

Correlation Effects in Thermotropic Liquid Crystals

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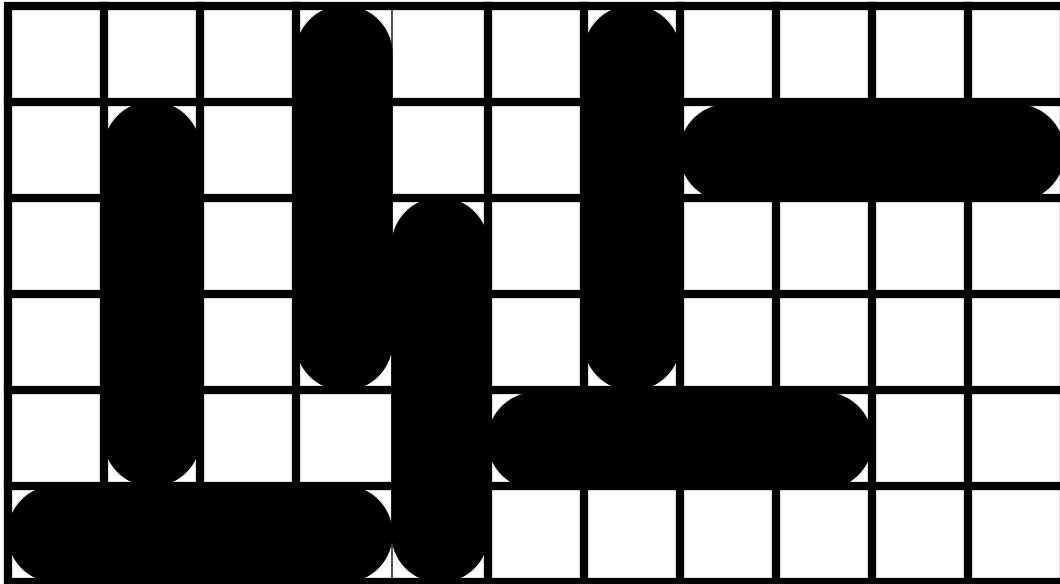
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● Flory 'Chimney' Theory for Rods

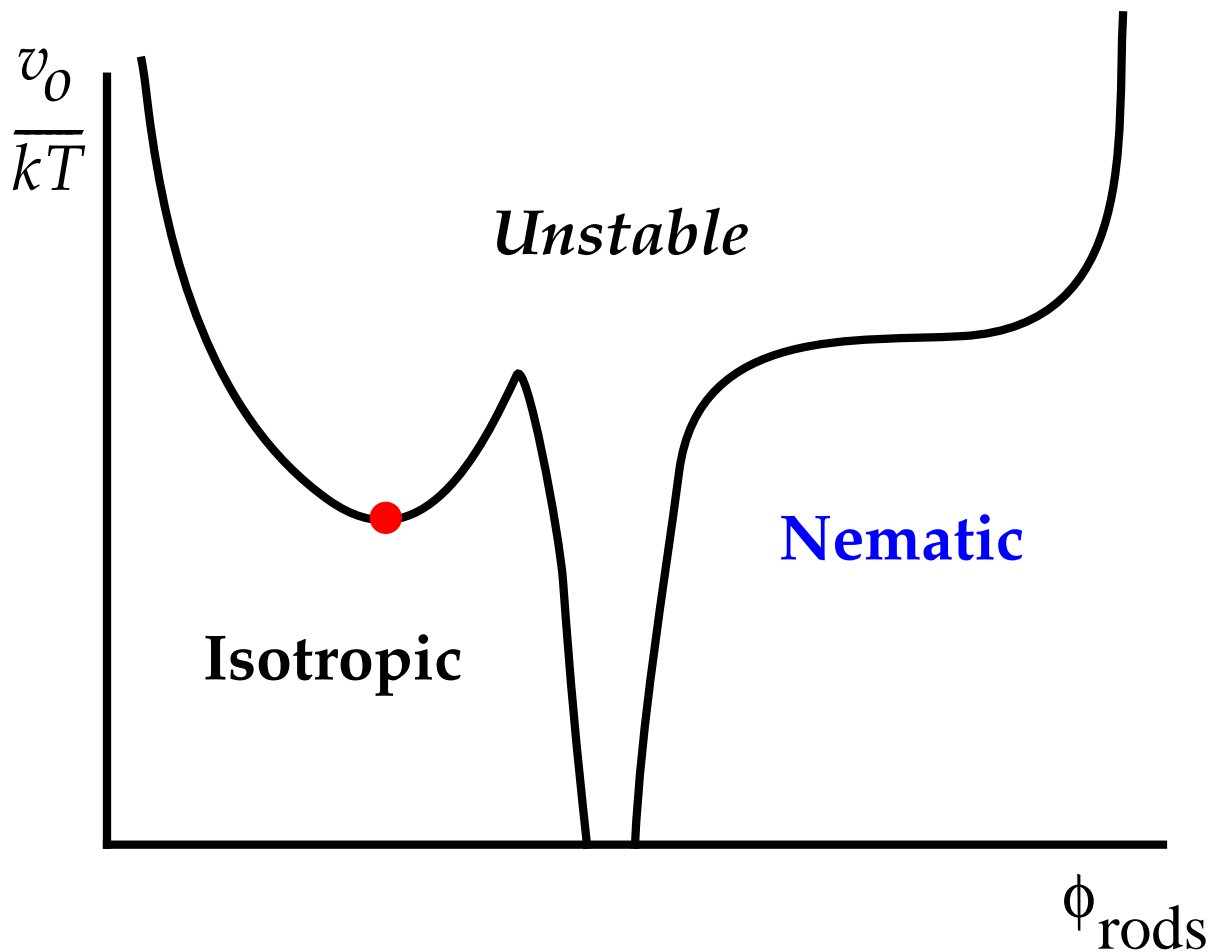
□ Entropy: incompressible lattice



- ↳ Rods align at high density
- Internal energy: mean field.
$$U = -v_0 \rho$$
 - ↳ Interactions favor high density states
 - ↳ High density increases ordering
- Mechanism: athermal, Onsager

● Chimney Phase diagram

- Chimney widens as v_0 increases (cooling).

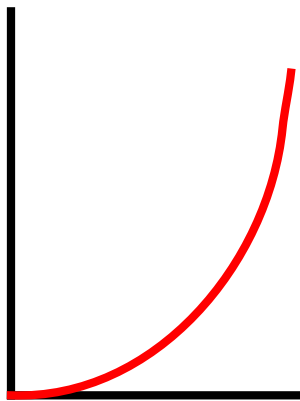


- Isotropic-**Nematic** coexistence pushed to small and high density.
- No attempt at including correlations in U

- **Effect that correlations might have**

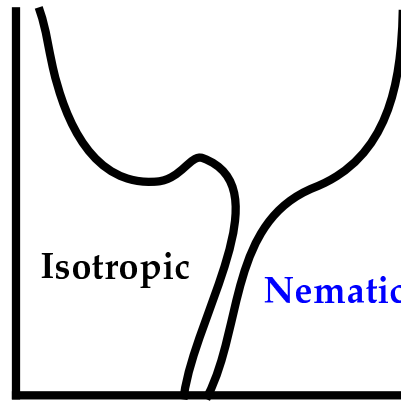
- **Favoring isotropic over nematic**

Energy



Alignment

$\frac{v_0}{kT}$

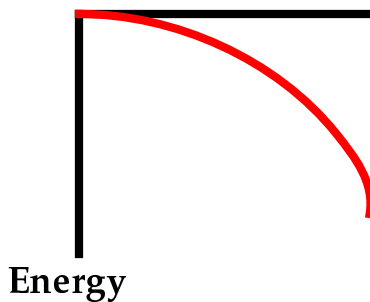


Have to go to higher density

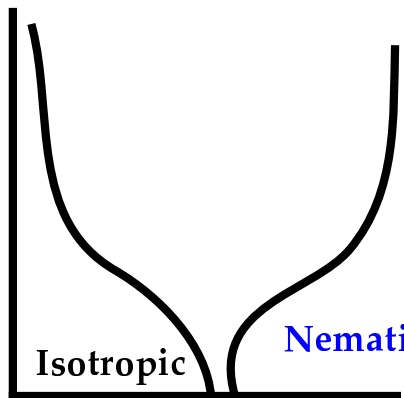
- ✦ Chimney leans: reentrancy.

- **Favoring nematic over isotropic (Meier-Saupe theory)**

Alignment



$\frac{v_0}{kT}$

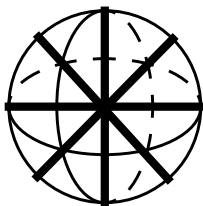


- **How to choose U ?**

● PRISM Theory for Thermotropics

- Order parameter: τ

$\tau = 0$
Isotropic



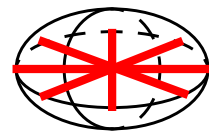
Pea

$\tau > 0$
Nematic



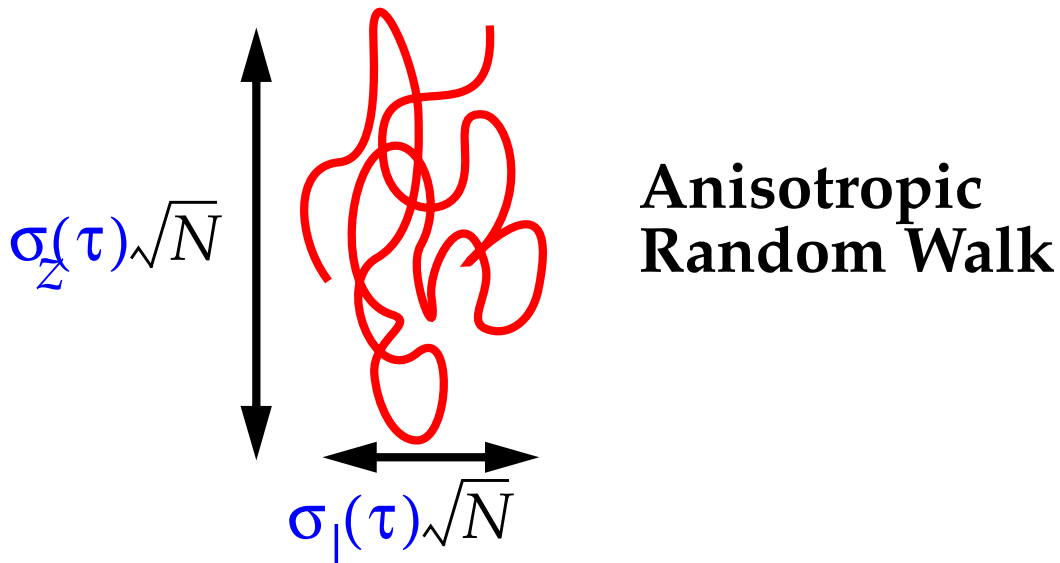
Rice

$\tau < 0$
Discotic



Lentil

- Anisotropy enters the single-chain scattering function: $\omega(\vec{q})$




- Compressibility route to get $S[\tau]$

● Free energy: Excluded Volume

- Orientation, τ determines $\omega(\vec{q})$.
- PRISM equation determines pair correlation function, $g(\vec{r})$ given
- Closure approximation for direct correlation function, $C[\vec{q}]$
 - ↪ “Wave vector cutoff closure”

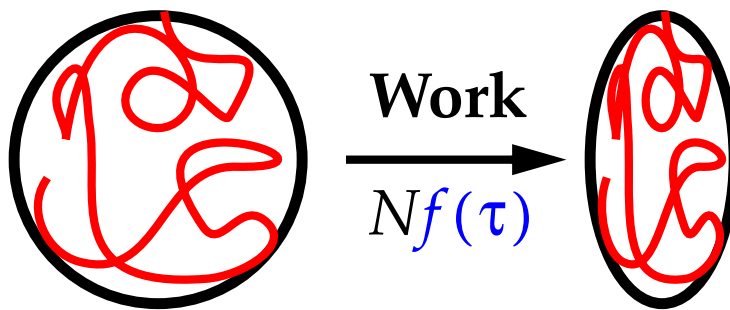
$$C(\vec{q}) = C_0 \quad \text{if } \|\vec{q}\| < \frac{\pi}{d}$$



- ↪ Direct correlations have range.
- **Hard-core constraint:** $g(\vec{r} = 0) \equiv 0$
- **Structure function, and compressibility, equation of state, free energy as a functional of τ**

● Free Energy: Orientation

- Need to do work to go from isotropic to aligned.



Gaussian chain:

$$f(\tau) = \log \frac{\sigma^3}{\sigma_{\perp}^2 \sigma_z}$$

- Stabilizes isotropic phase.

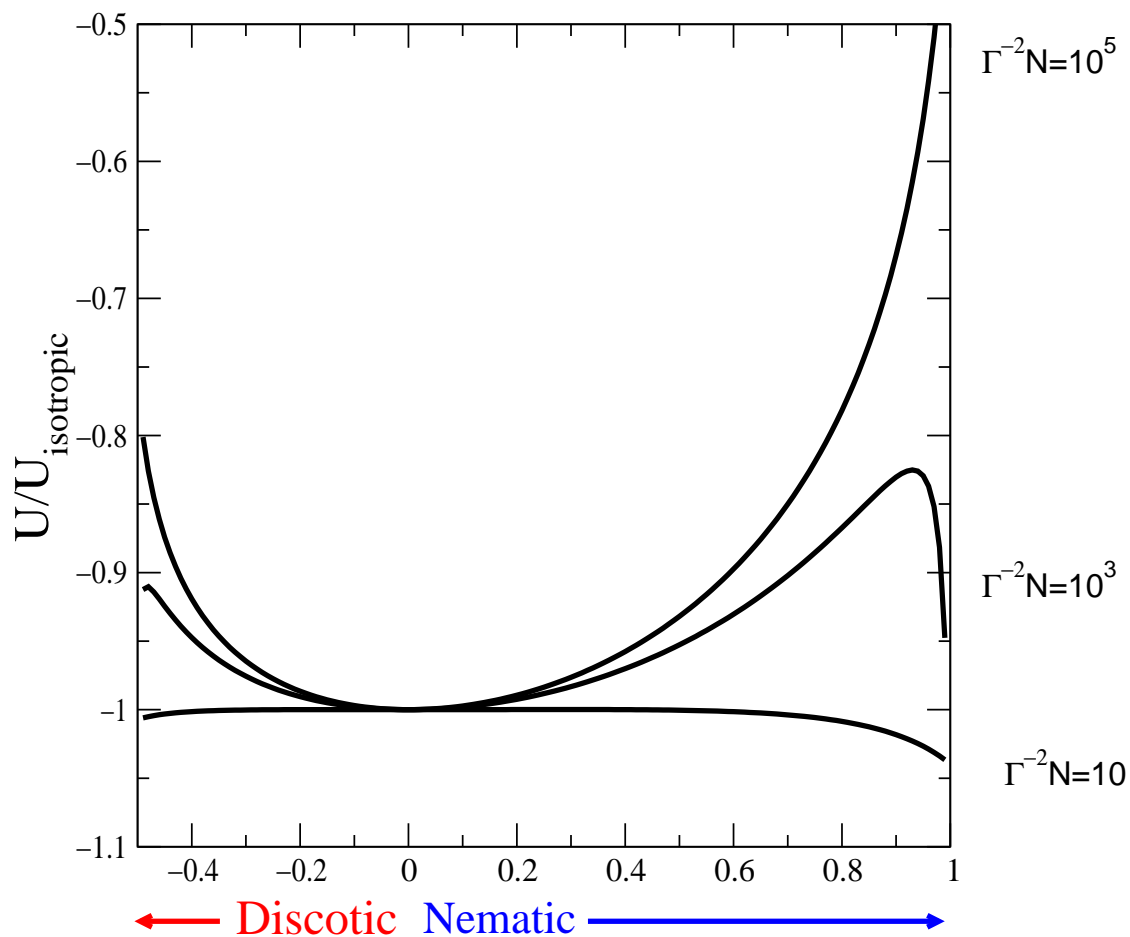
● Free Energy: Internal Energy

□ $U = \rho \int g(\vec{r}) v(\vec{r}),$ where $v(\vec{r})$ is pair-interaction.

□ Short-ranged interaction

$$v(r) = -\frac{v_0}{r/a} e^{-r/a}$$

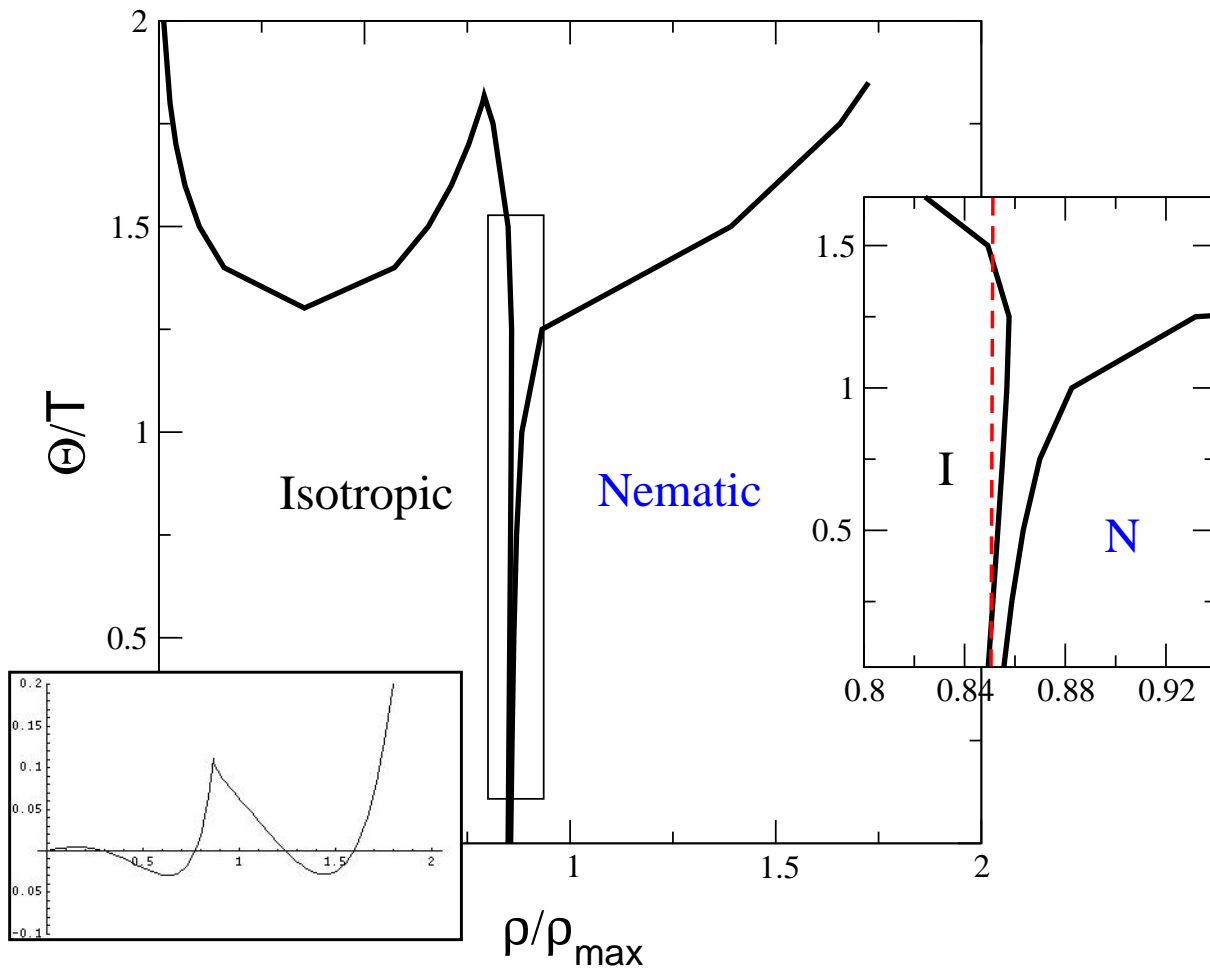
□ Pair-correlation depends on τ



● “Chimney” diagram

□ Parameters:

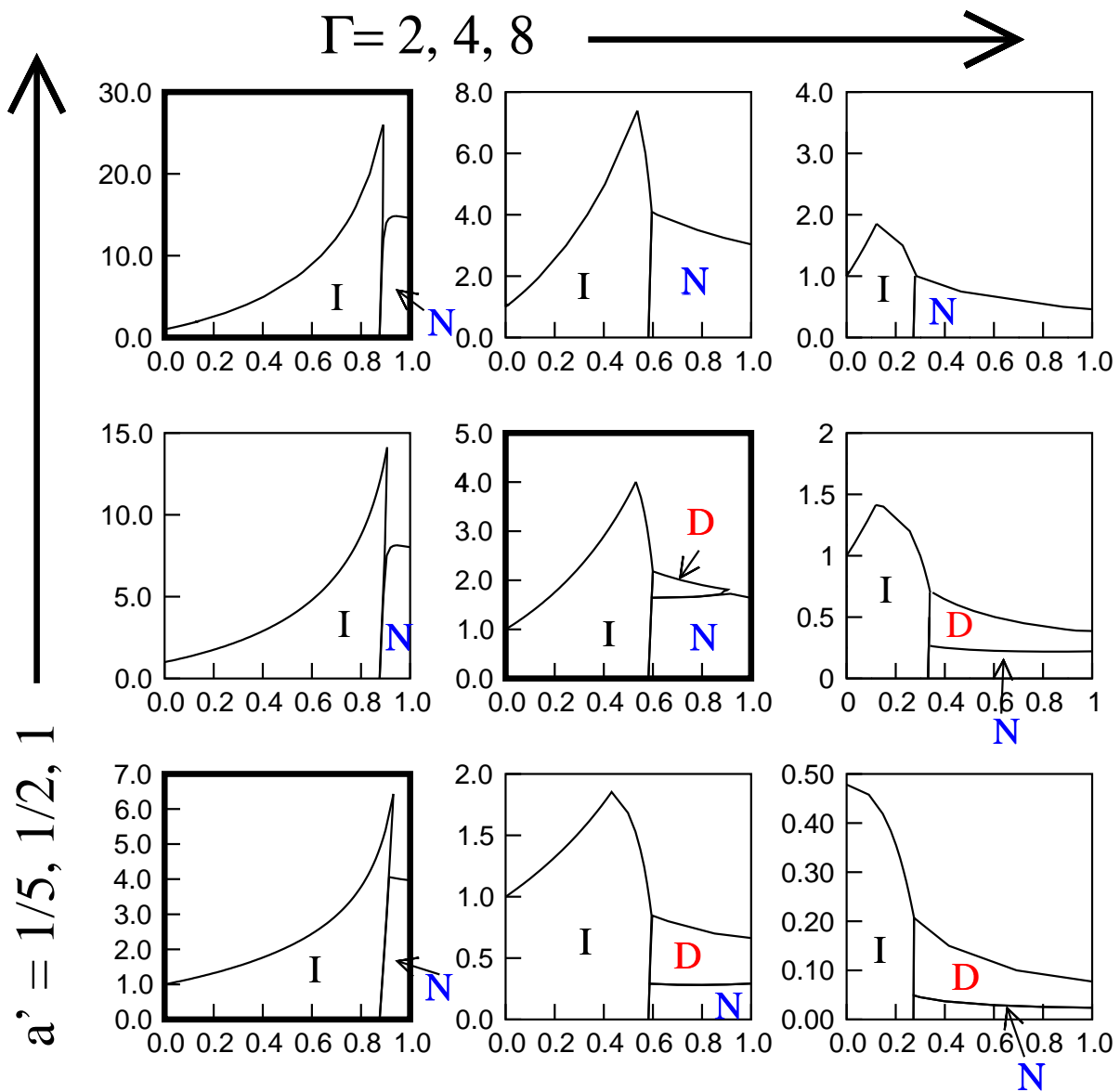
- ✦ Range of interaction $a=d$,
Statistical segment length = $2d$,
aspect ratio $\Gamma = 2, N = 100$.



- Correlations in U give reentrant Nematic.

- $N \Rightarrow \infty$, new phases.

- **Discotic ($\tau < 0$) stabilized by correlations in U**
Infinite N:

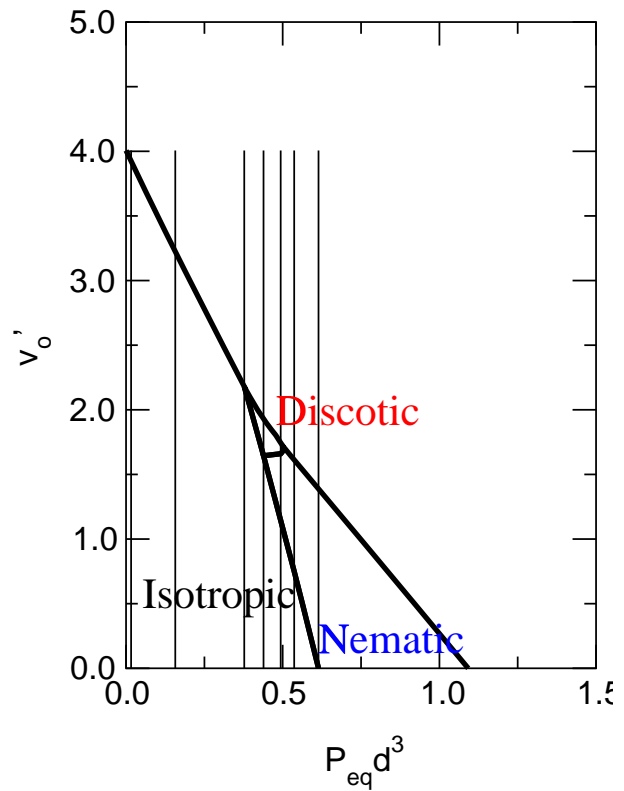
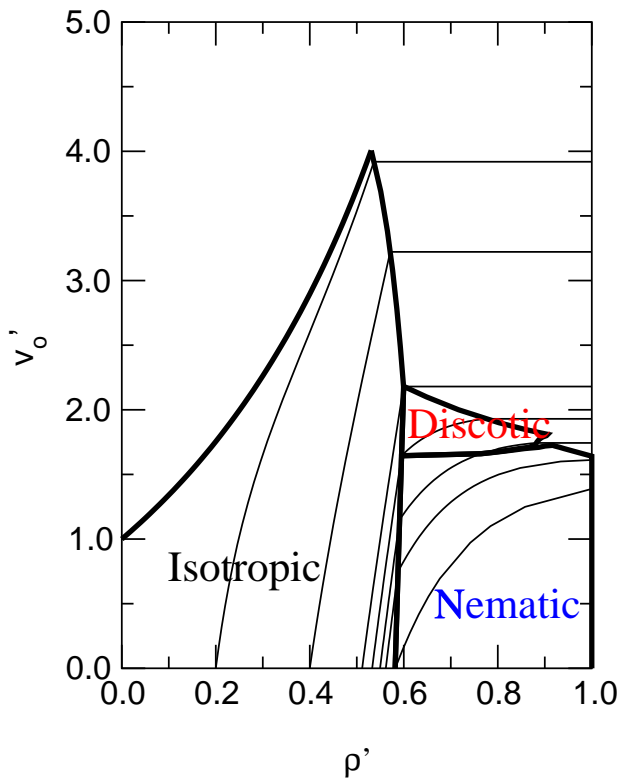


- **Details of an I-N-D transition.**

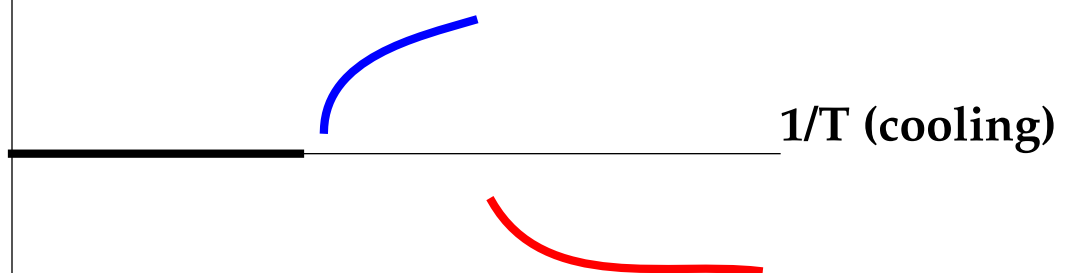
● Isotropic-Nematic-Discotic

□ Density and pressure:

$$\rho' - v_0', \quad \Gamma=4 \quad a'=1/2 \quad P_{eq} d^3 - v_0'$$



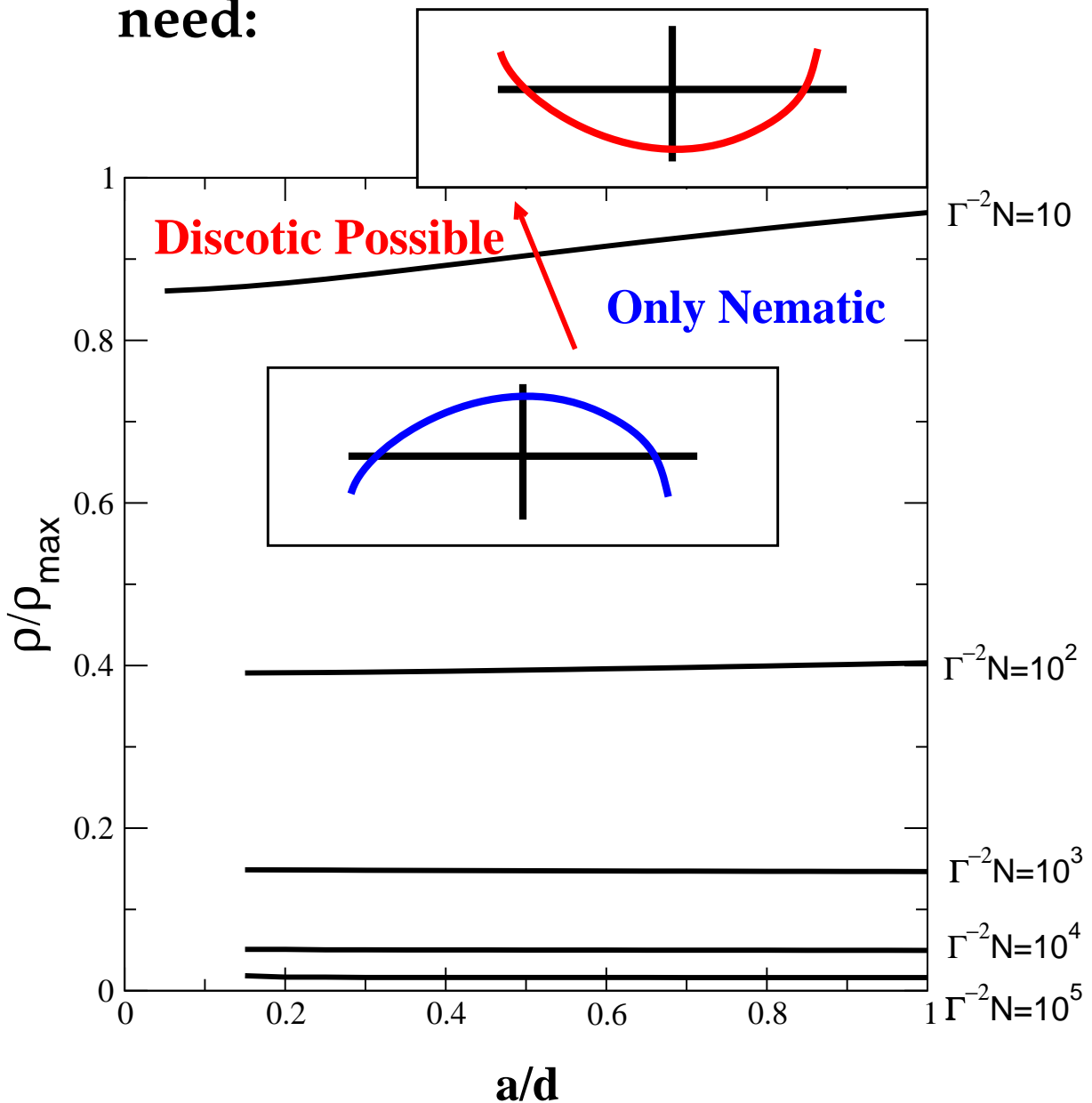
Orientation



□ Cooling: I-N-D, anti-alignment.

● **Condition for U affect diagram**

- **Reentrant nematic, and discotic need:**



- **Correlations are critical.**

● **Conclusion**

- **Constructed through PRISM and wave vector-cutoff closure free energy for nematics.**
- **Correlations are key both**
 - ↪ excluded-volume contribution to the free energy, and
 - ↪ internal energy.
- **Correlations produce**
 - ↪ Reentrant nematic phase
 - ↪ Discotic “anti-aligned” phase.