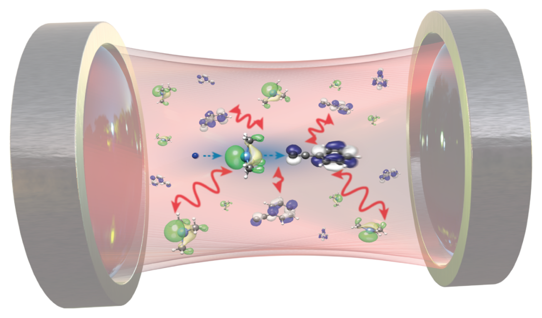
Lecture Outline



***Disclaimer:** The relevance of spin glass physics for polaritonic chemistry is unknown and considerable research efforts will be required to proof/disproof it. However, the presented spin glass concepts are generally established, and interesting to know about in any case…*

1. Discuss VSC simulation exercise („nuclear temperature“).
2. **Fundamentals of spin glasses** illustrated for Sherrington-Kirkpatrick (SK) model: Phase transition, free energy, replica symmetry breaking, order function, (off)-equilibrium properties…
3. „Trivial“ case: **Spherical Sherrington-Kirkpatrick (SSK)** model.
4. **Putting pieces together**: Interpret cavity-induced electron correlations with SSK model (introduces electronic temperature under VSC).

Repetition: DSE Correlation Spin Glass

Summary

unpublished

Prerequisites:

1. „Polarization-ordering“ for sufficiently strong collective light-matter coupling. **Collectively-degenerate electronic ground-state**.
2. **Quasi-dilute gas limit** with sufficient density of states (DSE inter-molecular correlations dominate over Coulomb correlations).
3. Source of **randomness**: E.g., molecular orientations with respect to cavity polarization.
4. Random DSE **fluctuations** musst be **sufficiently strong** $\propto T_c$ (critical temperature) for phase transition into a spin glass $(T < T_c)$.

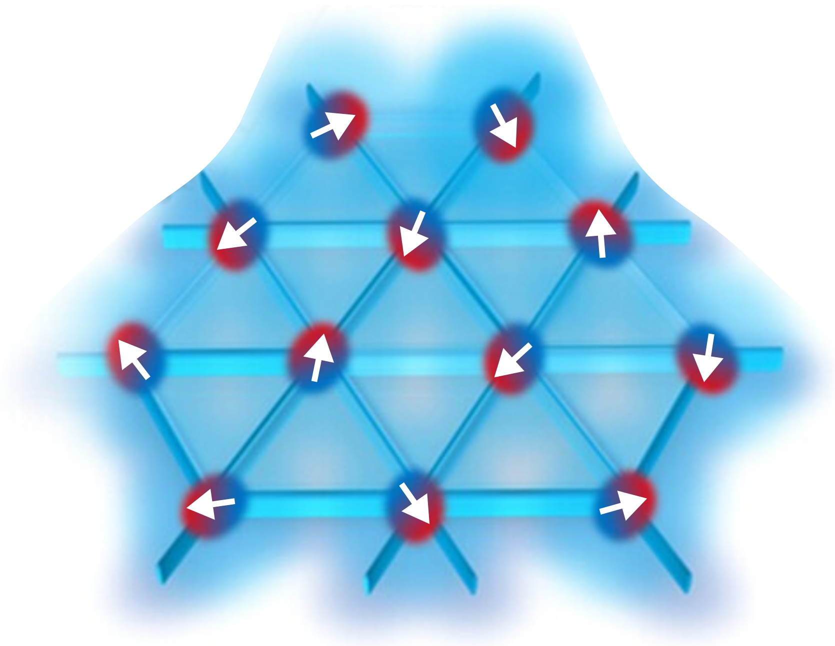
DSE Correlation Spin Glass:

$$\boxed{E_{\text{corr}}^{\text{DSE}} = -\sum_{i<j}^{N_J} s_i s_j J_{ij}, \ \sum_i s_i^2 = 1, \ \langle J_{ii} \rangle = 0,}$$

D. Sidler, M. Ruggenthaler and A. Rubio, arXiv:2409.08986, (2024)

Introduction to Theory of Spin Glasses

Blackboard: Famous Example: Sherrington - Kirkpatrick (SK) Model



SK

$$H_J(\boldsymbol{\sigma}) = -\sum_{j<i}^{N} J_{ij}\sigma_i\sigma_j$$

$$J_{ij} \sim \mathcal{N}(J_0/N, J^2/N) \qquad \sigma_i = \pm 1$$

Exact mean-field description at **temperature T**:

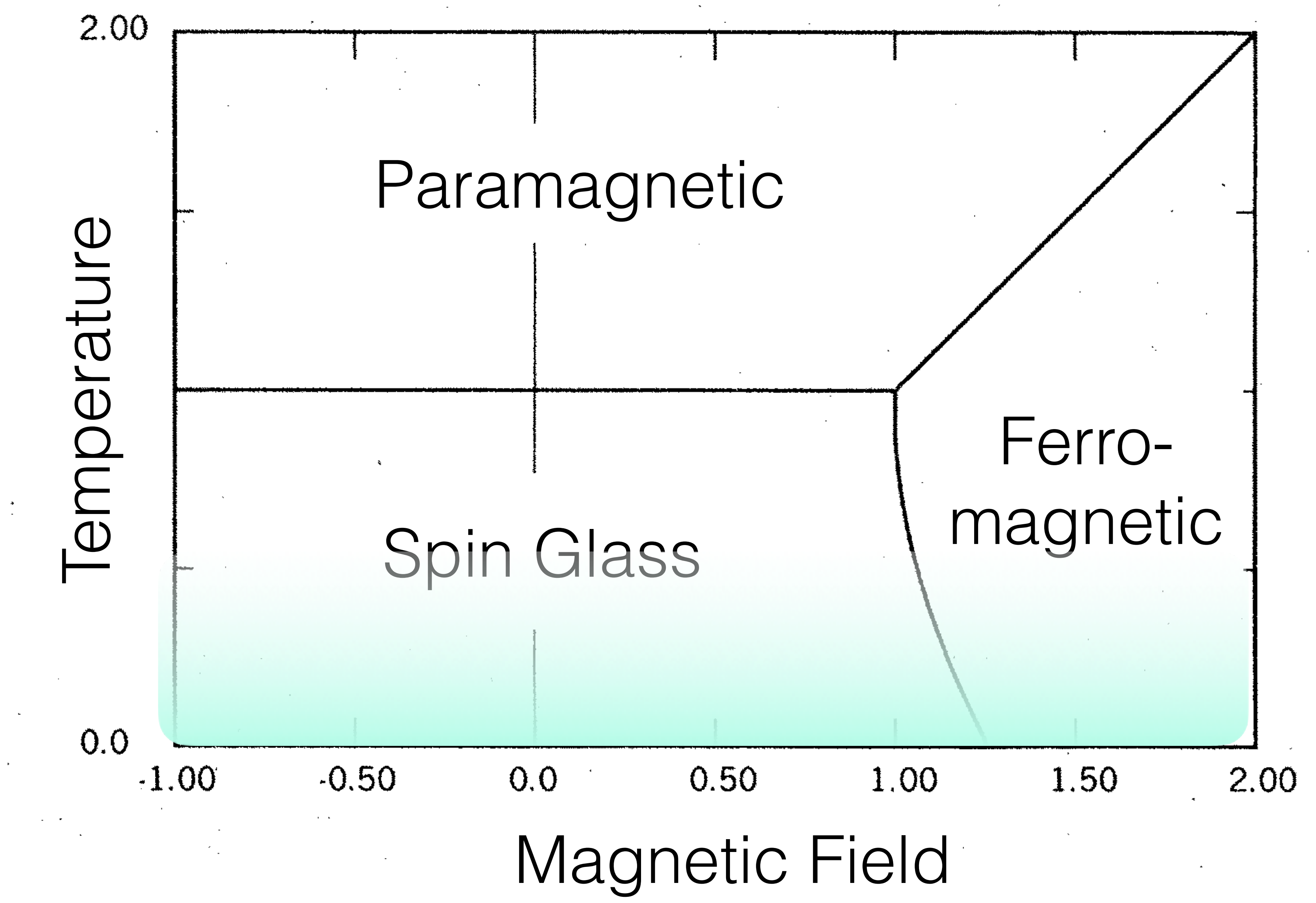
$$m(i) = \tanh\left(\frac{\sum_j J_{ij} m(j)}{k_B T}\right)$$

Magnetization: $m(i)_\alpha = \langle \sigma_i \rangle_{T,\alpha}$

Edwards-Anderson Order Parameter: $q_{EA} = \frac{\sum_i m(i)_\alpha m(i)_\alpha}{N} = \text{const. } \forall \alpha, J,$

Negative entropy: Something wrong!

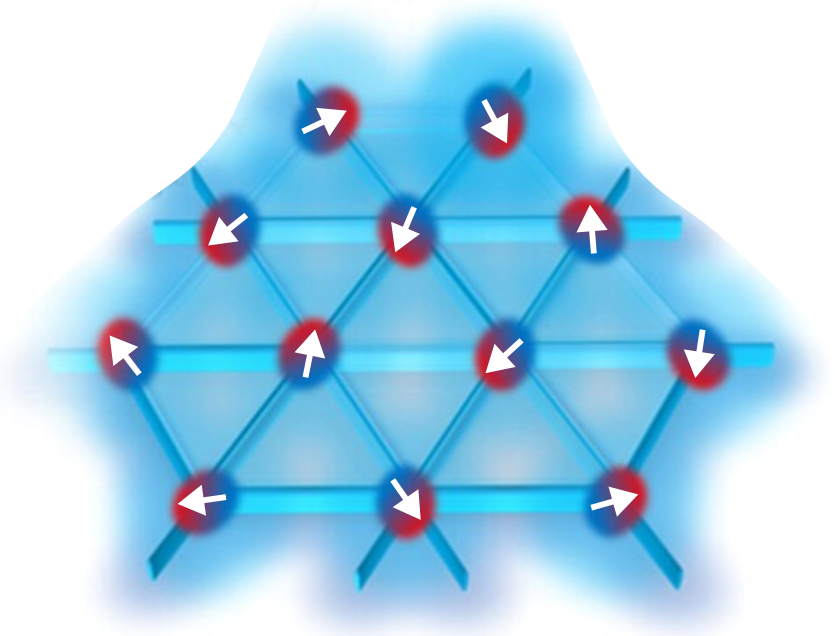
Phase Diagram



D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett (1975), J. R. L. de Almeida and D. J. Thouless (1977)

Introduction to Theory of Spin Glasses

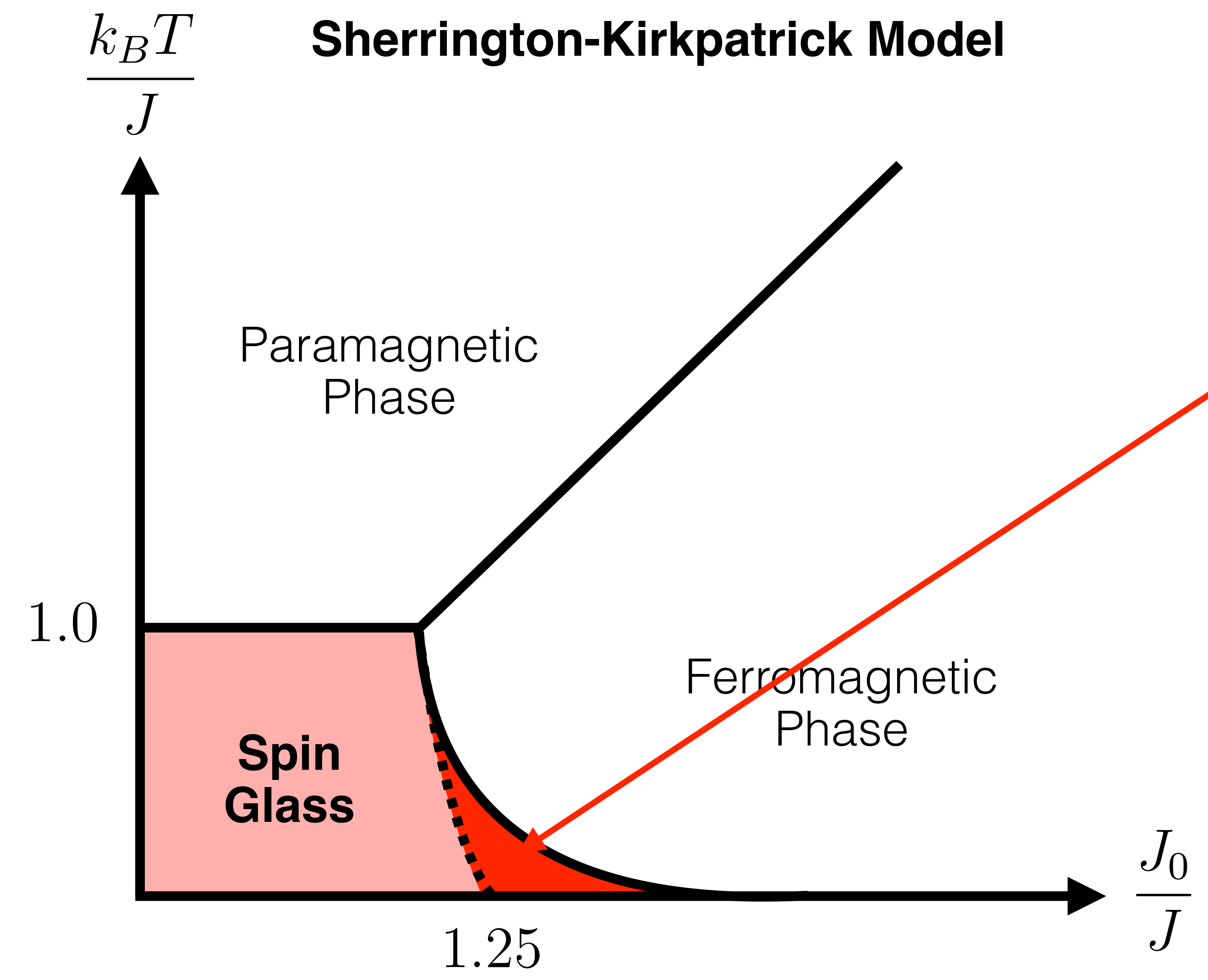
Blackboard: Free Energy and Replica Symmetry Breaking



$$
\begin{aligned}
F(T) &= -\lim_{N\to\infty} \frac{\overline{k_B T \log(Z_J(T,N))}}{N},\\
Z_J(T,N) &= 2^{-N} \sum_{\{\sigma\}} e^{-\frac{H_J(\sigma)}{k_B T}}.
\end{aligned}
$$

Replica Ansatz:

$$
\begin{aligned}
F_n(T) &= -\lim_{N\to\infty} \frac{\overline{k_B T (Z_J(T,N))^n}}{nN},\\
\cancel{F(T)} &\cancel{= \lim_{n\to 0} F_n(T).}
\end{aligned}
$$



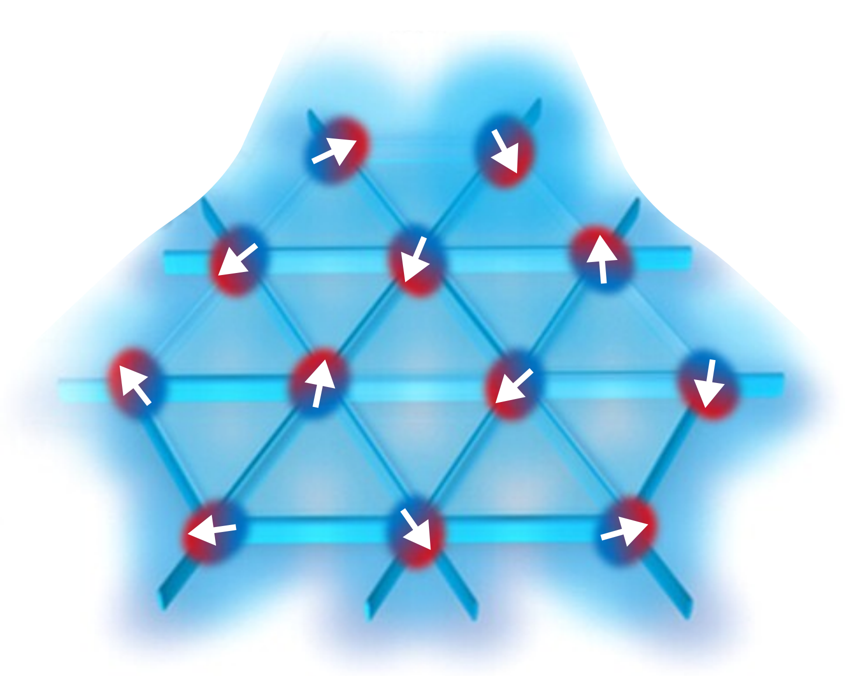
Borken replica symmetry triggers instability of ferromagnetic phase

Exact solution of SK model: Far reaching mathematical and physical consequences. **Nobel prize in physics 2021** (G. Parisi)

D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett (1975), J. R. L. de Almeida and D. J. Thouless (1977)
G. Parisi, Nobel Lecture in Rev. Mod. Phys. (2023)

Introduction to Theory of Spin Glasses

Order Parameter Distribution from Replica Symmetry Breaking in SK Model

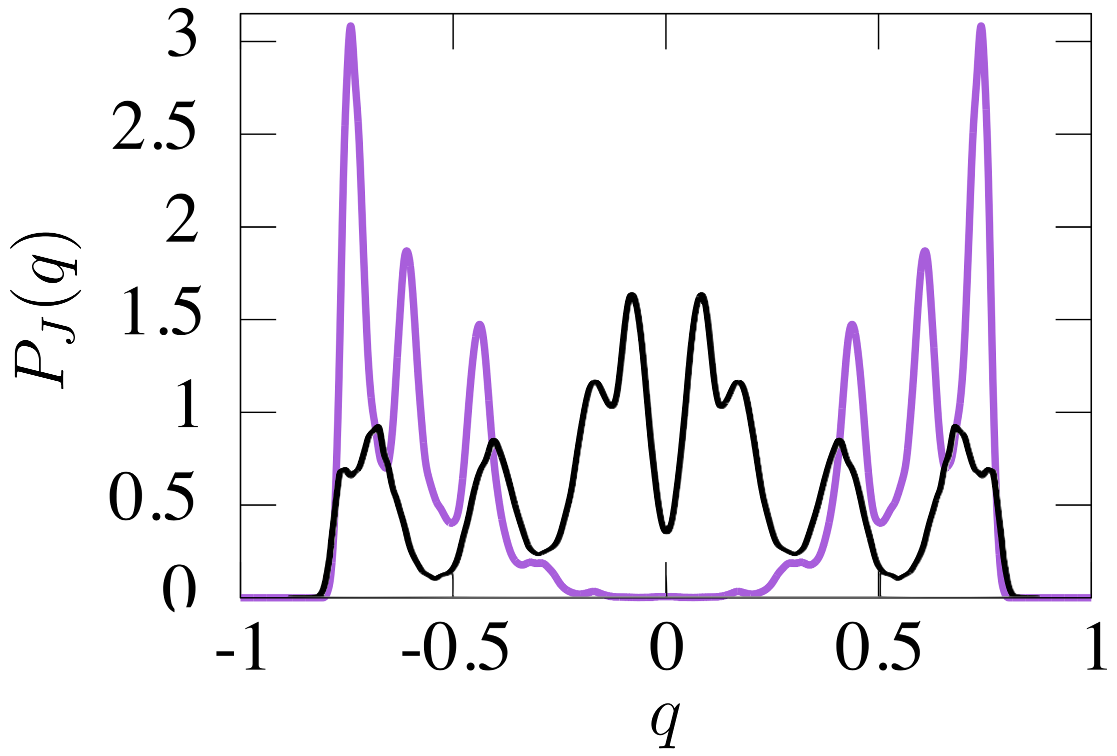


Parisi could show that spontaneous replica symmetry breaking leads to **order function** $q(x)$, instead of just one order parameter q.

The exact free energy of the SK model is given by determining $\max_{q(x)} F[q(x)]$ of a corresponding (non-trivial) PDE (not shown here).

The order function can be related to the **probability density** $P_J(q)$ of finding two states (solutions) α, γ with overlap $Q_{\alpha\gamma} = \dfrac{\sum_i m(i)_\alpha m(i)_\gamma}{N}$, in a given sample J. Remark: self-overlap $q_{EA} = Q_{\alpha\alpha}$.

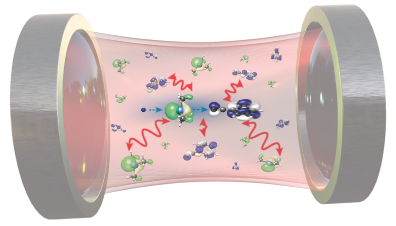
Order parameter distribution example



=> **Equilibrium overlap density** $P(q) = \langle P_J(q) \rangle_J$ is tricky to calculate!

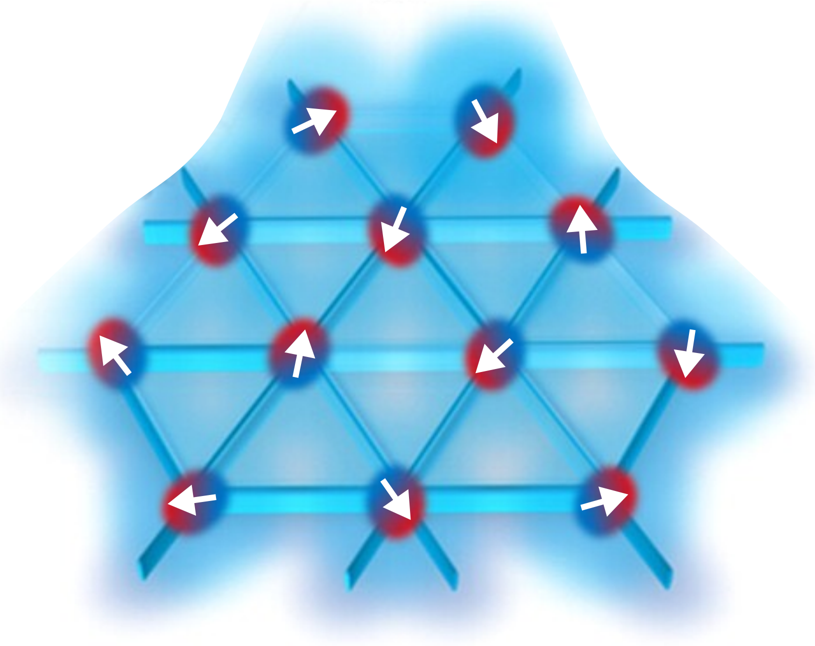
Remark: Making functional dependency of $q(x)$ explicit by inverting the probability density, yielding $x(q) = \int_0^q dq' P(q')$. (see off-equilibrium discussion of SSK model).

D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett (1975), J. R. L. de Almeida and D. J. Thouless (1977)
G. Parisi, Nobel Lecture in Rev. Mod. Phys. (2023)



Introduction to Theory of Spin Glasses

Equilibrium properties: Response to small external field perturbation

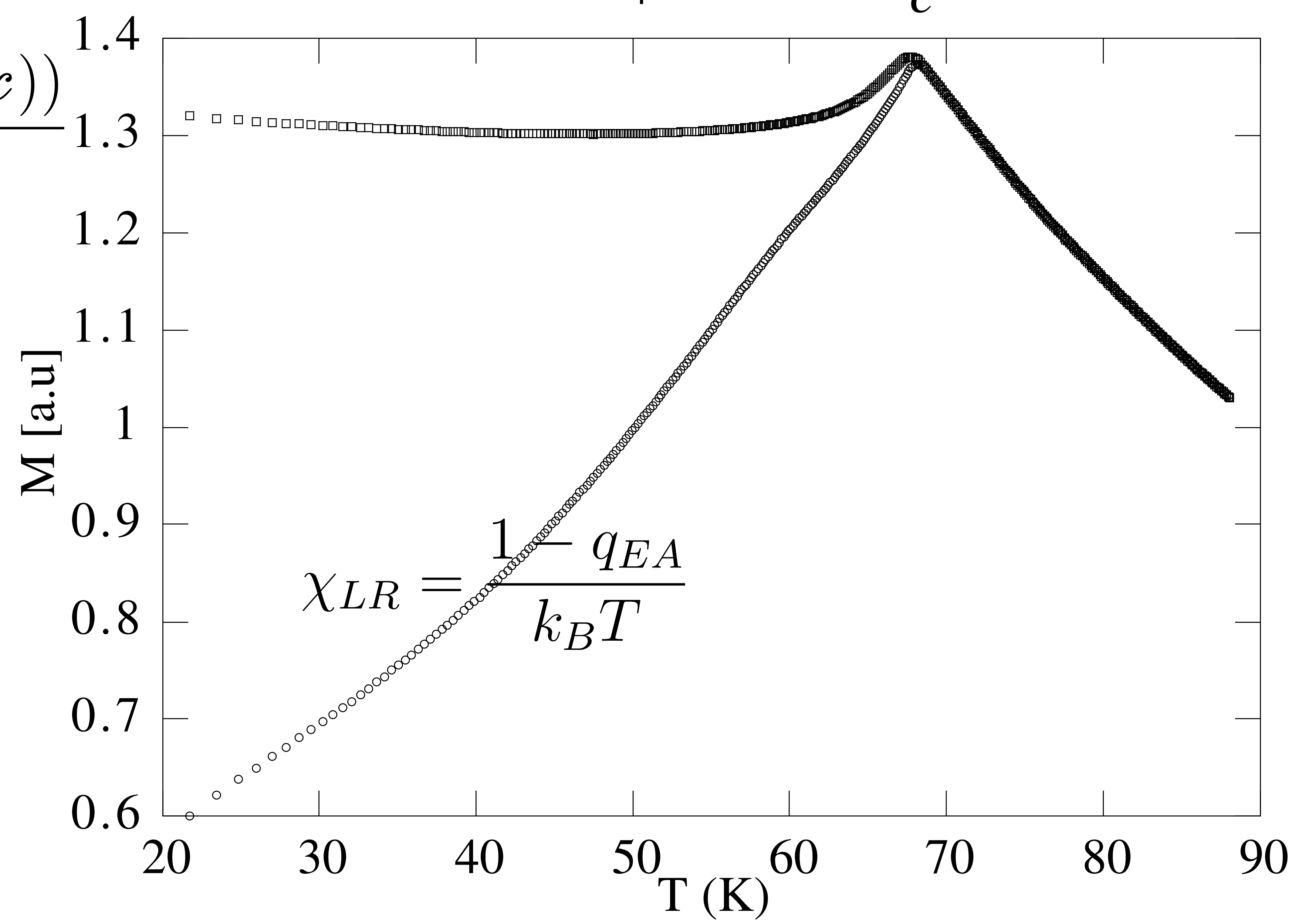


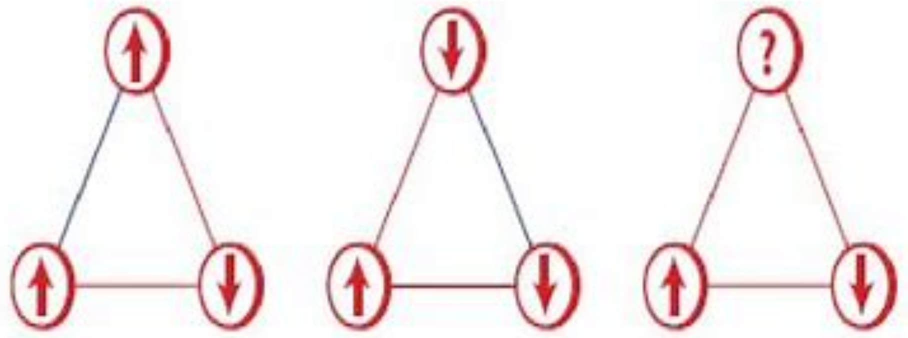
External magnetic field perturbation $H'(\boldsymbol{\sigma}) = h' \sum_i \sigma_i.$

Magnetic **equilibrium** (eq) **susceptibility** measured when applying first magnetic field, then cooling (system can relax to thermodynamically most favored state).

$$\chi_{eq} = \frac{\int dx(1 - q(x))}{k_B T}$$

Critical Temperature T_c



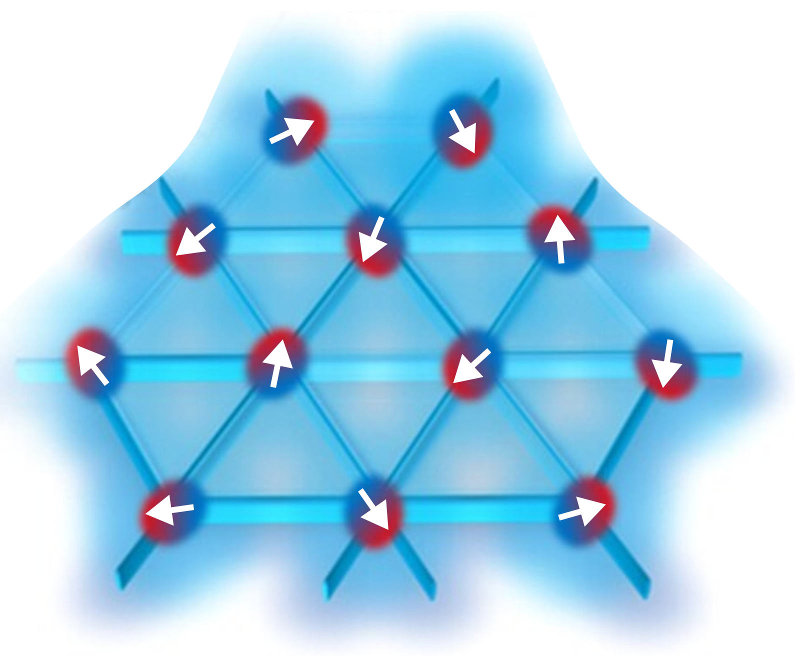


Linear response (LR) **susceptibility** measured, when applying first cooling, then magnetic field (**spin glass frustration:** System remains trapped and does not „reach“ equilibrium response).

D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett (1975), J. R. L. de Almeida and D. J. Thouless (1977)
G. Parisi, Nobel Lecture in Rev. Mod. Phys. (2023)

Introduction to Theory of Spin Glasses

Off-Equilibrium Properties: Correlations



Cooling to spin glass

$T < T_c$

Apply external magnetic field perturbation

$H'(\boldsymbol{\sigma}) = h' \sum_i \sigma_i.$

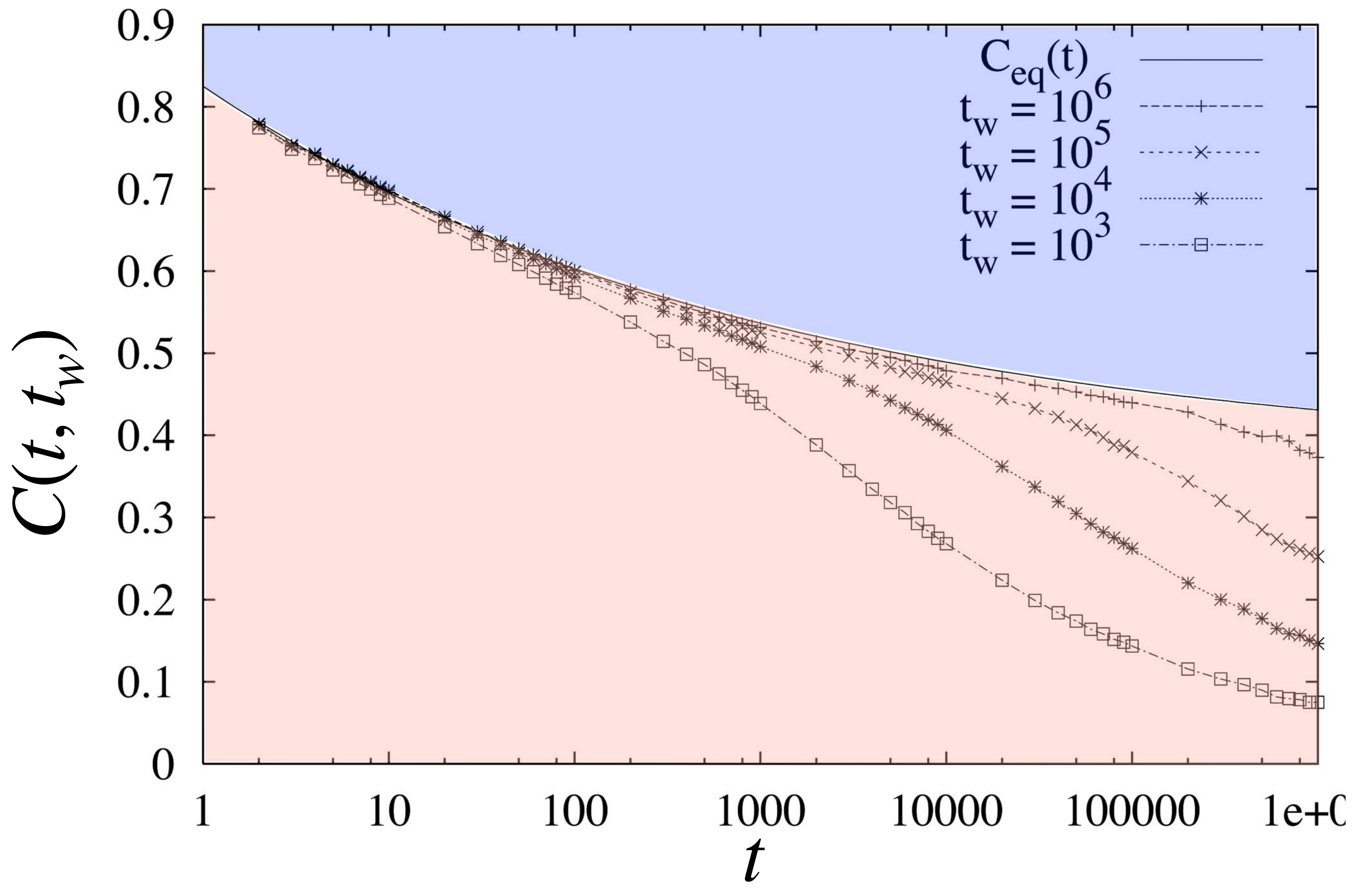
„Measurement"

time

0 t_w $t_w + t$

magnetic correlations $C(t, t_w) = \frac{1}{N}\sum_i^N \langle \sigma_i(t_w)\sigma_i(t_w+t)\rangle$

Ising Spin Glass (replica symmetry braking)



Stationary Correlations $C(t, t_w) \mapsto C_{eq}(t)$

Aging Regime $C(t, t_w) \neq C_{eq}(t)$

D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett (1975), J. R. L. de Almeida and D. J. Thouless (1977)
G. Parisi, Nobel Lecture in Rev. Mod. Phys. (2023)

Spherical Sherrington-Kirkpatrick (SSK) Model

Simple Analytic Free Energy Solution

Assume for discussion $J_0 = 0$

$$H_{SSK}(\boldsymbol{s}) = -\sum_{i<j}^{N_J} s_i s_j J_{ij}, \;\; J \sim \mathcal{N}(\cancel{J_0/N_J}, \tilde{J}^2/N_J).$$

Continuous spin variables

Spherical Constraint $\sum_i s_i^2 = N_J$

No replica symmetry breaking -> no order parameter function -> only EA order parameter: $q_{EA}^{\mathrm{SSK}} = 1 - T/T_c$

Phase transition at critical temperature $T_c = \tilde{J}/k_B$

Free Energy per spin without external magnetic field

$$F_{T,\tilde{J}} = \lim_{N_J \to \infty} F_{N_J,T,\tilde{J}} = \begin{cases} -\frac{\tilde{J}^2}{4k_BT} - \frac{1}{2}k_BT(1+\ln(2)) & \text{if } T \geq T_c, \;\; J_0 = 0 \\ \frac{1}{2}k_BT\ln\left(k_BT/(2\tilde{J})\right) - \tilde{J} + \frac{1}{4}k_BT & \text{if } T < T_c, \;\; J_0 = 0, \end{cases}$$

Spherical Sherrington-Kirkpatrick (SSK) Model

Properties: Modified fluctuations

Local (per spin) free energy fluctuations for $\tilde{J} = 1$:

$$F_{T,1} - F_{N_J,T,1} \propto \begin{cases} \frac{1}{N_J} \mathcal{N} & \text{if } T \geq T_c,\ J_0 = 0 \\ \frac{1}{N_J^{2/3}} TW_1 & \text{if } T < T_c,\ J_0 = 0, \end{cases}$$

Different fluctuation scaling in spin glass phase.

Different probability distribution among ensemble

Remark: In a cavity, „local in spin“ does **not** mean spatially localized.
Remember: we talk about delocalized inter-molecular correlations (excited HF orbitals).

$$F_{\text{corr}}^{\text{DSE}} \sim N_J F_{T,\tilde{J}}.$$

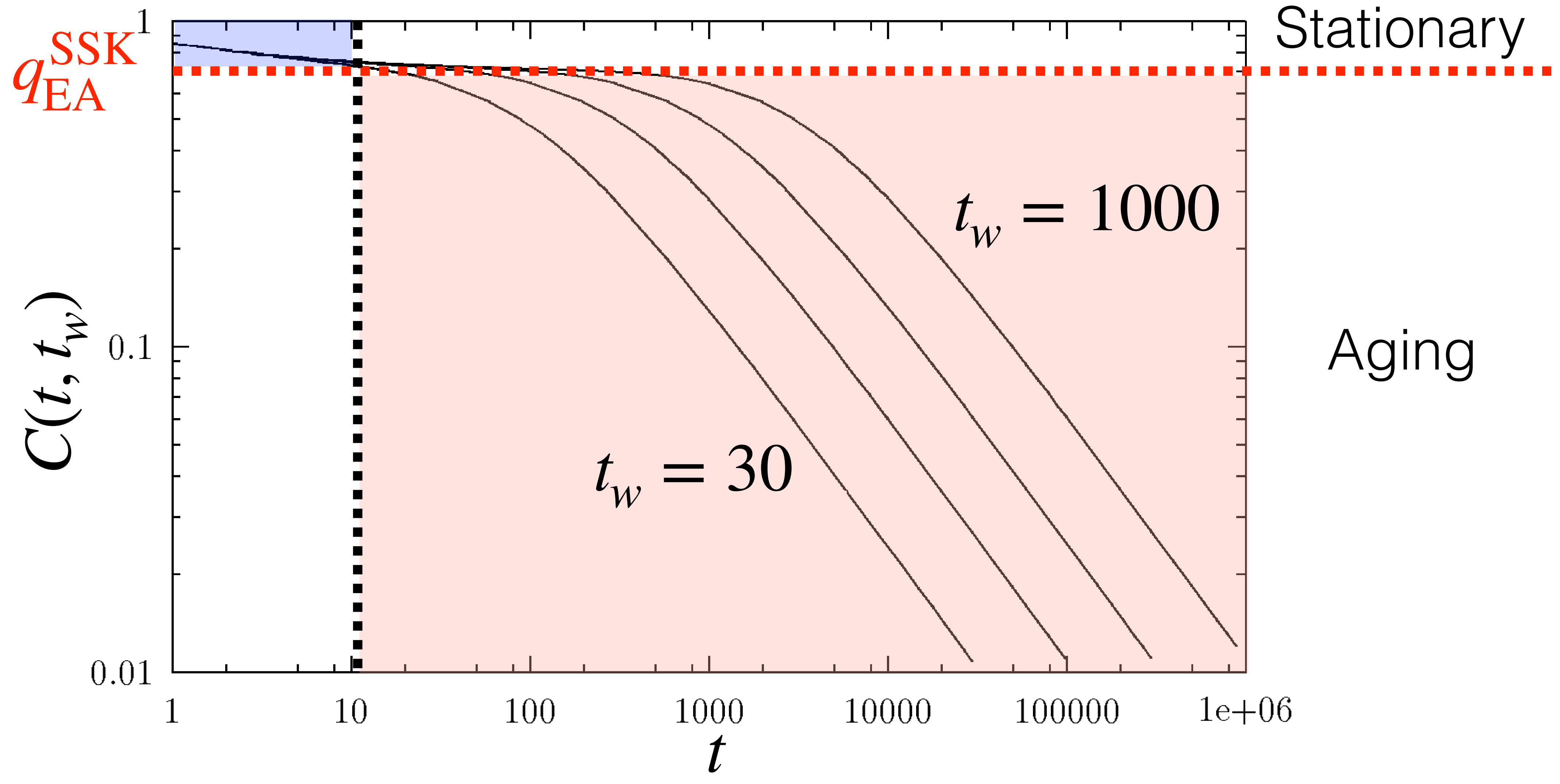
Spherical Sherrington-Kirkpatrick (SSK) Model

Non-equilibrium Dynamics / Correlations

Stationary correlation regime: $C(t,t_w) \sim C_s(t),\ t \ll t_w.$

Aging regime: $C(t,t_w) \sim \begin{cases} q_{EA}^{\rm SSK} = 1 - T/T_c & \text{if } t \approx t_w, \\ \text{slowly decaying to 0} & \text{if } t \gg t_w. \end{cases}$

SSK Model (no replica symmetry braking)



Dynamics of SSK model never reaches thermal equilibrium for almost any initial condition.

$$\boxed{\lim_{t_w \to \infty} C(t,t_w) = q_{EA},\ \forall t \text{ finite.}}$$

$$q_{EA} = 1 - T/T_c$$

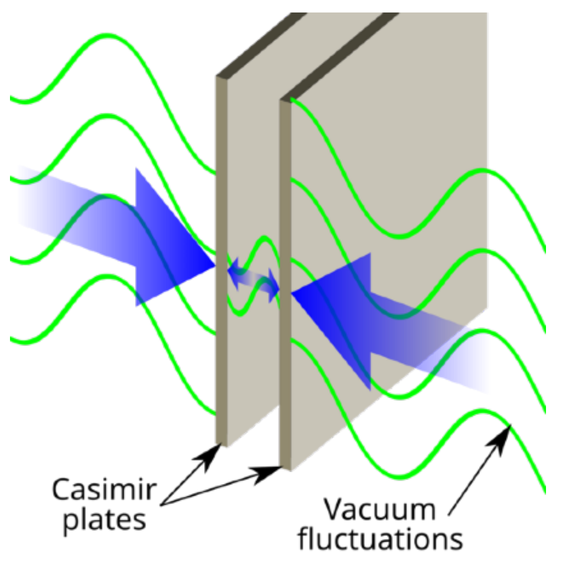
Spherical Sherrington-Kirkpatrick (SSK) Model

Blackboard: Interpreting Off-equilibrium

The Spin Glass Hypothesis

Cavity Induces Non-trivial Intermolecular Correlations

$$\mathscr{E}_{\boldsymbol{c}} \overset{\text{quasi-dilute}}{\approx} E_0 + E_{\boldsymbol{c}}^{\text{C,intra}} + \boxed{E_{\boldsymbol{c}}^{\text{DS,inter}}}$$



Source of (inter-molecular) **„random“** overlap integrals**:**

- molecular separation (weak for quasi-dilute gas)
- **molecular orientation (cavity breaks isotropy of space**!)

Spherical 2-spin <u>model</u> of a spin glass

$$\boxed{E_{\text{corr}}^{\text{DSE}}} = -\sum_{i<j}^{N_J} s_i s_j J_{ij}, \quad \sum_i s_i^2 = 1, \quad \langle J_{ii} \rangle = 0,$$

Random

Continuous spin constraint

Static analytic solution at finite temperature

$$F_{T,\tilde{J}} = \lim_{N_J \to \infty} F_{N_J,T,\tilde{J}} = \begin{cases} -\frac{\tilde{J}^2}{4k_B T} - \frac{1}{2}k_B T(1+\ln(2)) & \text{if } T \geq T_c, \ J_0 = 0 \\ \frac{1}{2}k_B T \ln\left(k_B T/(2\tilde{J})\right) - \tilde{J} + \frac{1}{4}k_B T & \text{if } T < T_c, \ J_0 = 0, \end{cases}$$

$$\boxed{F_{\text{corr}}^{\text{DSE}} \sim N_J F_{T,\tilde{J}}.}$$

J. M. Kosterlitz et al., Phys. Rev. Lett. 36, 20 (1976), D. Sidler, M. Ruggenthaler and A. Rubio, <u>arXiv:2409.08986</u>, (2024)

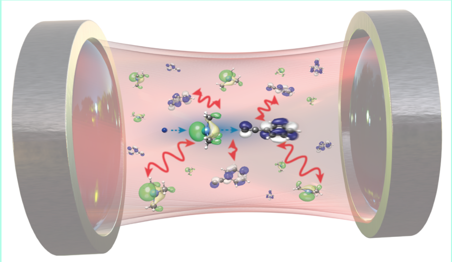
The Spin Glass Hypothesis

Implications of SSK Model on DSE Correlations

- Similar to solids, **electronic temperature** starts to play a role (spin glass phase transition).
- Cavity modifies **distribution** and (collective) **scaling behavior** of **inter-molecular electron correlations/fluctuations**.
- **Aging effect introduces explicit time-dependency on correlation energy (spin glass dynamics does not reach equilibrium).** Breaks Born-Oppenheimer picture.
- Breakdown of fluctuation-dissipation relation suggest cavity-induced **non-equilibrium thermodynamics.**

Time-dependent correlation energy for $T < T_c$

$$\mathscr{E}\big(\boldsymbol{R}(t), q_\beta(t)\big) \overset{T<T_c}{\mapsto} \mathscr{E}\big(\boldsymbol{R}(t), q_\beta(t)\boxed{, t}\big)$$



D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett (1975), J. R. L. de Almeida and D. J. Thouless (1977)
G. Parisi, Nobel Lecture in Rev. Mod. Phys. (2023), D. Sidler, M. Ruggenthaler and A. Rubio, arXiv:2409.08986, (2024)
C. M. Bustamante, D. Sidler, M. Ruggenthaler and A. Rubio, J. Chem. Phys. 161, 244101 (2024)

Spherical Sherrington-Kirkpatrick (SSK) Model

Limitations / Unknowns

- Random probability distribution of J_{ij} not known.
- Resulting modified SSK spin glass features not known.
- Time-dependent parameters enter spin glass problem (nuclei and displacement field).

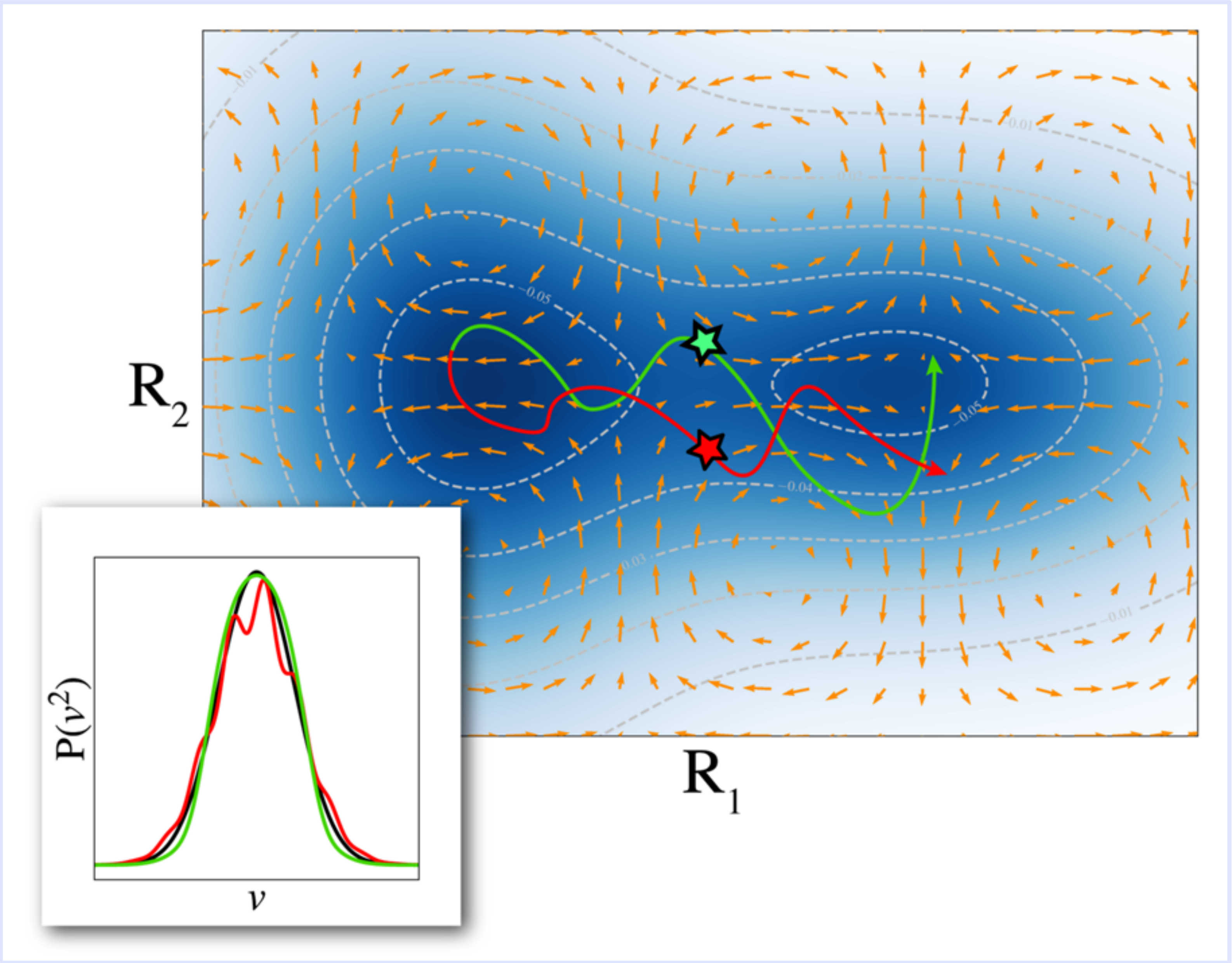
  Here we have assumed them to be static. „Act as periodic local magnetic fields“
- Role of different time-scales not known (waiting time vs. vibrational time-scales etc.)

What About the Nuclei?

Stochastic Resonance Hypothesis

Classical Cavity Born-Oppenheimer Molecular Dynamics Hamiltonian

$$H^{\mathrm{npt}}\big(\mathbf{R}(t), q_\beta(t), t\big) = H^{\mathrm{m}}\big(\mathbf{R}(t), q_\beta(t)\big) + \frac{p_\beta^2}{2} + \frac{\omega_\beta^2}{2}\left(q_\beta - \frac{X_\beta}{\omega_\beta}\right) + E_0\big(\mathbf{R}(t), q_\beta(t)\big) + \boxed{E_{\mathrm{corr}}\big(\mathbf{R}(t), q_\beta(t), t\big)}$$

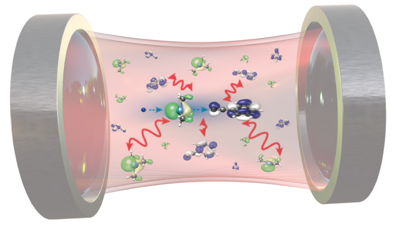


Cavity-modified Electronic Correlations:
Spin glass dynamics (aging) introduce explicit **time-dependent electronic forces.**

Add (nuclear) temperature:
Classical Langevin equations of motion.

Non-conservative forces imply non-canonical (!) dynamics and possibly stochastic resonances.

D. Sidler et al., J. Chem. Phys. 156, 230901 (2022), D. Sidler et al., J. Chem. Theory Comput. 19, 23, 8801 (2023)



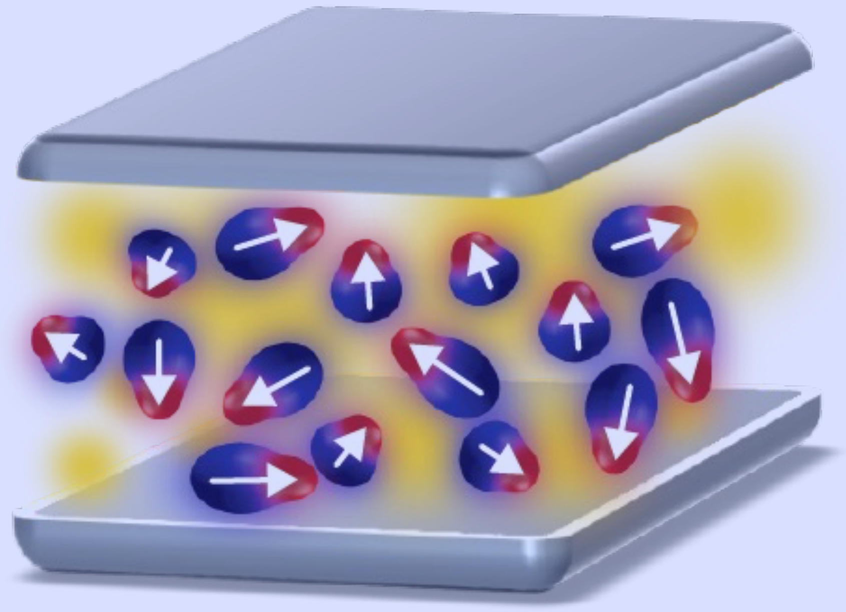
Assembling the Pieces

Non-trivial Feedback in VSC

Electronic Structure

$$\langle\Psi|\sum_{i}^{N_e}\left\{\frac{\hat{\boldsymbol{p}}_i^2}{2}-\frac{1}{2}\sum_{l}^{N_N}\frac{Z_n}{|\hat{\boldsymbol{r}}_i-\boldsymbol{R}_l|}+\frac{1}{2}\sum_{j}^{N_e}\frac{1}{|\hat{\boldsymbol{r}}_i-\hat{\boldsymbol{r}}_j|}\right\}$$

$$+\left(\frac{1}{2}\hat{x}^2+\hat{x}X-\omega_\beta\hat{x}q_\beta\right)|\Psi\rangle$$



Seed of VSC:
Collectively induced polarization instability. Replica symmetry breaking & (dynamic) frustration.

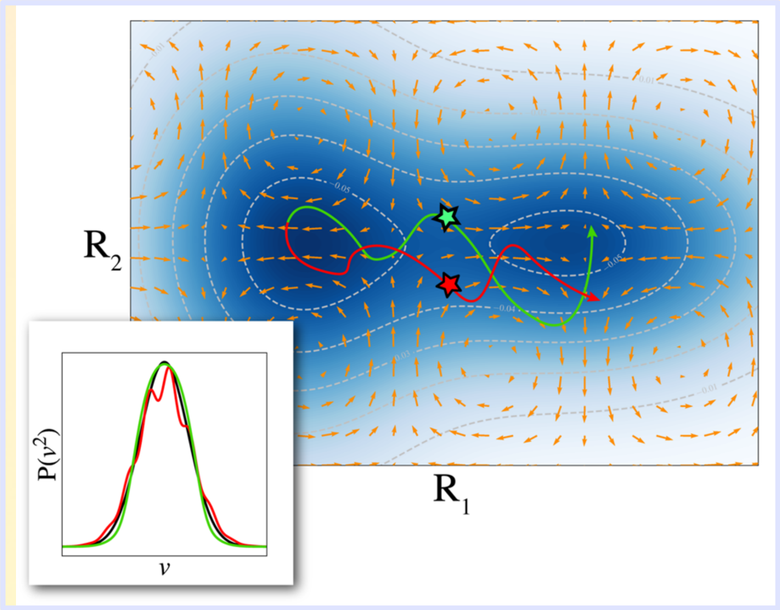
?

European Research Council
Established by the European Commission
Synergy Grants

PhD/Postdoc positions available at MPSD Hamburg!

Nuclei

$$H^{\mathrm{npt}} := H_{\mathrm{m}}^{\mathrm{n}}+\sum_{\alpha=1}^{M}\left(\frac{p_\alpha^2}{2}+\frac{\omega_\alpha^2}{2}\left(q_\alpha-\frac{X_\alpha}{\omega_\alpha}\right)^2+\langle\psi_0|\hat{H}_e(\mathbf{R},\underline{q})|\psi_0\rangle\right)$$



Stochastic Resonances:
non-equilibrium thermodynamics

Displacement Field

Summary and Conclusion

Spin glass phase transition could be the **missing theoretical piece that „localizes“ collective strong coupling**, i.e., modifies fluctuations and introduces off-equilibrium effects that modify chemistry (rare events), at least if all prerequisites are met.
=> Validation / verification requires considerable future research efforts.