Mathematical Theories of Liquid Crystals

II. The Maier-Saupe Theory

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Summary

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Introduction

The Maier-Saupe theory of liquid crystals is perhaps the most successful microscopic theory proposed so far to explain the **condensation** of the **nematic phase**. MAIER & SAUPE (1958)

In essence, it rests on **three** conceptual pillars:

- it is a **mean-field** theory;

- it considers only **attractive** interactions between molecules;

- it applies only to **homogeneous** phases.

Helmholtz Free Energy

We consider a dynamical system with N **_identical_** particles in the Hamiltonian formalism.

Lagrangian

$$\mathcal{L}(\mathsf{q}, \dot{\mathsf{q}}) := \mathcal{K}(\mathsf{q}, \dot{\mathsf{q}}) - \mathcal{U}(\mathsf{q})$$

$\mathsf{q} = (q_1, \ldots, q_N) \in \mathcal{Q}^N$ generalized coordinates

$\mathcal{Q}$ single particle configuration space

$\dot{\mathsf{q}} = (\dot{q}_1, \ldots, \dot{q}_N)$ generalized velocities

$\mathcal{K}$ kinetic energy

$\mathcal{U}$ potential energy

Hamiltonian

$$\mathcal{H}(\mathsf{q}, \mathsf{p}) := \mathcal{K} + \mathcal{U}$$

$p_j := \dfrac{\partial \mathcal{L}}{\partial \dot{q}_j}$ conjugate momenta

equations of motion

$$\dot{\mathsf{q}} = \frac{\partial \mathcal{H}}{\partial \mathsf{p}}$$

$$\dot{\mathsf{p}} = -\frac{\partial \mathcal{H}}{\partial \mathsf{q}}$$

$\mathcal{Q}^N \times \mathbb{R}^N \subset \mathbb{R}^{2N}$ phase space

canonical ensemble

Imagine a great many **replicas** of the system described by the same Hamiltonian $\mathcal{H}$, but differing in the occupation of the phase space, as a result, for example, of different initial conditions. Different ensembles differ in their **probability density** ϱ. Gibbs(1902)

In the *canonical* ensemble,

$$\varrho_0(\mathsf{q}, \mathsf{p}) := \frac{1}{Z} \mathrm{e}^{-\frac{1}{kT}\mathcal{H}(\mathsf{q}, \mathsf{p})}$$

k Boltzmann constant
T absolute temperature

partition function

$$Z := \int_{\mathbb{R}^N} \mathrm{d}\mathsf{p} \int_{\mathcal{Q}^N} \mathrm{d}\mathsf{q} \, \mathrm{e}^{-\frac{1}{kT}\mathcal{H}(\mathsf{q}, \mathsf{p})}$$

Helmholtz free energy

$$F := -kT \ln Z.$$

The number of particles N, the volume V they occupy, and the temperature T hidden in F are parameters. Equilibrium thermodynamics results from differentiating F with respect to them. For example,

$$P = -\frac{\partial F}{\partial V} \quad \text{is the pressure}$$

Amended configurational partition function

We reduce Z to a purely configurational quantity, by integrating out the momenta components of $\mathcal{H}$. For a canonical $\mathcal{H}$, purely ***quadratic*** in p, this amounts to extracting a factor (depending on T) out of Z, which in turn only affects F by an inessential additive constant.

$$Z_N := \frac{1}{N!} \int_{\mathcal{Q}^N} \mathrm{e}^{-\frac{1}{kT}\mathcal{U}(\mathsf{q})} \mathrm{d}\mathsf{q} \qquad F_N := -kT \ln Z_N$$

A classical justification for introducing the correcting factor $\frac{1}{N!}$ is to account for the indistinguishability of the particles comprising the system.

It has long been known (apparently, to Gibbs himself) that failing to introduce this correcting factor would make the theory vulnerable to ***Gibbs' paradox*** for the entropy of mixing ideal gases.

Pairwise Interactions

We assume that the N particles only interact *in pairs*

$$\mathcal{U}(\mathsf{q}) = \frac{1}{2} \sum_{i \neq j=1}^{N} U(q_i, q_j)$$

$$U : \mathcal{Q} \times \mathcal{Q} \to \mathbb{R}$$
$$U(q_i, q_j) = U(q_j, q_i)$$

In *general*, $U(q_1, q_2)$ comprises the whole energy involved in the interaction between particles q_1 and q_2. It includes both slowly varying, long-range potentials, typically responsible for the *attraction* between particles, and rapidly varying, short-range potentials, typically responsible for the *repulsion* between particles, often steric in nature. We call *soft* the former component of U and *hard* the latter.

typical potential
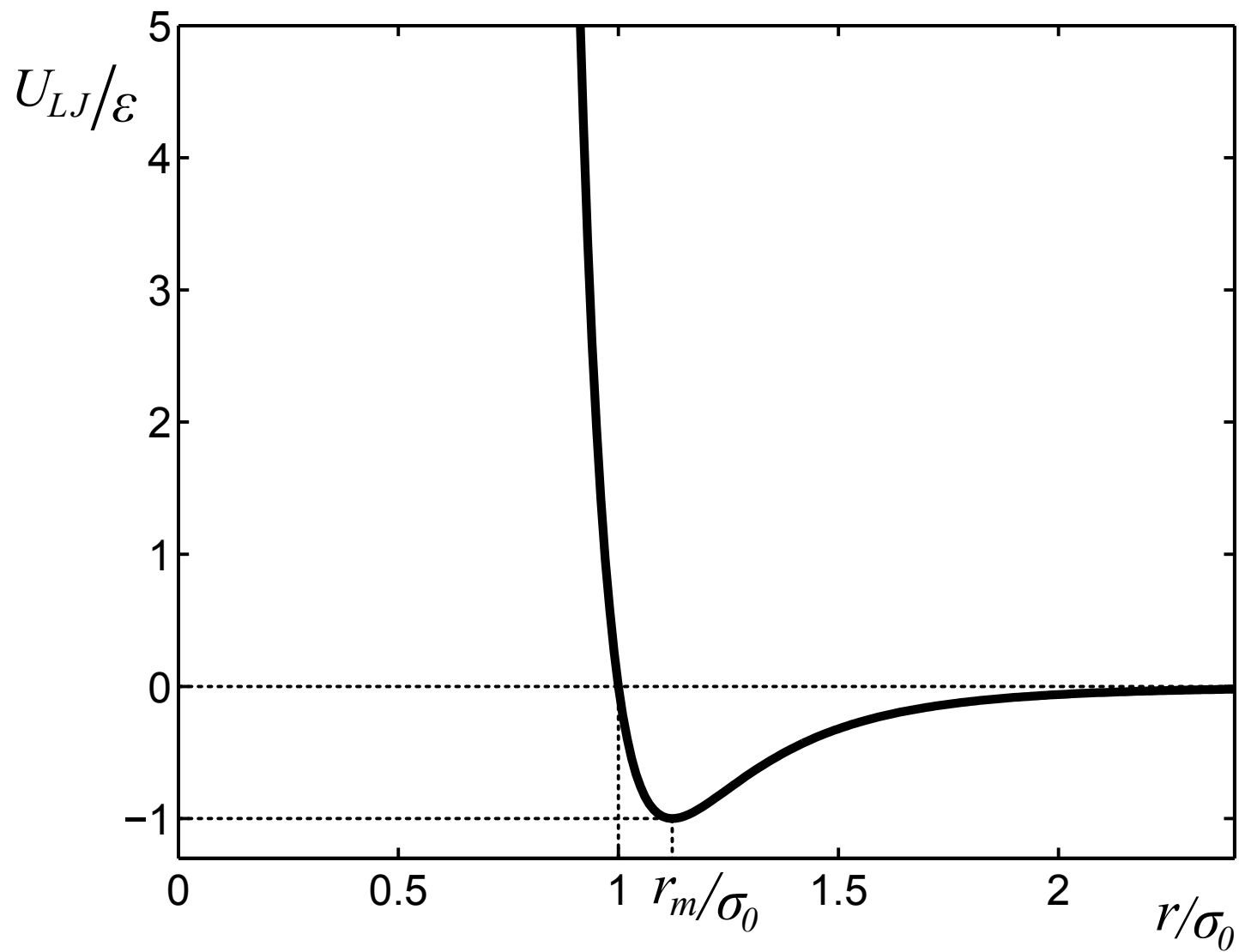
Soft and Hard Interactions

U can be ***decomposed*** into the sum of its attractive (soft) and repulsive (hard) components:

$$U(q_1, q_2) = U^{(A)}(q_1, q_2) + U^{(R)}(q_1, q_2)$$

Though, to some extent, such a decomposition is ***arbitrary***, the distinctive feature of $U^{(R)}$ is its ***abrupt divergence*** when the interacting particles tend to come ***in contact*** with one another.

$U^{(R)}$ is often assumed to be arbitrarily close to zero when the interacting particles are close to one another, and to ***diverge*** to $+\infty$ as they touch.

The ***divergence*** of $U^{(R)}$ makes it questionable taking ***averages*** of repulsive interactions.

only attractions

An ***assumption*** of the Maier-Saupe theory is to ignore repulsive interactions:

$$U^{(R)} \equiv 0$$

computing the free energy

$$F_N = -\,kT \ln \frac{1}{N!} \int_{\mathcal{Q}^N} \left(\mathrm{e}^{-\frac{1}{2}\frac{1}{kT}\sum_{j=2}^{N} U^{(A)}(q_1,q_j)} \right) \mathrm{d}q_1$$

$$\times \cdots$$

$$\times \left(\mathrm{e}^{-\frac{1}{2}\frac{1}{kT}\sum_{j=1}^{N-1} U^{(A)}(q_N,q_j)} \right) \mathrm{d}q_N$$

$$= -\,kT \ln \frac{1}{N!} \int_{\mathcal{Q}^N} \prod_{h=1}^{N} I_h \,\mathrm{d}q_1 \mathrm{d}q_2 \ldots \mathrm{d}q_N$$

$$I_h(q_1,\ldots,q_N) := \mathrm{e}^{-\frac{1}{2}\frac{1}{kT}\sum_{j=1,j\neq h}^{N} U^{(A)}(q_h,q_j)}$$

Mean-Field Free Energy

Mathematically, a mean-field theory is an *approximation* that *replaces* complicated expressions, difficult to evaluate, which involve *many* individual particles and their mutual interactions, with simpler expressions, easier to evaluate, which involve a single, *effective* particle.

Physically, it is as if the actions exchanged by particles were *replaced* by an *effective* field that *all* particles produce and feel at the same time.

$$\approx \quad \text{here means "}\textit{replaced}\text{ by"}$$

$$\frac{1}{2} \sum_{j=1, j\neq h}^{N} U^{(A)}(q_h, q_j) \approx \mathcal{E}(q_h)$$

$$I_h(q_1, \ldots, q_N) \approx \mathcal{I}(q_h) := e^{-\frac{1}{kT}\mathcal{E}(q_h)}$$

$\mathcal{E}$ single-particle *effective potential*

mean-field free energy

$$F_N = -kT \ln \frac{1}{N!} \int_{\mathcal{Q}^N} \prod_{h=1}^{N} I_h \, \mathrm{d}q_1 \mathrm{d}q_2 \ldots \mathrm{d}q_N$$

$$\approx -kT \ln \frac{1}{N!} \left(\int_{\mathcal{Q}} e^{-\frac{1}{kT}\mathcal{E}(q)} \mathrm{d}q \right)^N =: F_N^{(\mathrm{mf})}$$

upper estimate

It follows from Gibbs-Bogoliubov inequality (and an equivalent approach to mean-field theory) that the **mean-field** free energy is **larger** than the **true** free energy it replaces.

<div align="right">GARTLAND & VIRGA (2010)</div>

remark

For a deformable particle the configuration space $\mathcal{Q}$ will also allow for extra configurational degrees of freedom in addition to the usual translational and orientational ones.

Density Functional Theory

- The mean-field free energy $F_N^{(\mathrm{mf})}$ is a scalar depending on (N, V, T) only in a parametric form.

- Considering, within the **canonical ensemble**, how particles are **distributed** in the configuration space $\mathcal{Q}$, we construct a theory where the mean-field free energy becomes a **functional** $\mathscr{F}$ of the distribution **density**.

$$\textit{distribution (number) density}$$

$$\rho := \mathcal{Q} \to \mathbb{R}^+ \qquad \int_{\mathcal{Q}} \rho(q)\mathrm{d}q = N$$

$$\textit{effective potential}$$

$$\frac{1}{2} \sum_{j=1, j \neq h}^{N} U^{(A)}(q_h, q_j) \approx \mathcal{E}(q_h) \quad \to \quad \mathcal{E}(q) := \frac{1}{2} \int_{\mathcal{Q}} \rho(q') U^{(A)}(q, q')\mathrm{d}q'$$

partitioning $\mathcal{Q}$

$$\mathcal{Q} = \bigcup_{i=1}^{M} \mathcal{Q}^{(i)}$$

We split the system in a ***great number***, say M, of ***subsystems***

N_i number of particles in the ith subsystem

$q^{(i)} \in \mathcal{Q}^{(i)}$ ***core*** of the ith subsystem

$\mathcal{Q}^{(i)} \subset \mathcal{Q}$ region occupied by the ith subsystem

Δq_i measure of $\mathcal{Q}^{(i)}$

discretizing ρ

$$\rho : \mathcal{Q} \to \mathbb{R}^+ \qquad \rho_i := \rho\left(q^{(i)}\right) \qquad N_i = \rho_i \Delta q_i \qquad \sum_{i=1}^{M} N_i = N$$

free-energy additivity

$$F_N^{(\mathrm{mf})} = \sum_{i=1}^{M} F_{N_i}^{(\mathrm{mf})}$$

$$F_{N_i}^{(\mathrm{mf})} = -kT \ln \frac{1}{N_i!} \left(\int_{\mathcal{Q}^{(i)}} e^{-\frac{1}{kT}\mathcal{E}(q)} \mathrm{d}q \right)^{N_i}$$

$$F_N^{(\mathrm{mf})} = -kT \sum_{i=1}^{M} \ln \frac{1}{N_i!} \left(\frac{N_i}{\rho_i} e^{-\frac{1}{kT}\mathcal{E}^{(i)}} \right)^{N_i}$$

$$\mathcal{E}^{(i)} := \mathcal{E}\left(q^{(i)} \right)$$

Stirling's approximation

$$\ln \left(\frac{1}{N_i!} N_i^{N_i} \right) \approx N_i$$

Free-energy functional

$$F_N^{(\mathrm{mf})} \approx - kT \sum_{i=1}^{M} N_i \left(\ln \frac{1}{\rho_i} - \frac{\mathcal{E}^{(i)}}{kT} \right) - kTN$$

Disregarding the last addendum, as it does not depend on ρ, we justify the definition

$$\mathscr{F}[\rho] := kT \int_{\mathcal{Q}} \rho(q) \ln \rho(q) \mathrm{d}q + \frac{1}{2} \int_{\mathcal{Q}^2} \rho(q') \rho(q) U^{(A)}(q', q) \mathrm{d}q' \mathrm{d}q$$

$$\mathscr{E}[\rho] := \frac{1}{2} \int_{\mathcal{Q}^2} \rho(q') \rho(q) U^{(A)}(q', q) \mathrm{d}q' \mathrm{d}q$$

$$\int_{\mathcal{Q}} \rho(q) \mathrm{d}q = N$$

Maier-Saupe Free Energy

Here we apply the general mean-field theory presented so far to London **dispersion forces** interactions between **non-polar** molecules.

London dispersion forces

- Liquid crystal molecules are thought of as being both **neutral** and with **no** permanent **dipole**.

- However, **instantaneous** dipoles can arise in a molecule and the electric field thus created can **polarize** a nearby molecule.

- Though the (time) average of dipoles **vanishes** in each molecule, the average energy between induced dipoles **does not** vanish and results in an **attractive** interaction.

- This basic interaction mechanism can easily be understood classically, but the evaluation of the induced dipole can only be achieved via a **quantum mechanics** (perturbative) computation, relying on a number of **approximations**.

Unsöld approximation

Assume that all states in the molecules that contribute to their dispersion interaction have excitation energies close to E_0.

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UNSÖLD (1927), LONDON (1930,1937)

dispersion energy

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$$U_{\text{disp}} = -\frac{C}{r^6}\mathbf{U}(\boldsymbol{e}_r)\boldsymbol{\alpha}_{\text{mol}}\mathbf{U}(\boldsymbol{e}_r) \cdot \boldsymbol{\alpha}'_{\text{mol}} \qquad C = \frac{3}{4}\frac{E_0}{(4\pi)^2}$$

<div align="center">

r distance between molecular centres

$\boldsymbol{\alpha}_{\text{mol}}, \boldsymbol{\alpha}'_{\text{mol}}$ molecular polarizability tensors

$\mathbf{U}(\boldsymbol{e}_r) := \boldsymbol{e}_r \otimes \boldsymbol{e}_r - \frac{1}{3}\mathbf{I}$

$\boldsymbol{e}_r$ unit vector along the line joining molecular centres

</div>

degrees of freedom

Molecules are treated as rigid particles:

$$\mathcal{Q} = \mathcal{B} \times \Omega$$

$\mathcal{B}$ region in space of volume V

Ω orientational manifold

$$q = (\boldsymbol{x}, \omega)$$

$\boldsymbol{x}$ position vector of molecular centre

ω orientational degrees of freedom (e.g. Euler angles)

attractive potential

$$U^{(A)}(q, q') := \begin{cases} U_{\mathrm{disp}} & r \geqq R \\ 0 & r < R \end{cases}$$

spatially homogeneous density

$$\rho(q) = \underbrace{\rho_0}_{\frac{N}{V}} \varrho(\omega)$$

$$\int_{\mathcal{Q}} \rho(q)\mathrm{d}q = N \int_{\Omega} \varrho(\omega)\mathrm{d}\omega = N \quad \Rightarrow \quad \int_{\Omega} \varrho(\omega)\mathrm{d}\omega = 1$$

effective potential

$$\mathcal{E}(\boldsymbol{x},\omega) = \frac{1}{2}\int_{\mathscr{B}\times\Omega} \rho_0 \varrho(\omega')U^{(A)}(\boldsymbol{x},\omega;\boldsymbol{x}',\omega')\mathrm{d}\boldsymbol{x}'\mathrm{d}\omega'$$

$$= -\frac{1}{2}\int_{\Omega}\left(\int_{R}^{\infty}\frac{C\rho_0}{r^4}\int_{\mathbb{S}^2}\mathbf{U}(\boldsymbol{e}_r)\boldsymbol{\alpha}_{\mathrm{mol}}(\omega)\mathbf{U}(\boldsymbol{e}_r)\mathrm{d}r\mathrm{d}A(\boldsymbol{e}_r)\right)\cdot\boldsymbol{\alpha}_{\mathrm{mol}}(\omega')\varrho(\omega')\mathrm{d}\omega'$$

$$= -\frac{2\pi C\rho_0}{135R^3}\int_{\Omega}\boldsymbol{\alpha}_{\mathrm{mol}}(\omega)\cdot\boldsymbol{\alpha}_{\mathrm{mol}}(\omega')\varrho(\omega')\mathrm{d}\omega' + \mathrm{constant}$$

in the ***thermodynamic limit***, $N,V \to \infty$ with ρ_0 unchanged.

uniaxial molecules

$$\Omega = \mathbb{S}^2$$

$$\boldsymbol{\alpha}_{\mathrm{mol}}(\omega) = (\alpha_\parallel - \alpha_\perp)\mathbf{q}(\omega) + \frac{1}{3}(2\alpha_\perp + \alpha_\parallel)\mathbf{I}$$

$$\mathbf{q}(\omega) = \boldsymbol{m}(\omega) \otimes \boldsymbol{m}(\omega) - \tfrac{1}{3}\mathbf{I} \quad \text{molecular tensor}$$

$$\mathcal{E}(\boldsymbol{x}, \omega) = -\frac{1}{2}U_0 \int_{\mathbb{S}^2} \mathbf{q}(\omega) \cdot \mathbf{q}(\omega')\varrho(\omega')\mathrm{d}\omega' \qquad U_0 := \frac{\pi}{45R^3}\frac{(\alpha_\parallel - \alpha_\perp)^2}{(4\pi)^2}E_0\rho_0$$

$$= -\frac{1}{2}U_0' \int_{\mathbb{S}^2} P_2(\boldsymbol{m}(\omega) \cdot \boldsymbol{m}(\omega'))\varrho(\omega')\mathrm{d}\omega' \qquad U_0' := \frac{2}{3}U_0$$

$\mathcal{E}$ is independent of $\boldsymbol{x}$

$$\mathcal{E}(\omega) = -\frac{1}{2}U_0 \int_{\mathbb{S}^2} \mathbf{q}(\omega) \cdot \mathbf{q}(\omega')\varrho(\omega')\mathrm{d}\omega'$$

Free-energy functional

$$\mathscr{F}[\rho] := kT \int_{\mathcal{Q}} \rho(q) \ln \rho(q) \mathrm{d}q + \frac{1}{2} \int_{\mathcal{Q}^2} \rho(q') \rho(q) U^{(A)}(q', q) \mathrm{d}q' \mathrm{d}q$$

$$= kT \int_{\mathcal{Q}} \rho(q) \ln \rho(q) \mathrm{d}q + \int_{\mathcal{Q}} \mathcal{E}(\omega) \rho(q) \mathrm{d}q$$

$$q = (\boldsymbol{x}, \omega)$$

$$\rho(q) = \rho_0 \varrho(\omega)$$

$$\mathscr{F}_{\mathrm{MS}}[\rho] = kTN \int_{\mathbb{S}^2} \varrho(\omega) \ln(\rho_0 \varrho(\omega)) \mathrm{d}\omega$$

$$- \frac{1}{2} U_0 N \int_{\mathbb{S}^2 \times \mathbb{S}^2} \varrho(\omega') \varrho(\omega) \mathbf{q}(\omega') \cdot \mathbf{q}(\omega) \mathrm{d}\omega' \mathrm{d}\omega$$

$$\int_{\mathbb{S}^2} \varrho(\omega) \mathrm{d}\omega = 1$$

(dimensionless) free-energy per particle

$$F_{\mathrm{MS}}[\varrho] := \frac{1}{NkT}\mathscr{F}_{\mathrm{MS}}[\rho] = \int_{\mathbb{S}^2} \varrho(\omega)\ln\varrho(\omega)\mathrm{d}\omega$$

$$- \frac{1}{2}\beta \int_{\mathbb{S}^2\times\mathbb{S}^2} \varrho(\omega')\varrho(\omega)\mathbf{q}(\omega')\cdot\mathbf{q}(\omega)\mathrm{d}\omega'\mathrm{d}\omega$$

$$\beta := \frac{U_0}{kT} \quad \text{dimenionless reciprocal temperature}$$

first variation

$$\delta F_{\mathrm{MS}}(\varrho)[\delta\varrho] = \int_{\mathbb{S}^2}\left[(1-\lambda) + \ln\varrho(\omega) - \beta\left(\int_{\mathbb{S}^2}\mathbf{q}(\omega')\varrho(\omega')\mathrm{d}\omega'\right)\cdot\mathbf{q}(\omega)\right]\delta\varrho(\omega)\mathrm{d}\omega$$

λ Lagrange multiplier for $\int_{\mathbb{S}^2}\varrho(\omega)\mathrm{d}\omega = 1$

equilibrium density

$$\varrho_{\mathrm{eq}}(\omega) = \frac{\mathrm{e}^{\beta\left(\int_{\mathbb{S}^2} \mathbf{q}(\omega')\varrho_{\mathrm{eq}}(\omega')\mathrm{d}\omega'\right)\cdot\mathbf{q}(\omega)}}{\int_{\mathbb{S}^2} \mathrm{e}^{\beta\left(\int_{\mathbb{S}^2} \mathbf{q}(\omega')\varrho_{\mathrm{eq}}(\omega')\mathrm{d}\omega'\right)\cdot\mathbf{q}(\omega)}\mathrm{d}\omega} = \frac{\mathrm{e}^{\beta\mathbf{Q}\cdot\mathbf{q}(\omega)}}{\int_{\mathbb{S}^2} \mathrm{e}^{\beta\mathbf{Q}\cdot\mathbf{q}(\omega)}\mathrm{d}\omega}$$

$$\mathbf{Q} = \int_{\mathbb{S}^2} \mathbf{q}(\omega')\varrho_{\mathrm{eq}}(\omega')\mathrm{d}\omega'$$

- The integral equilibrium equation for ϱ_{eq} becomes the ***self-consistency*** equation for the order tensor $\mathbf{Q}$.

- $\mathbf{Q} = \mathbf{0}$, and $\varrho_{\mathrm{eq}} = \varrho_0 \equiv \frac{1}{4\pi}$, is a solution for all β.

(rescaled) equilibrium free energy

$$f_{\mathrm{MS}}(\beta, \mathbf{Q}) := \frac{1}{\beta}\left(F_{\mathrm{MS}}[\varrho_{\mathrm{eq}}] + \ln 4\pi\right) = \frac{1}{2}\mathbf{Q}\cdot\mathbf{Q} - \frac{1}{\beta}\ln\left(\frac{1}{4\pi}\int_{\mathbb{S}^2} e^{\beta\mathbf{Q}\cdot\mathbf{q}(\omega)}\mathrm{d}\omega\right)$$

$$f_{\mathrm{MS}}(\beta, \mathbf{0}) = 0 \quad \text{for all} \quad \beta$$

critical points

$$\frac{\partial f_{\mathrm{MS}}}{\partial \mathbf{Q}} = \mathbf{Q} - \frac{\int_{\mathbb{S}^2}\mathbf{q}(\omega)e^{\beta\mathbf{Q}\cdot\mathbf{q}(\omega)}\mathrm{d}\omega}{\int_{\mathbb{S}^2}e^{\beta\mathbf{Q}\cdot\mathbf{q}(\omega)}\mathrm{d}\omega}$$

$$\frac{\partial f_{\mathrm{MS}}}{\partial \mathbf{Q}} = \mathbf{0} \quad \Leftrightarrow \quad \mathbf{Q} = \langle\mathbf{q}\rangle_{\varrho_{\mathrm{eq}}}$$

The critical points of f_{MS} are solutions to the ***self-consistency*** equation for $\mathbf{Q}$ and have necessarily ***admissible*** eigenvalues.

critical point properties

- We regard $f_{\mathrm{MS}}(\beta, \cdot)$ as defined in the ***whole space*** of symmetric traceless tensors.

- But $f_{\mathrm{MS}}(\beta, \mathbf{Q})$ represents the mean-field free energy only at its critical points $\mathbf{Q}$. Its non-critical values are physically irrelevant.

- For given β, the order tensor $\mathbf{Q}$ at which $f_{\mathrm{MS}}(\beta, \cdot)$ attains its ***least critical value*** represents the ***stable*** equilibrium phase.

- $\mathbf{Q} = \mathbf{0}$ is a critical point of $f_{\mathrm{MS}}(\beta, \cdot)$ for all values of β.

- $f_{\mathrm{MS}}(\beta, \cdot)$ is an ***isotropic*** function:
$$f_{\mathrm{MS}}(\beta, \mathbf{R}\mathbf{Q}\mathbf{R}^{\mathsf{T}}) = f_{\mathrm{MS}}(\beta, \mathbf{Q}) \qquad \forall\, \mathbf{R} \in \mathsf{O}(3).$$

- If $\mathbf{Q} \neq \mathbf{0}$ is a critical point of $f_{\mathrm{MS}}(\beta, \cdot)$, then $\mathbf{Q}$ is ***uniaxial***.

FATKULLIN & SLASTIKOV (2005)

LIU, H. ZHANG & P. ZHANG (2005)

$$\mathbf{Q} = S\left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I}\right) + T\left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y\right).$$

reduced free energy

$$f_{\mathrm{MS}}(\beta, \mathbf{Q}) = f_{\mathrm{s}}(\beta, S, T)$$

$$f_{\mathrm{s}}(\beta, S, T) := \frac{1}{3}S^2 + T^2 - \frac{1}{\beta}\ln\frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\mathrm{e}^{\beta g_{\mathrm{s}}(\vartheta,\varphi;S,T)}\sin\vartheta\mathrm{d}\vartheta$$

$$g_{\mathrm{s}}(\vartheta, \varphi; S, T) = S\left(\cos^2\vartheta - \frac{1}{3}\right) + T\sin^2\vartheta\cos 2\varphi$$

coercivity

$$|g_{\mathrm{s}}| < \frac{2}{3}|S| + |T| \quad \Rightarrow \quad f_{\mathrm{s}}(\beta, S, T) > \frac{1}{3}S^2 + T^2 - \frac{2}{3}|S| - |T|$$

- $f_{\mathrm{s}}(\beta, \cdot, \cdot)$ enjoys a 6-fold symmetry in the ***admissible triangle***.

- All critical points of $f_{\mathrm{s}}(\beta, \cdot, \cdot)$ lie on the ***uniaxial lines***.
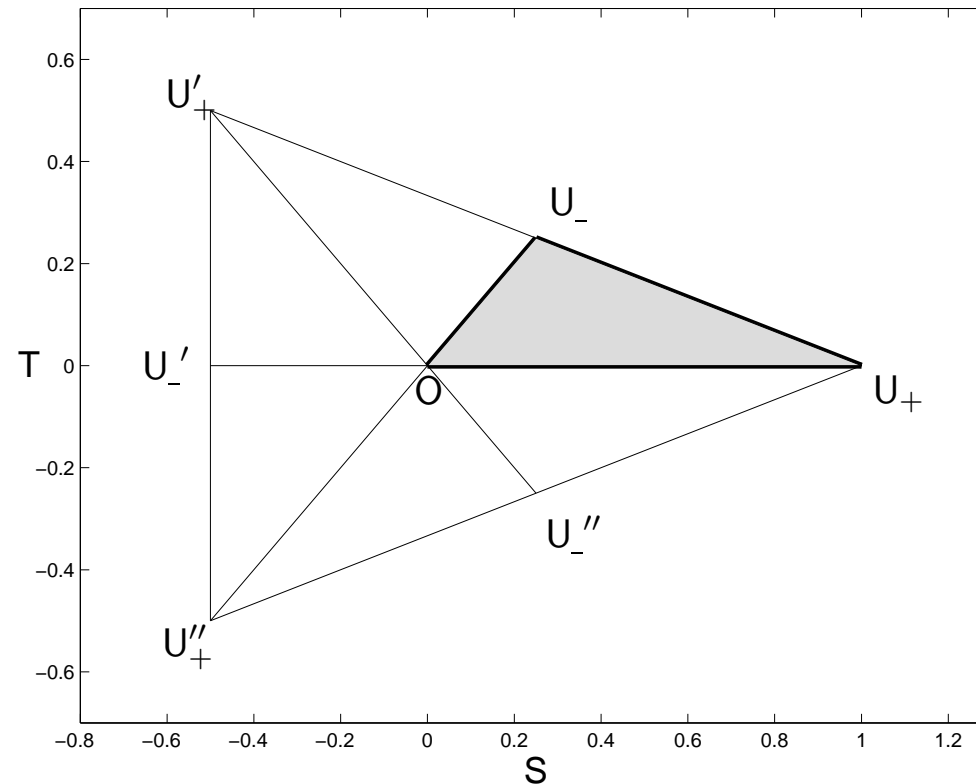
We shall restrict the search for the critical values of f_{s} to $T = 0$.

restricted free energy

$$\frac{\partial f_{\mathrm{s}}}{\partial T}(\beta, S, 0) = 0 \quad \forall\ \beta,\ S$$

$$\Downarrow$$

All critical points $(S_0, 0)$ of $f_{\mathrm{s}}(\beta, \cdot, \cdot)$ are critical points of

$$f_{\mathrm{u}}(\beta, S) := f_{\mathrm{s}}(\beta, S, 0) = \frac{1}{3}S^2 - \frac{1}{\beta}\ln\frac{1}{2}\int_0^\pi e^{\beta S\left(\cos^2\vartheta - \frac{1}{3}\right)}\sin\vartheta\,\mathrm{d}\vartheta$$

$$f_{\mathrm{u}}(\beta, S) = \frac{1}{3}S^2 - \frac{2}{3}S - \frac{1}{\beta}\ln\left(\frac{\mathsf{daw}\left(\sqrt{\beta S}\right)}{\sqrt{\beta S}}\right)$$

$$\mathsf{daw}(x) := e^{-x^2}\int_0^x e^{t^2}\,\mathrm{d}t$$

Dawson's integral
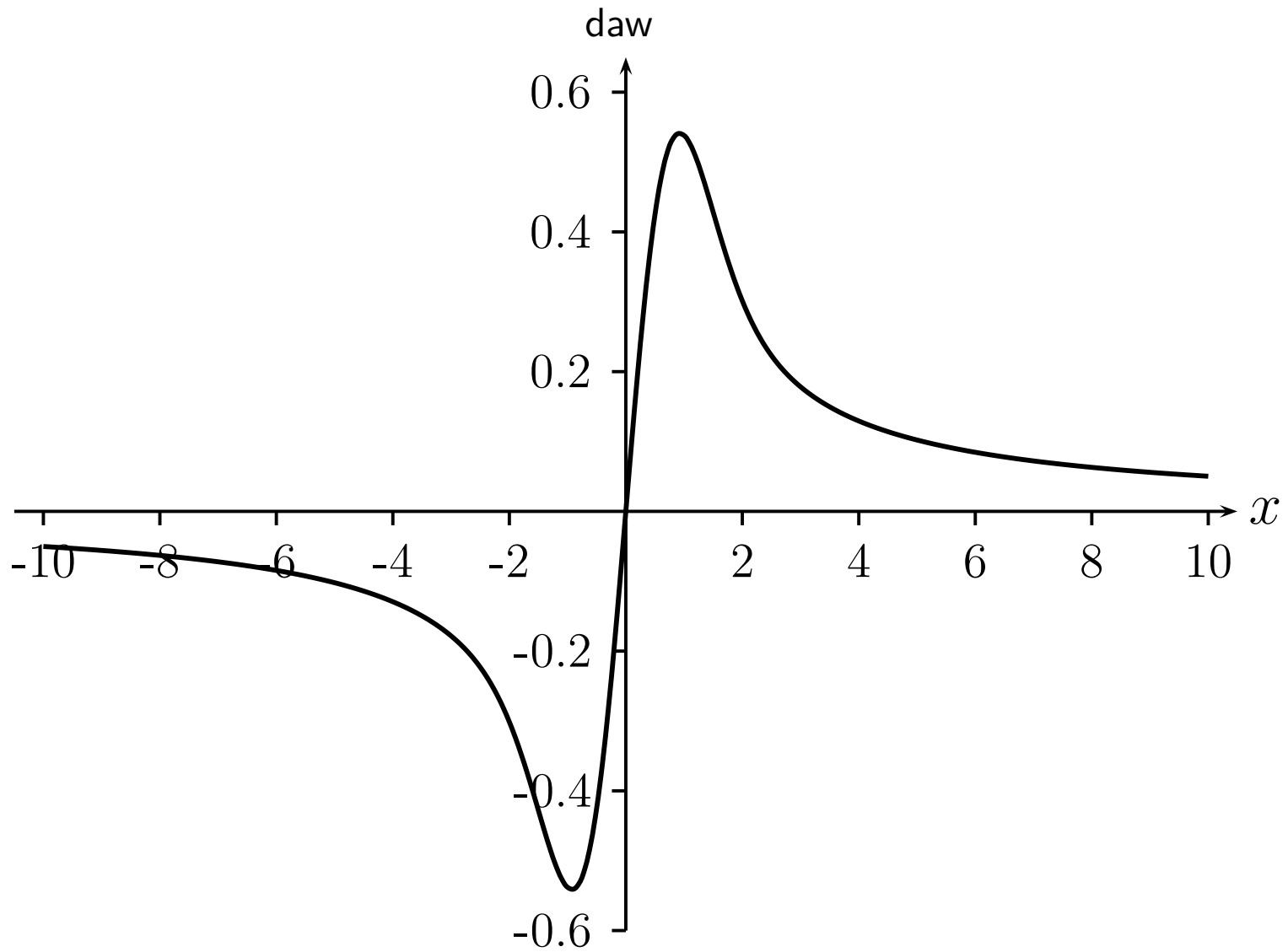
change of variables

$$x := \beta S$$

$$f_{\mathrm{u}}\left(\beta, \frac{x}{\beta}\right) = \frac{1}{\beta}\left\{\frac{1}{3\beta}x^2 - \frac{2}{3}x - \ln\left(\frac{\mathsf{daw}\left(\sqrt{x}\right)}{\sqrt{x}}\right)\right\}$$

equilibria

$$\frac{\partial f_{\mathrm{u}}}{\partial S} = \frac{2x}{3}\left(\frac{1}{\beta} - G(x)\right)$$

$$G(x) := \frac{3}{4x\sqrt{x}\,\mathsf{daw}\left(\sqrt{x}\right)} - \frac{3}{4x^2} - \frac{1}{2x}$$

$$\lim_{x \to 0} G(x) = \frac{2}{15}$$

$$G(x) \approx \frac{1}{x} \quad \text{for} \quad x \to +\infty \qquad G(x) \approx -\frac{1}{2x} \quad \text{for} \quad x \to -\infty$$

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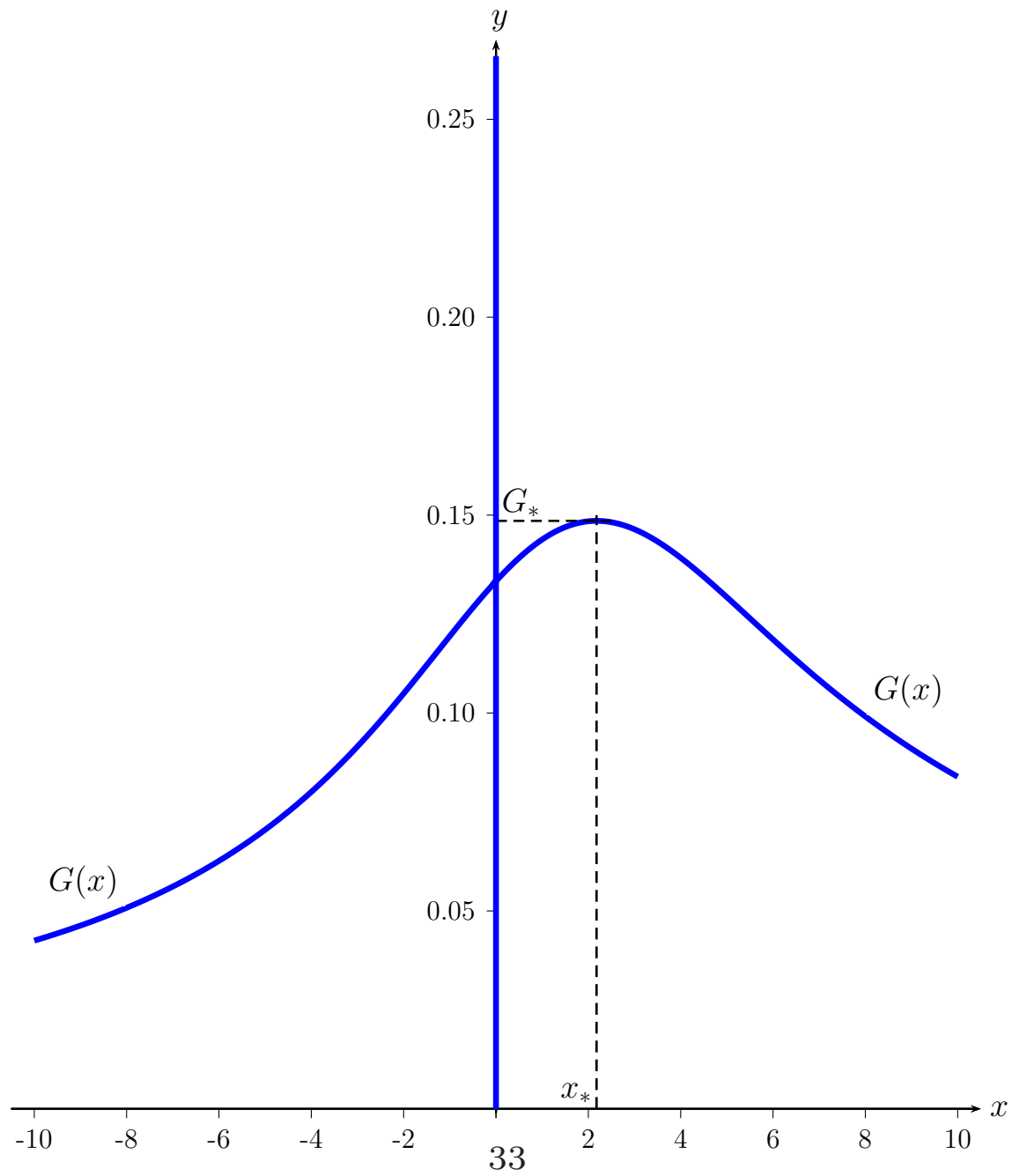
local uniaxial stability

- For $\frac{1}{\beta} > G_* \doteq 0.149$ there is only **one** equilibrium solution, $S = 0$.

- For $\frac{1}{\beta} < G_* \doteq 0.149$ there are **two extra** equilibrium solutions.

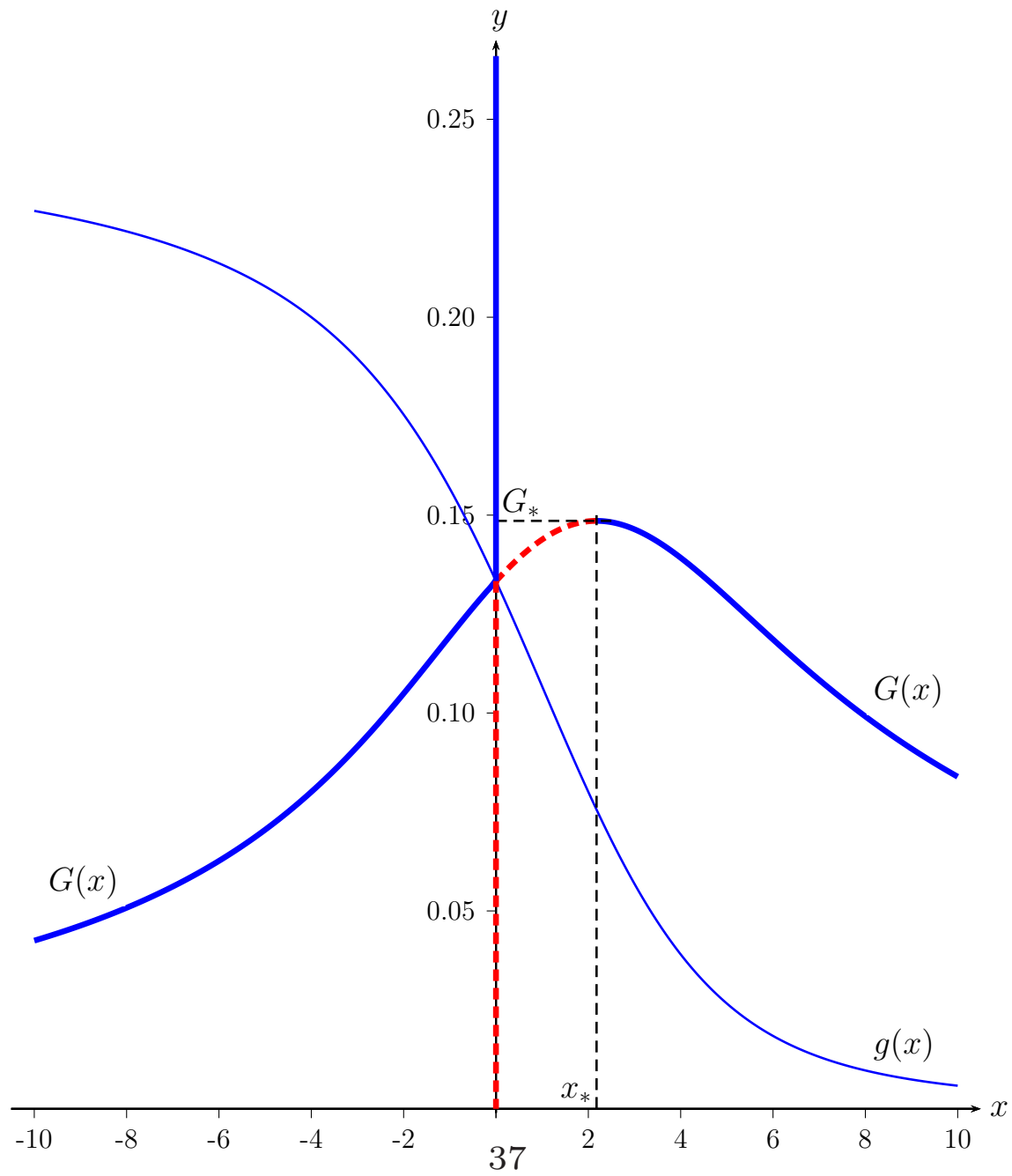- One of the extra solutions has $S < 0$ for $\frac{1}{\beta} < \frac{2}{15}$.

$$\frac{\partial^2 f_{\mathrm{u}}}{\partial S^2} = \frac{2\beta}{3} \left\{ \underbrace{\left(\frac{1}{\beta} - G(x) \right)}_{0 \text{ at equilibrium}} - xG'(x) \right\}$$
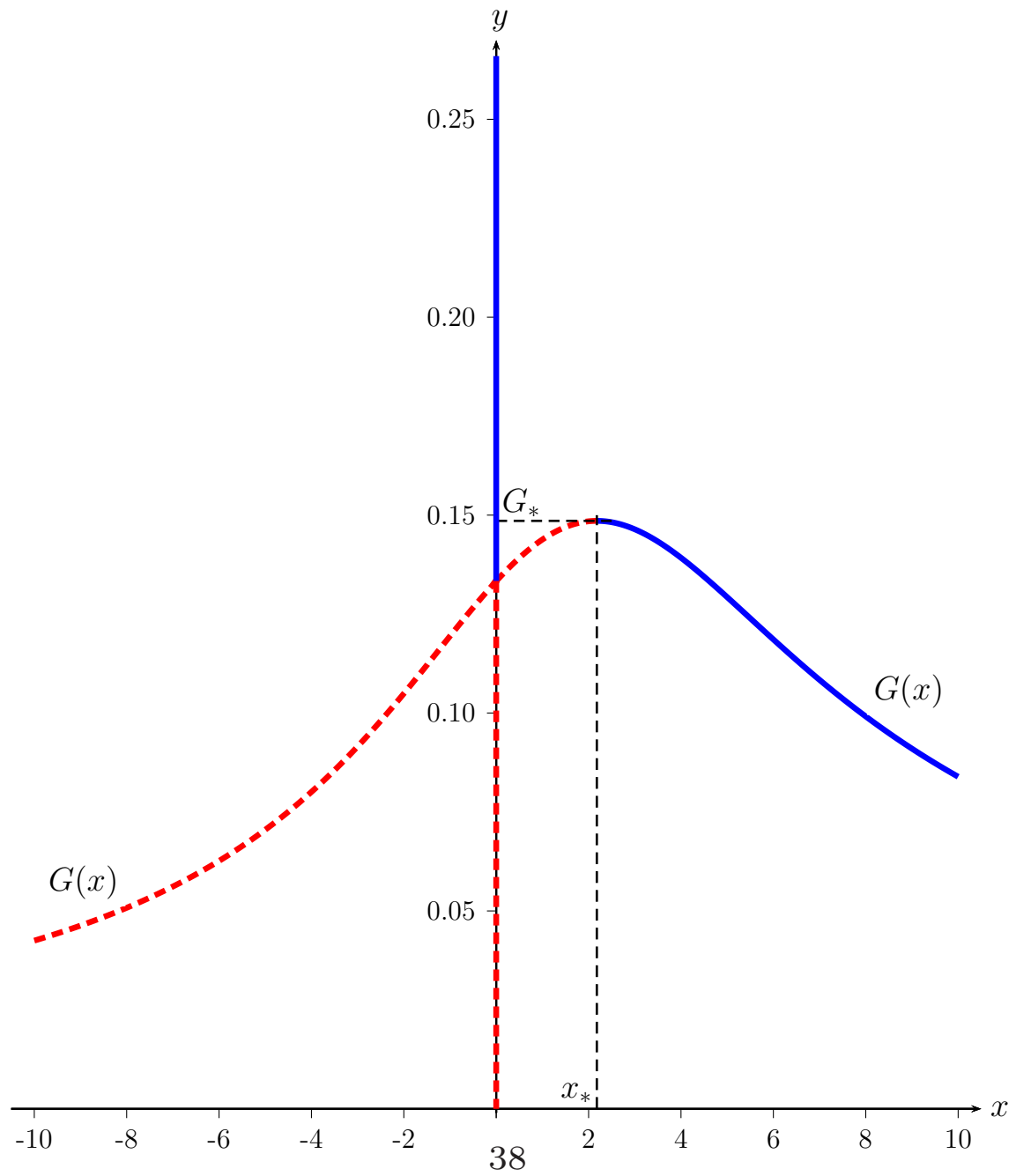
34
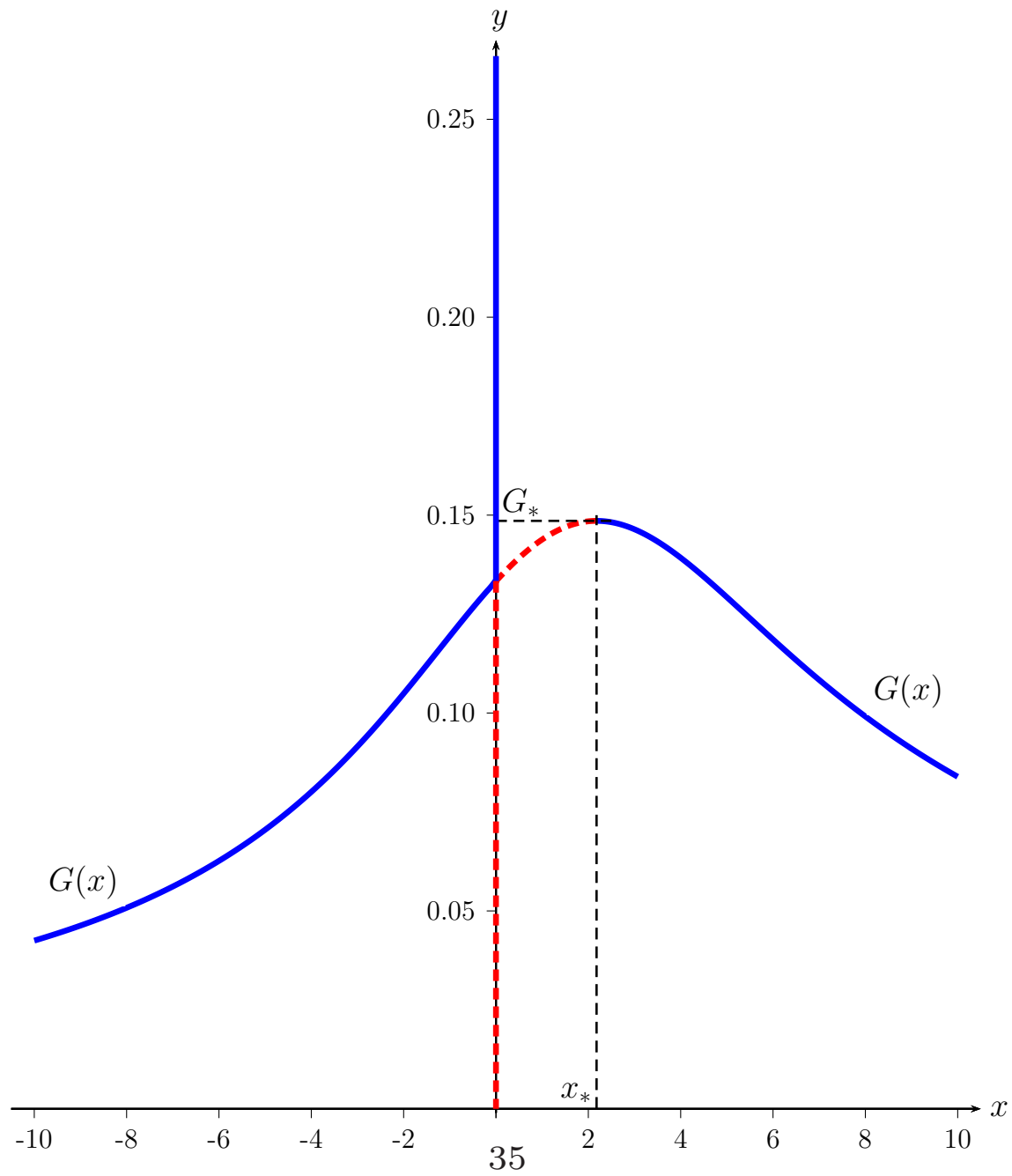
local biaxial stability

$$f_{\mathrm{s}}(\beta, S, T) = f_{\mathrm{u}}(\beta, S) + \beta \underbrace{\left(\frac{1}{\beta} - g\left(\beta S\right) \right)}_{\color{red}{G(\beta S) - g(\beta S)}} T^2 + O\left(T^4\right)$$

$$g(x) := \frac{1}{4} + \frac{1}{4x} + \frac{3}{16x^2} - \frac{1}{8\sqrt{x}\,\mathsf{daw}\left(\sqrt{x}\right)} - \frac{3}{16x\sqrt{x}\,\mathsf{daw}\left(\sqrt{x}\right)}.$$

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absolute minimizer

- The free energy vanishes on the isotropic phase:

$$f_{\mathrm{u}}(\beta, 0) = 0$$
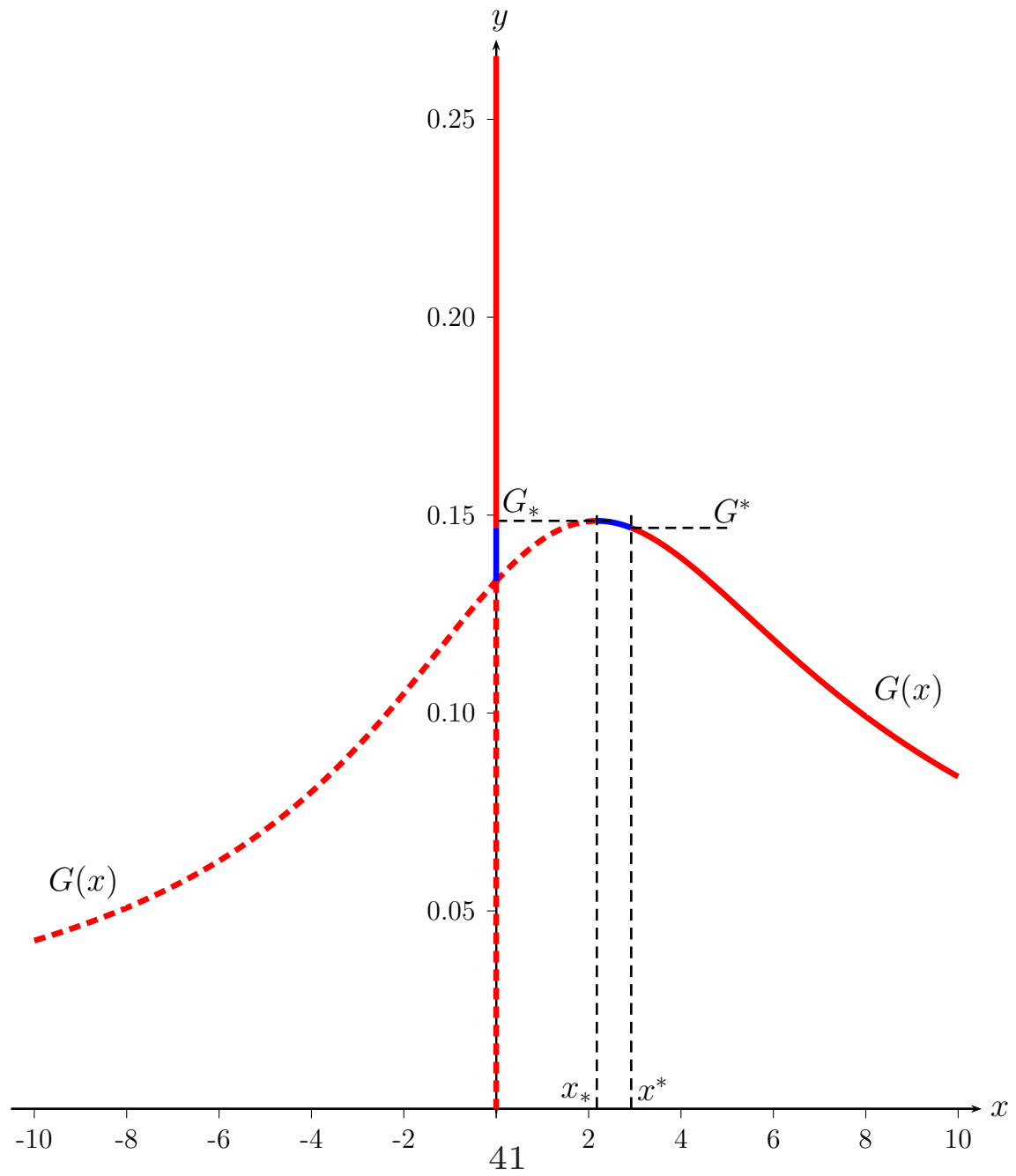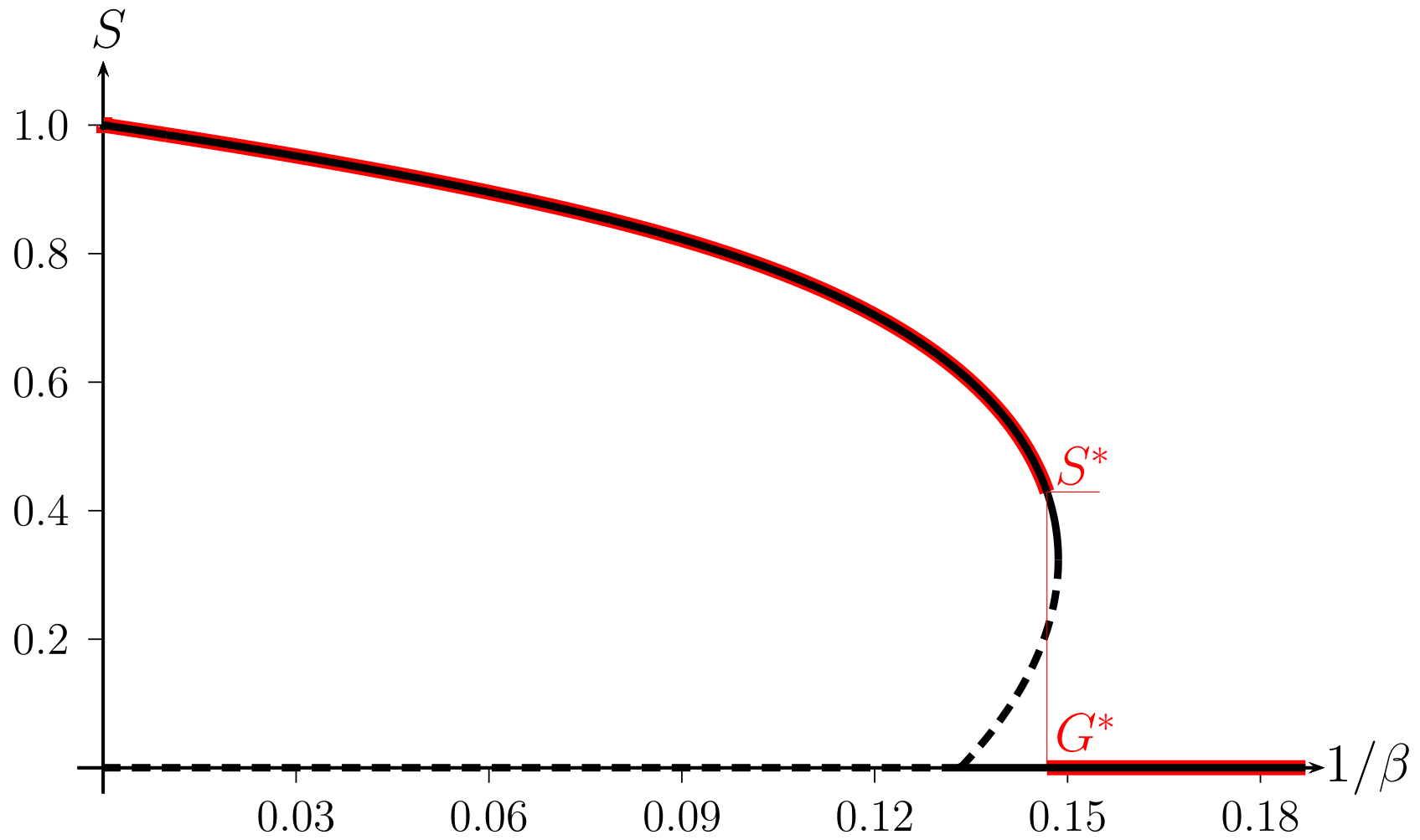
- The free energy of the competing locally stable nematic phase is ***negative*** whenever

$$G(x) < F(x)$$

$$F(x) := \frac{1}{x} + \frac{3}{x^2} \ln \left(\frac{\mathsf{daw}\left(\sqrt{x}\right)}{\sqrt{x}} \right)$$

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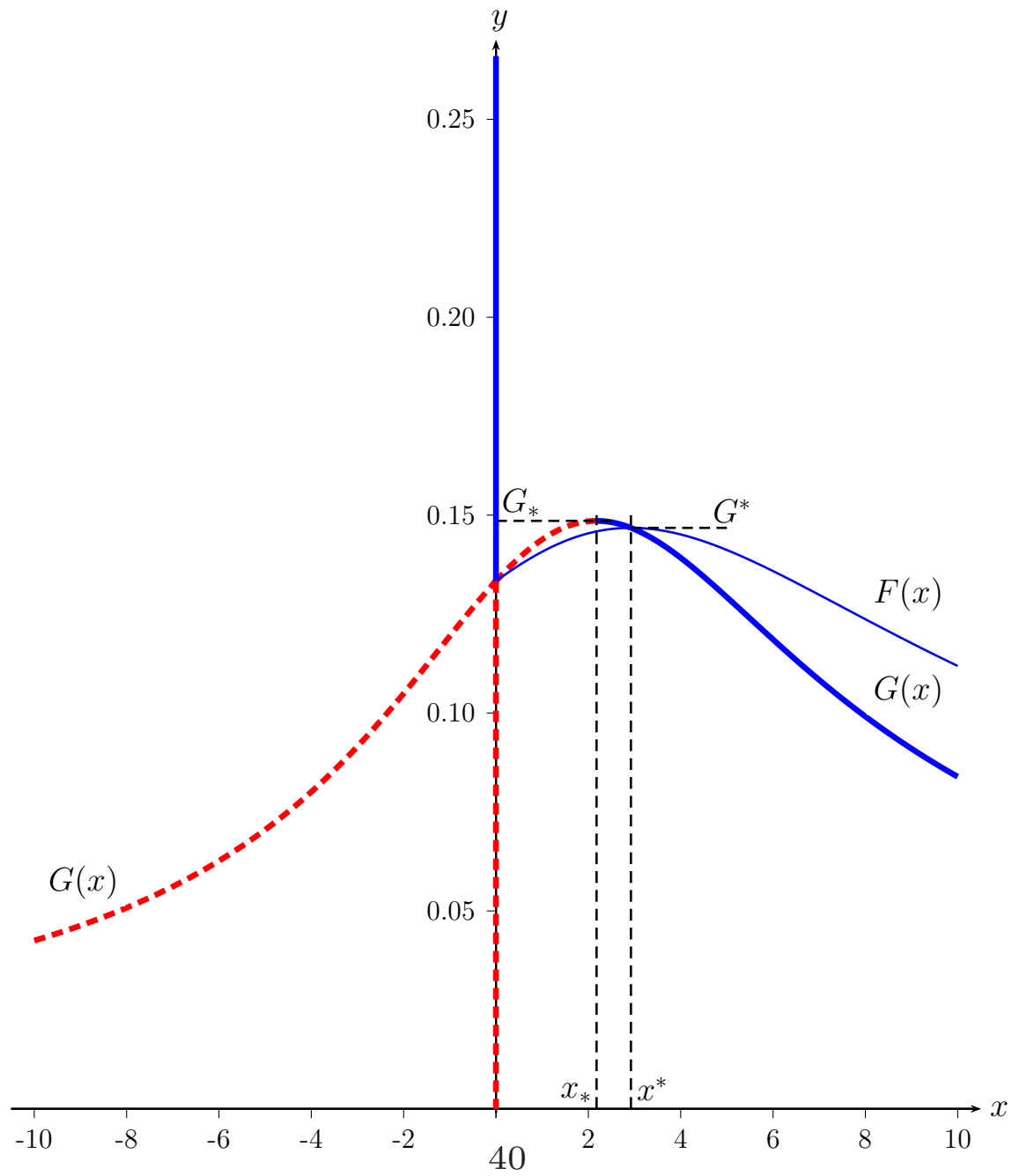
$$x^* \doteq 2.923 \qquad G^* \doteq 0.147 \qquad S^* = x^* G^* \doteq 0.429$$

Sources

- I. FATKULLIN & V. SLASTIKOV, Critical points of the Onsager functional on a sphere, *Nonlinearity*, **18**, 2005, 2565–2580.

- E.C. GARTLAND, JR., & E.G. VIRGA, Minimum principle for indefinite mean-field free energies, *Arch. Rational Mech. Anal.*, **196**, 2010, 143–189.

- J.W. GIBBS, *Elementary Principles in Statistical Mechanics*, Charles Scribners's Sons, New York, 1902. Digitally reprinted by Cambridge University Press, Cambridge, 2010.

- H. LIU, H. ZHANG & P. ZHANG, Axial symmetry and classification of stationary solutions of Doi-Onsager equation on the sphere with Maier-Saupe potential, *Comm. Math. Sci.*, **3**, 2005, 201–208.

- F. LONDON, The general theory of molecular forces, *Trans. Faraday Soc.*, **33**, 1937, 8–26.

- W. Maier & A. Saupe, Eine einfache molekulare Theorie des nematischen kristallinflüssigen Zustandes, **Z. Naturforsch.**, **13a**, 1958, 564–566.

- P. Palffy-Muhoray, M.Y. Pevnyi, E.G. Virga & X. Zheng, The effects of particle shape in orientationally ordered soft materials, in **Mathematics and Materials**, vol. **23**, PCMS Series, AMS, 2017, **in press**.

- M. Kleman & O.D. Lavrentovich, **Soft Matter Physics: An Introduction**, Springer-Verlag, New York, 2003.

- J.V. Selinger, **Introduction to the Theory of Soft Matter: From Ideal Gases to Liquid Crystals**, Springer, Cham, 2016.

- A.M. Sonnet & E.G. Virga, **Dissipative Ordered Fluids: Theories for Liquid Crystals**, Springer Science, New York, 2012.

- A. UNSÖLD, Quantentheorie des Wasserstoffmolekülions und der Born- Landéschen Abstoßungskräfte, *Z. Phys.*, **43**, 1927, 563–574.