Correlation Effects in Thermotropic Liquid Crystals

Galen T. Pickett

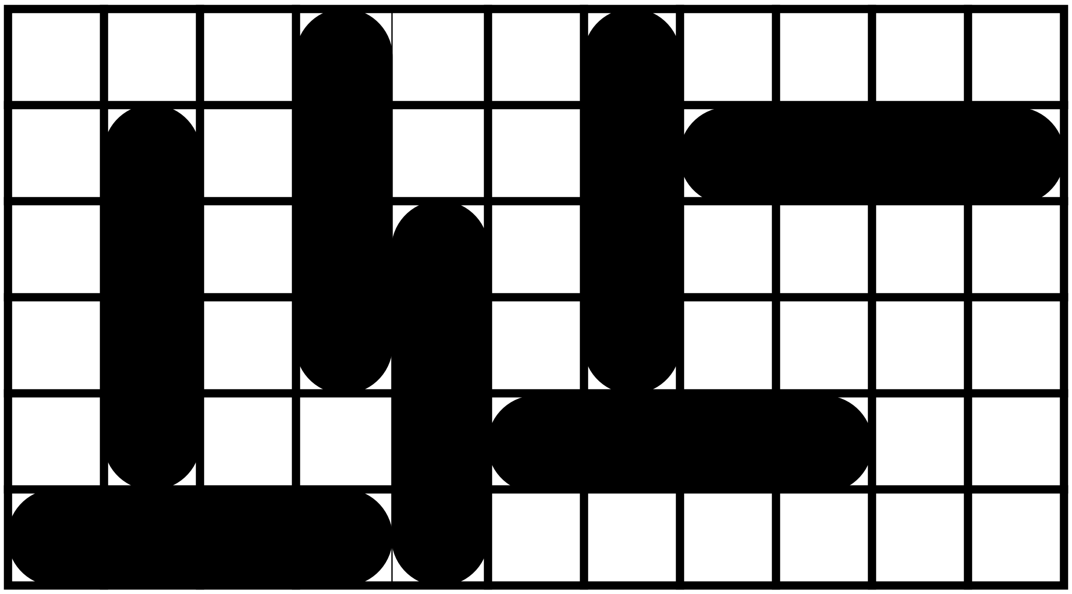
Dept. of Physics and Astronomy, Cal State Long Beach

Kenneth S. Schweizer

Dept. of Materials Sciences and Engineering, University of Illinois at Urbana-Champaign

● Flory 'Chimney' Theory for Rods

- **Entropy: incompressible lattice**



  - Rods align at high density

- **Internal energy: mean field.**

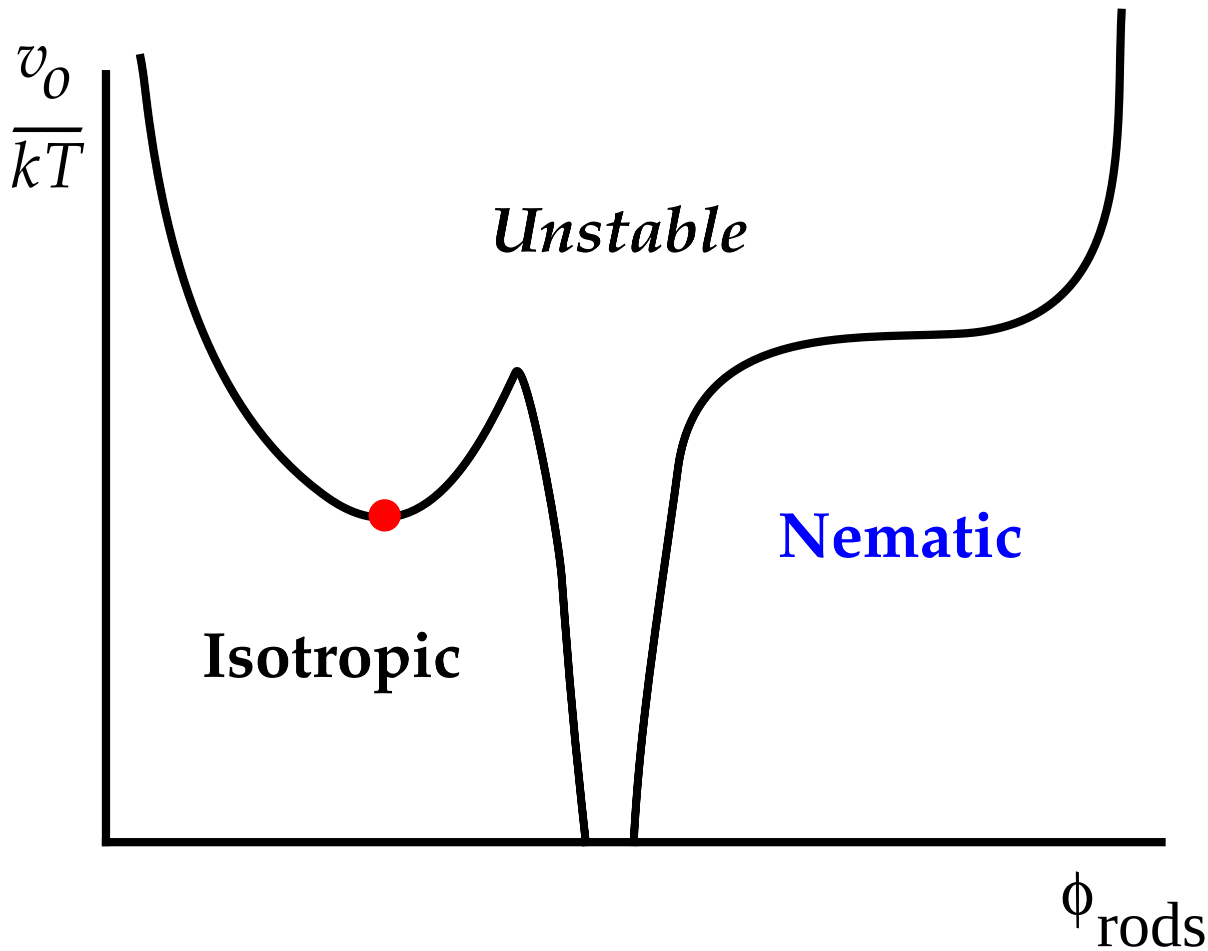
$$U = -v_0 \rho$$

  - Interactions favor high density states
  - High density increases ordering

- **Mechanism: athermal, Onsager**

- **Chimney Phase diagram**

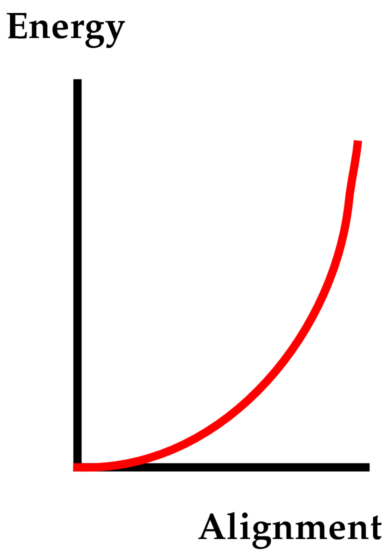
- **Chimney widens as v_0 increases (cooling).**

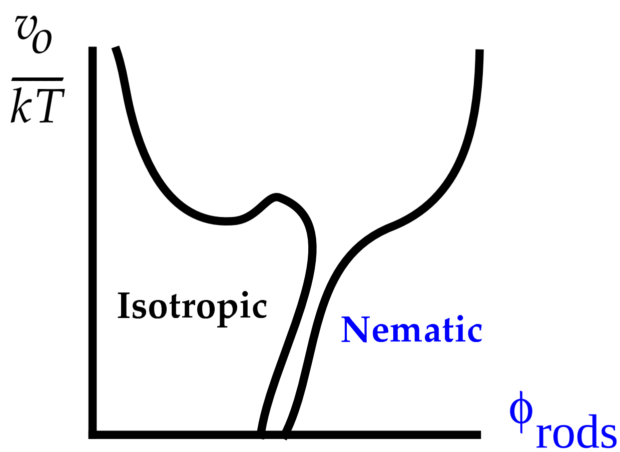


- **Isotropic-Nematic coexistence pushed to small and high density.**
- **No attempt at including correlations in U**

- **Effect that correlations might have**

  - **Favoring isotropic over nematic**

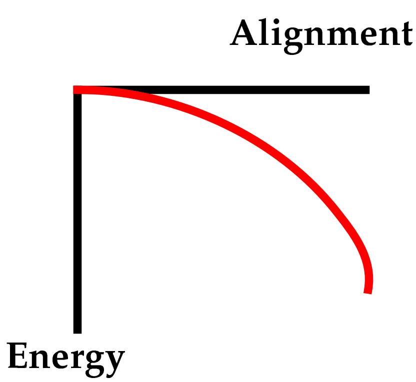


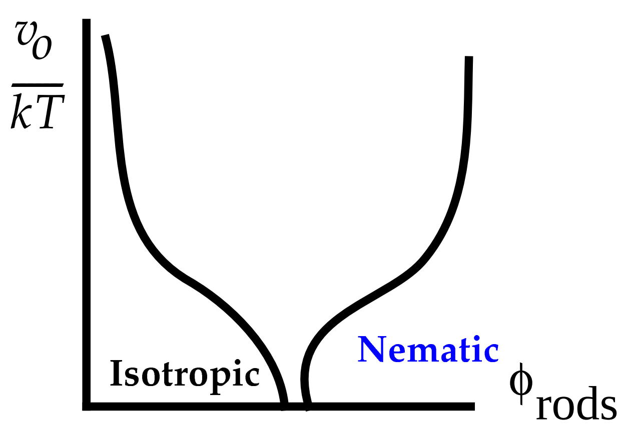


Have to go to higher density

    - Chimney leans: reentrancy.

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



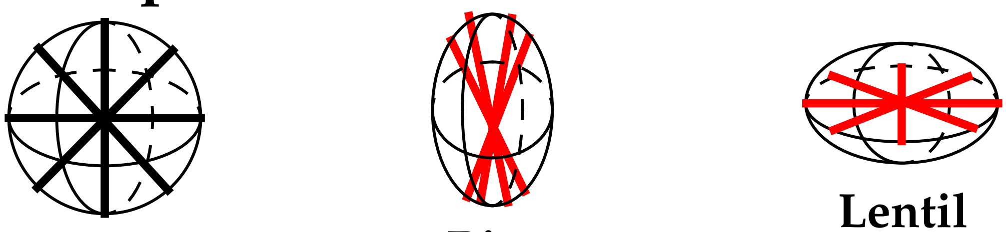


  - **How to choose U?**

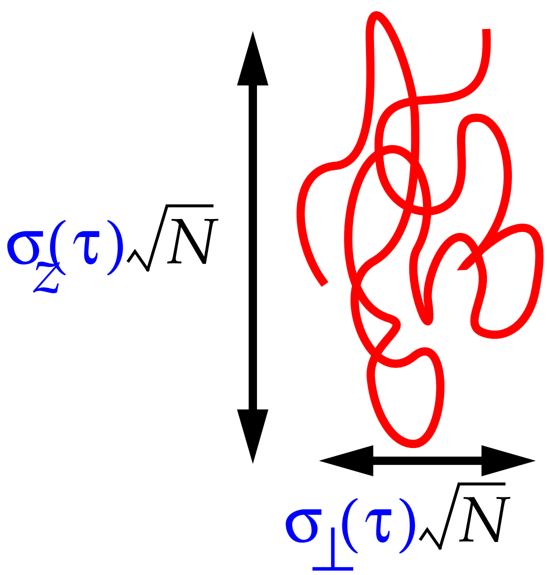
• PRISM Theory for Thermotropics

- **Order parameter: τ**

$\tau = 0$	$\tau > 0$	$\tau < 0$
Isotropic	**Nematic**	**Discotic**



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



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

• Free energy: Excluded Volume

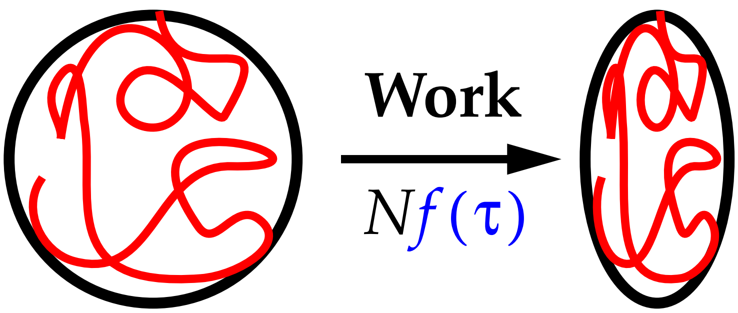
- **Orientation, τ determines $\omega(\vec{q})$.**
- **PRISM equation determines pair correlation function, $g(\vec{r})$ given**
- **Closure approximation for direct correlation function, $C[\vec{q}]$**
  - "Wave vector cutoff closure"

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

  - 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.**

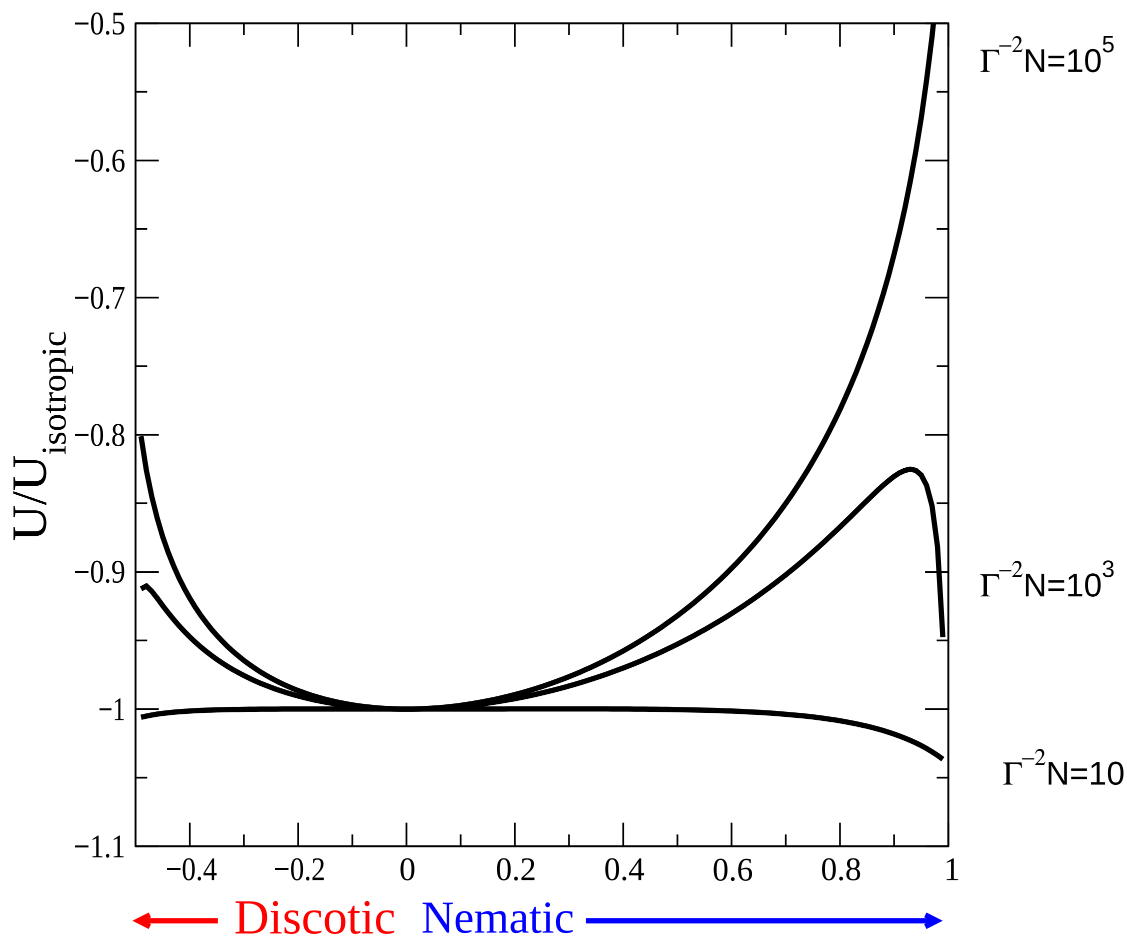
- **Free Energy: Internal Energy**

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

- **Short-ranged interaction**

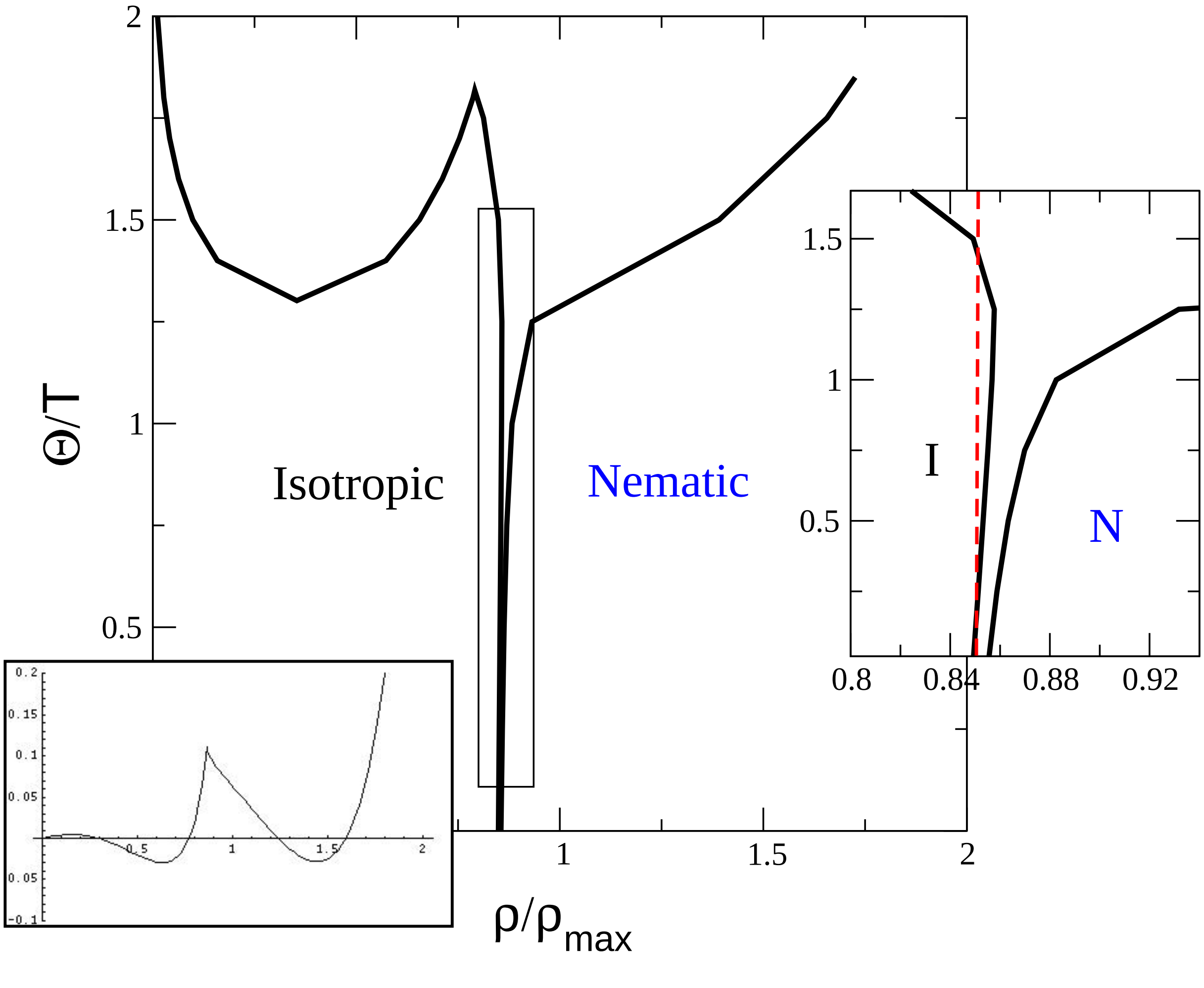
$$v(r) = -\frac{v_o}{r/a} e^{-r/a}$$

- **Pair-correlation depends on τ**



- **“Chimney” diagram**

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

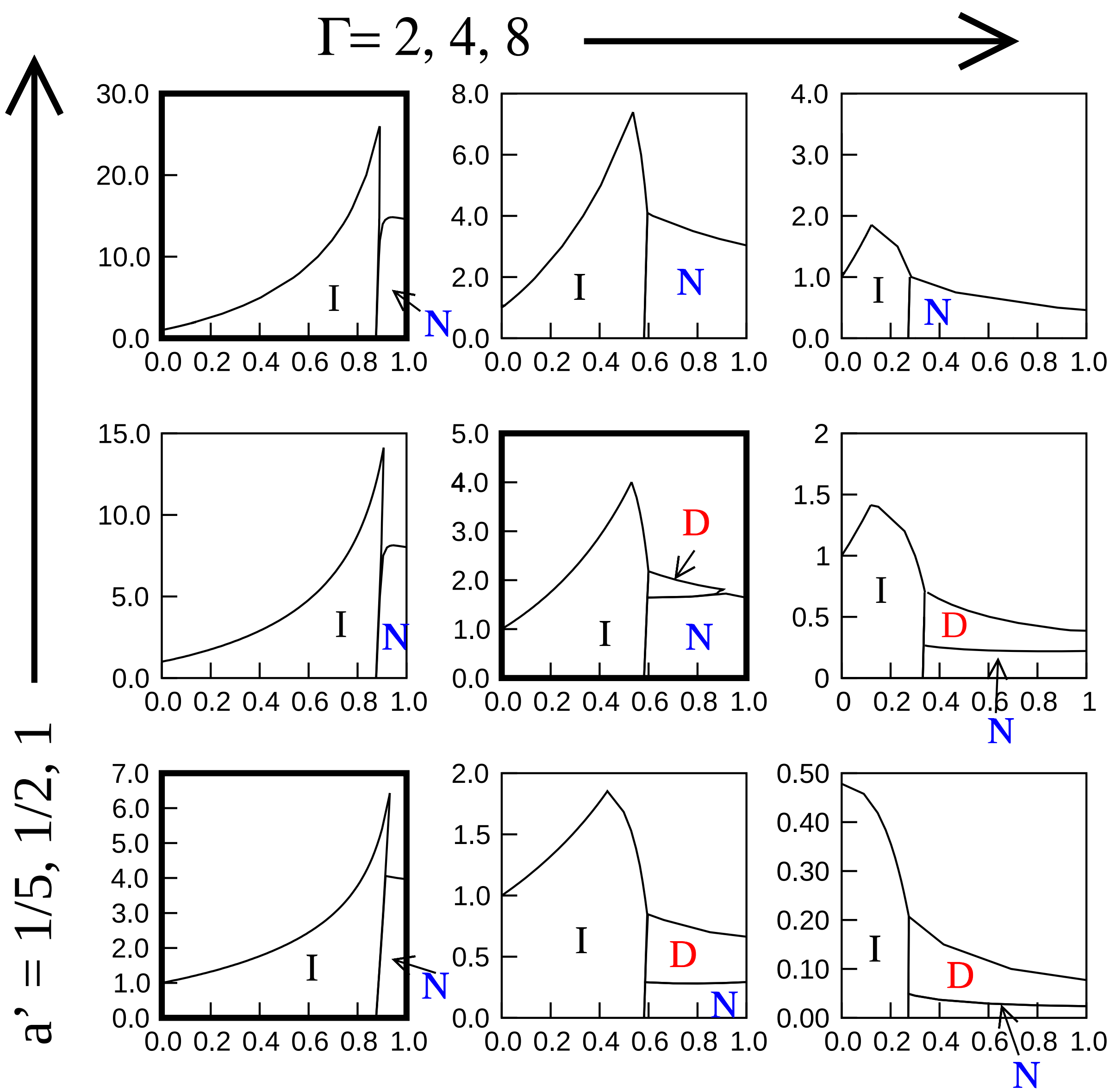


- **Correlations in U give reentrant Nematic.**

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

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

Infinite N:

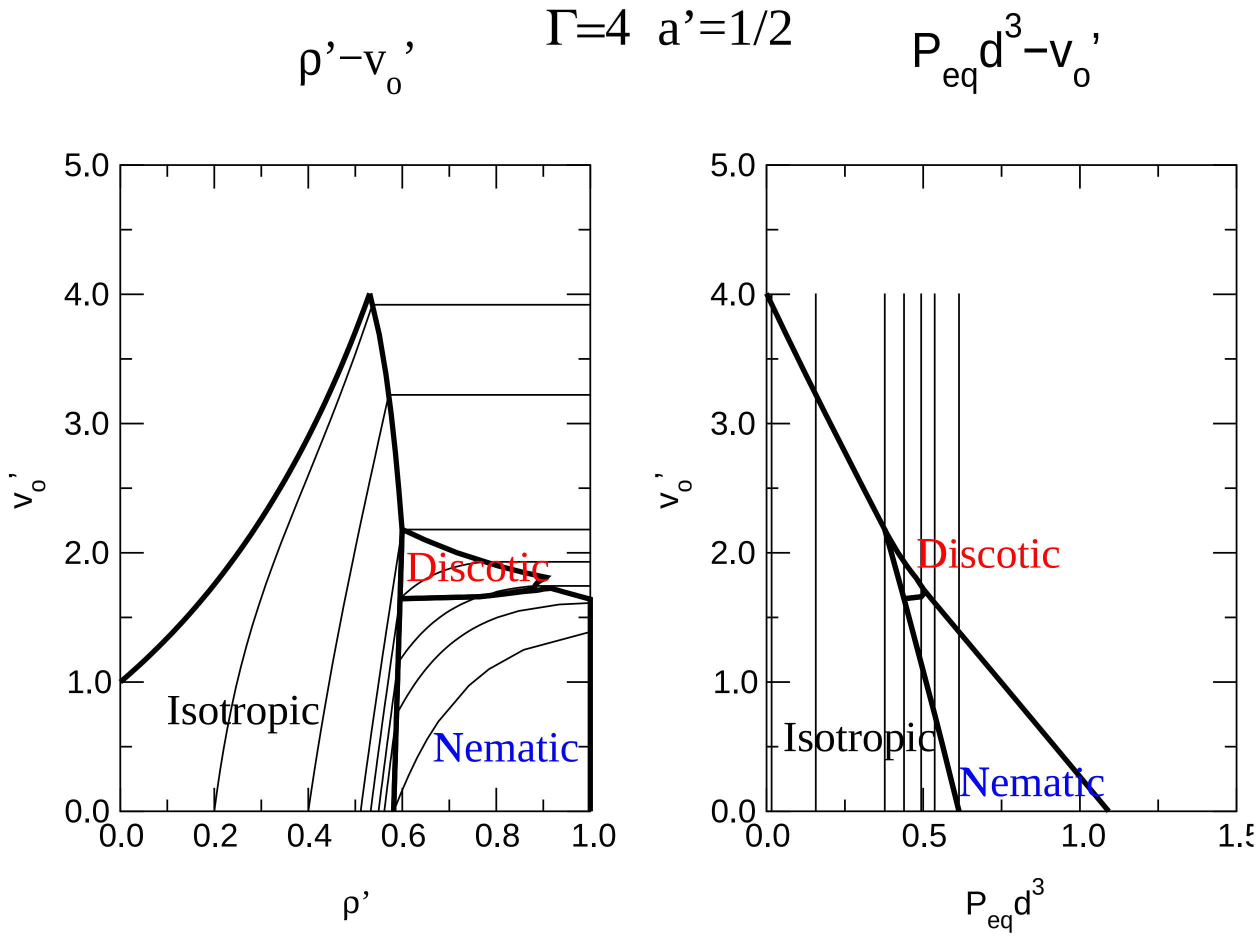


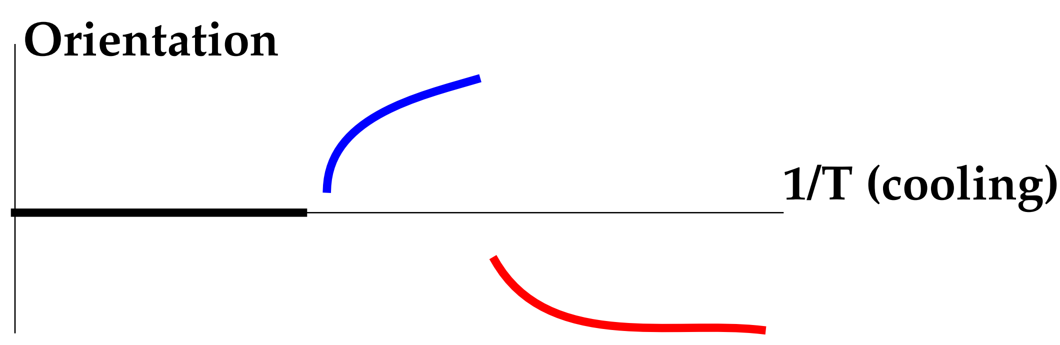
- **Details of an I-N-D transition.**

● Isotropic-Nematic-Discotic

❑ Density and pressure:

Γ=4 a'=1/2

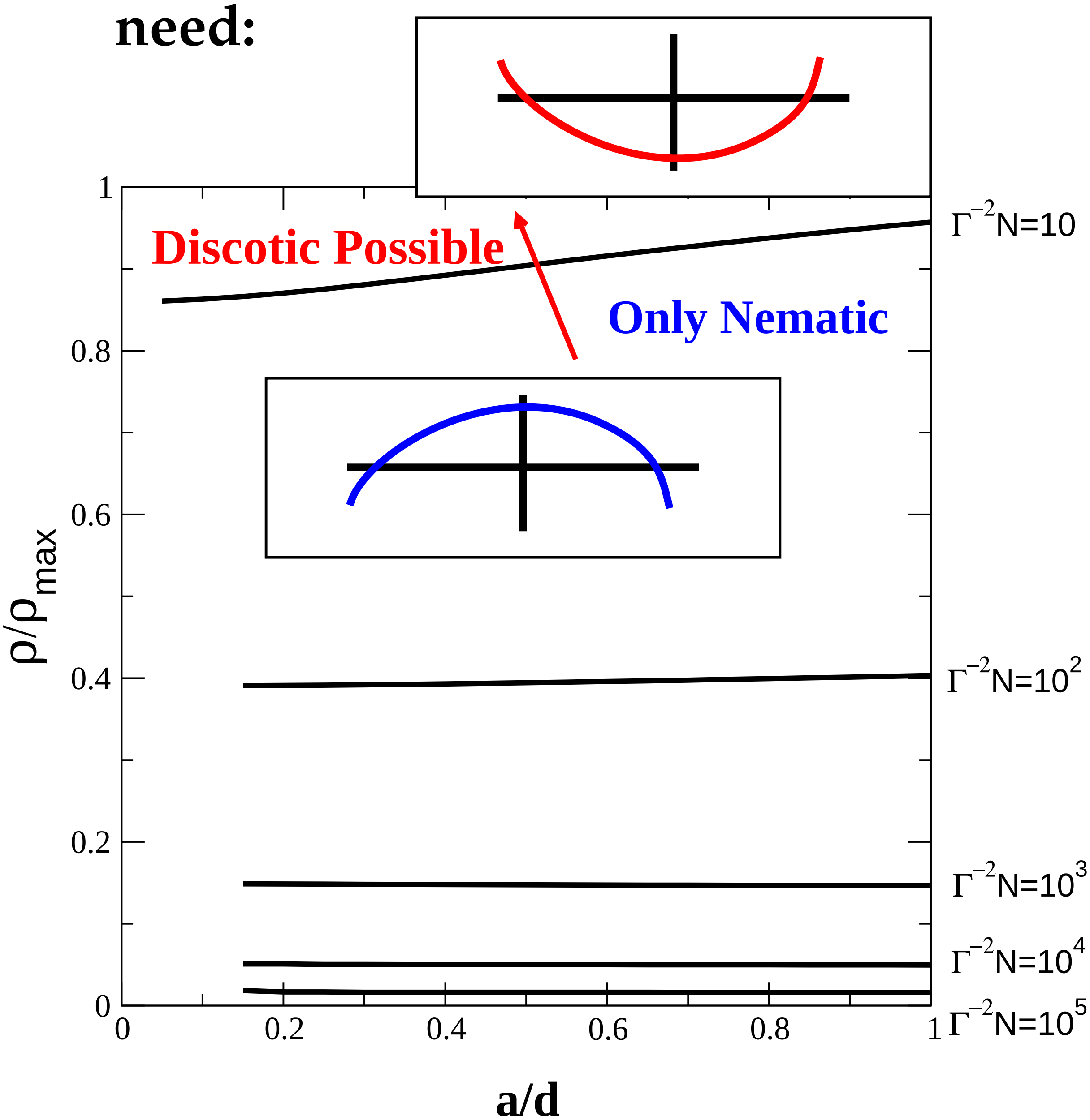




❑ Cooling: I-N-D, anti-alignment.

- 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.