Phase separation in negatively non-additive hard-sphere mixtures

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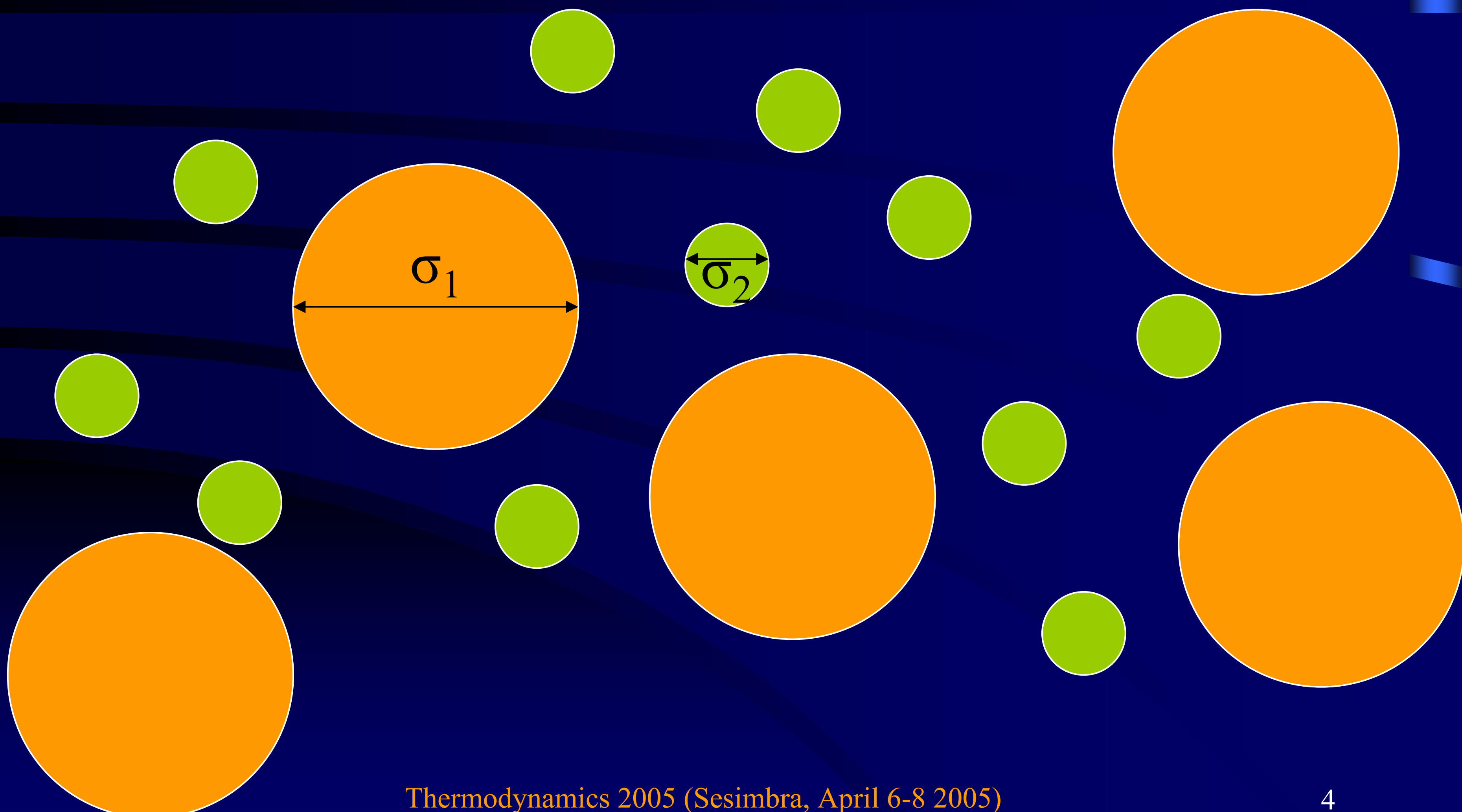
Entropy-driven phase transitions

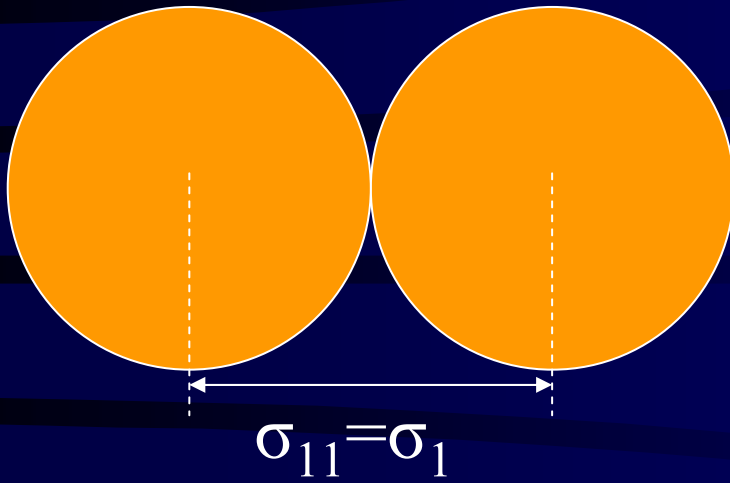
- In hard-sphere systems the internal energy is independent of density.
- Therefore, phase transitions are entropy-driven and the relevant thermodynamic parameter is not temperature but density.

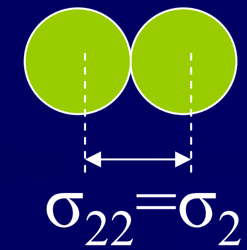
Examples

- **Fluid → crystal freezing transition in hard spheres.** The loss in entropy associated with nonuniformity is compensated at sufficiently large densities ($\eta > 0.49$) by the gain associated with a larger free-volume per particle.
- **Isotropic → nematic transition in a system of *thin* hard rods.** The loss in orientational entropy can be compensated (at large enough densities) by the gain in translational entropy.

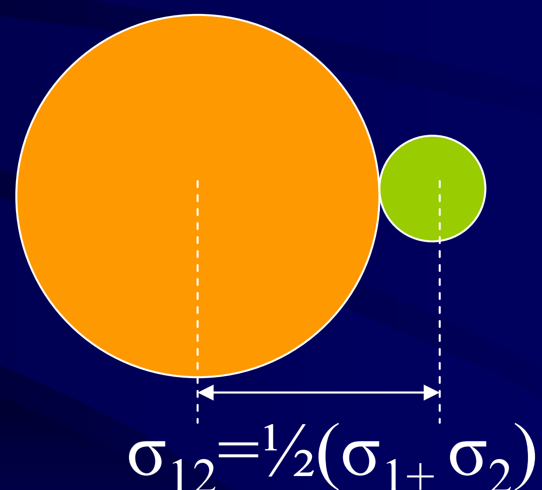
Binary mixture of hard spheres



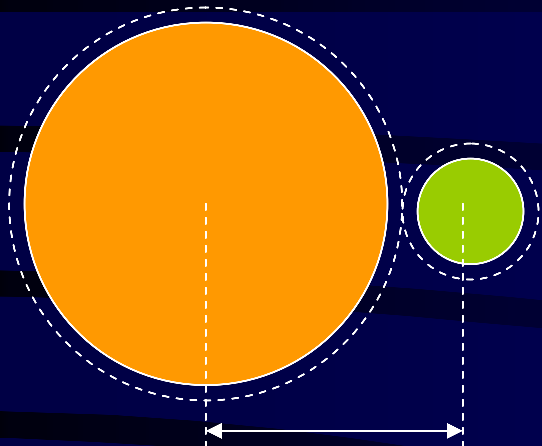




Additive spheres

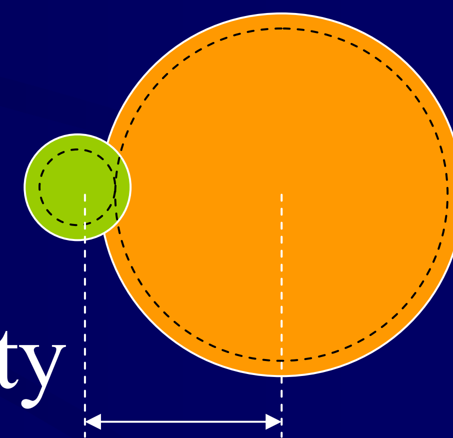


Non-additive hard spheres



Positive non-additivity

$\sigma_{12} > \frac{1}{2}(\sigma_1 + \sigma_2)$

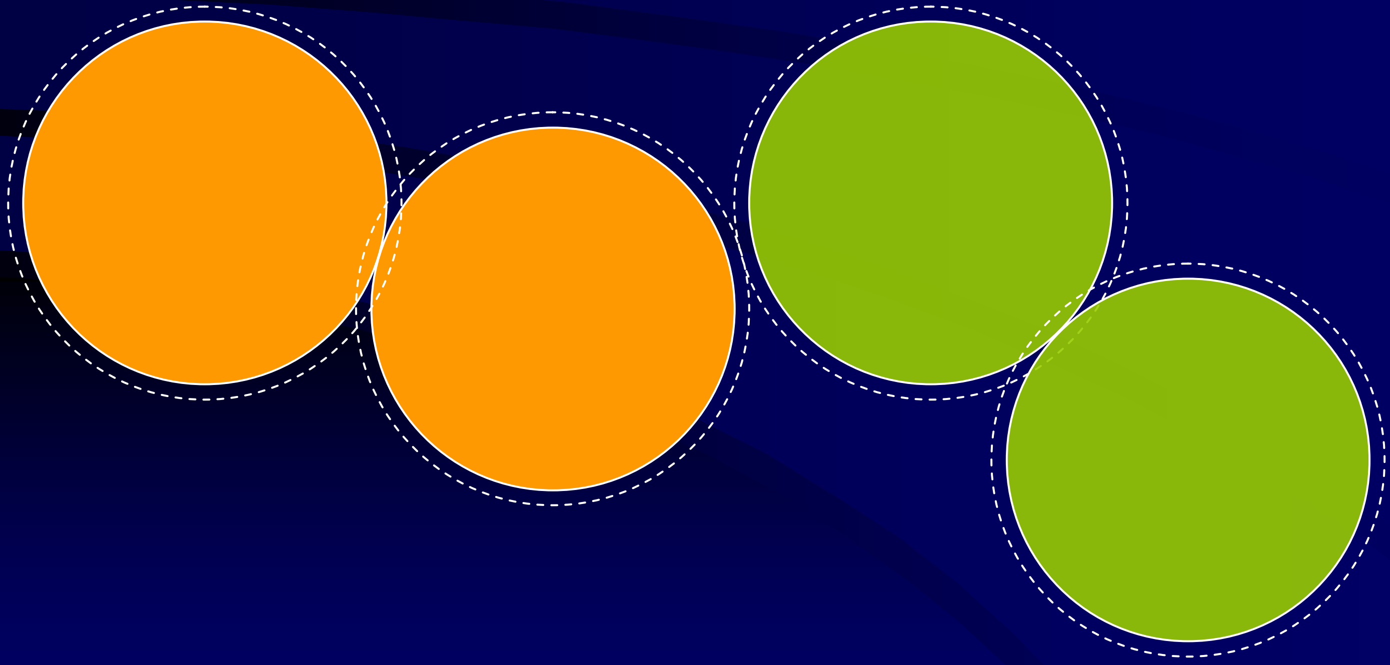


Negative non-additivity

$\sigma_{12} < \frac{1}{2}(\sigma_1 + \sigma_2)$

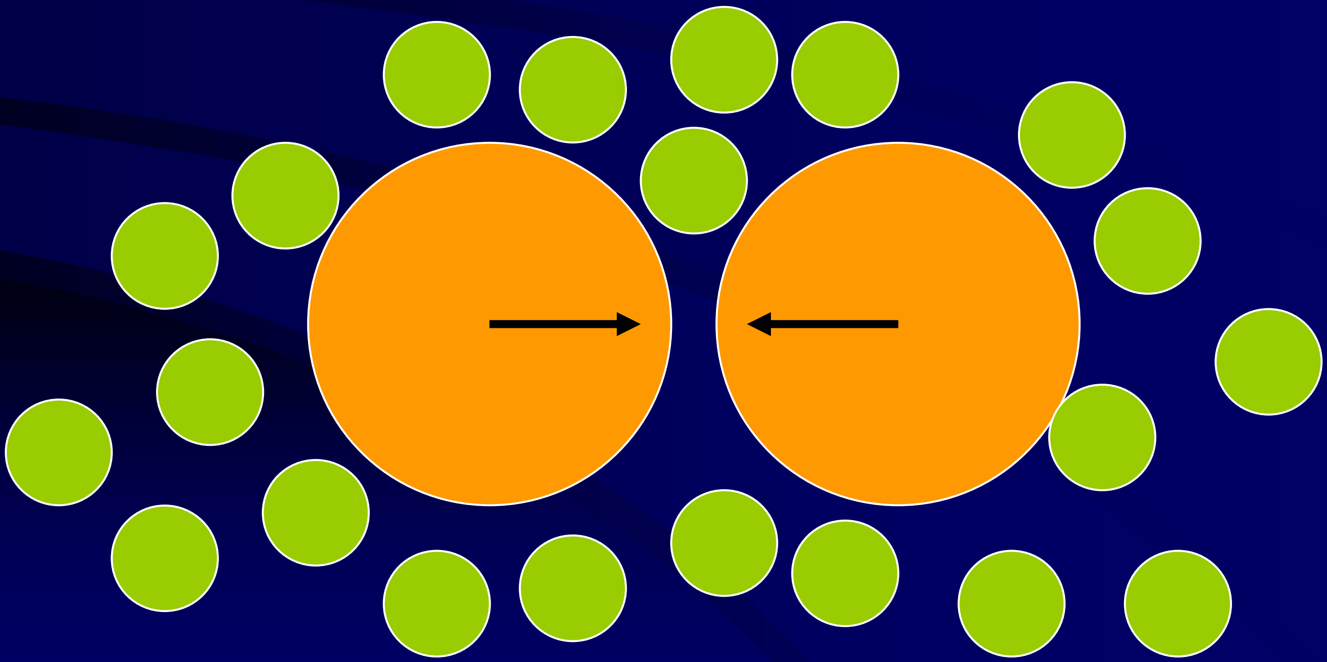
Demixing transition in *positively non-additive* mixtures

- Even in symmetric mixtures ($\sigma_1=\sigma_2$), phase separation can occur due to entropic effects (*homo-coordination*).



Demixing transition in *additive* mixtures

- *Osmotic depletion*: If the size ratio $\gamma \equiv \sigma_2/\sigma_1$ is small enough, the small spheres can induce an effective *attraction* between the large spheres.



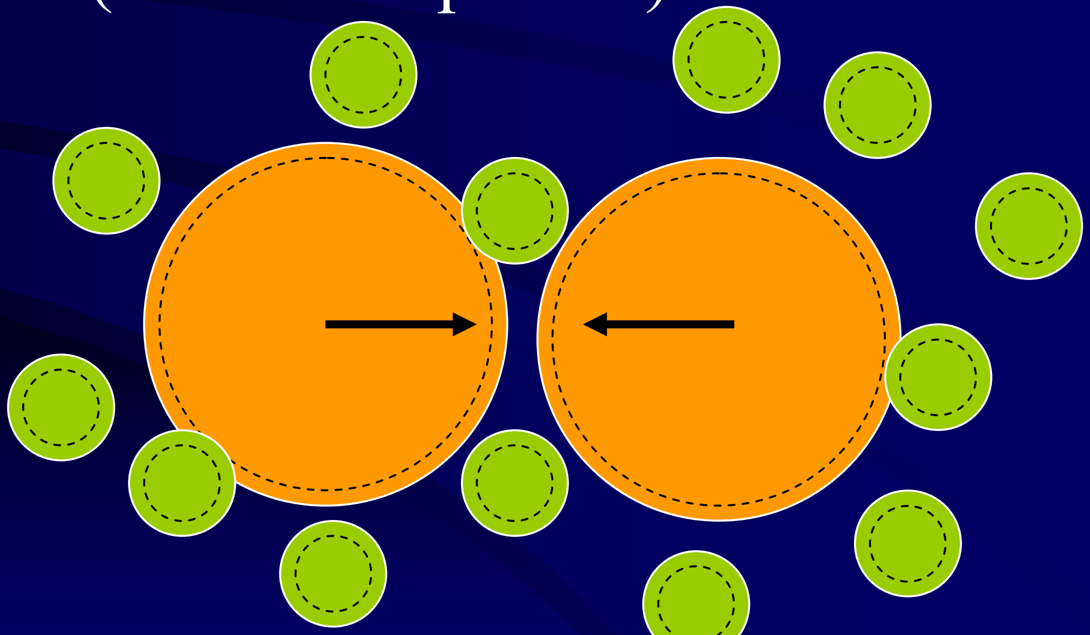
- Demixing in *additive* mixtures is a very elusive effect.

- If demixing exists, it is possibly metastable with respect to the freezing transition.

Can demixing occur in *asymmetric* mixtures with *negative* non-additivity?

- Two competing effects:

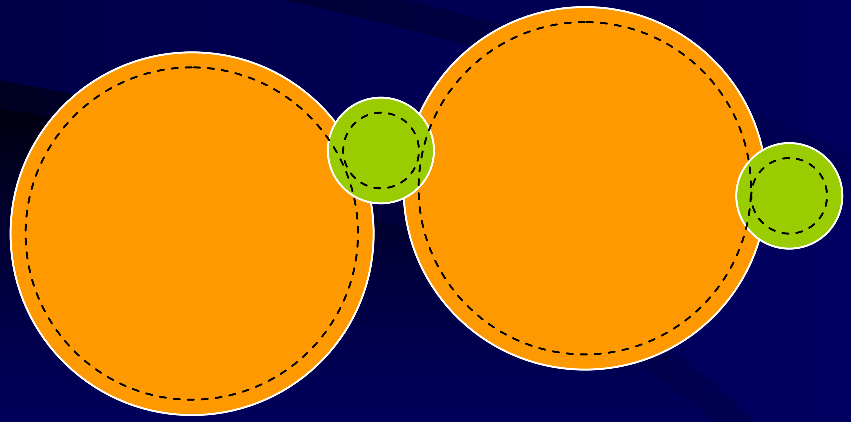
1. Size asymmetry ($\gamma \equiv \sigma_2/\sigma_1 \ll 1$) favors phase separation (osmotic depletion).



Can demixing occur in *asymmetric* mixtures with *negative* nonadditivity?

- Two competing effects:

2. Negative non-additivity [$\sigma_{12}<\frac{1}{2}(\sigma_1+\sigma_2)$] favors mixing (hetero-coordination).



Our strategy: infinitely many dimensions ($d \to \infty$)

- H. L. Frisch and J. Percus, *High dimensionality as an organizing device for classical fluids*, Phys. Rev. E **60**, 2942 (1999):

  "[In high spatial dimensionality], fluctuations are reduced by high effective coordination number, so, e.g., interfaces tend to be even sharper, and *one generally expects clean caricatures of any thermodynamic phenomenology that indeed extends to higher dimensionality*."

Relevant quantities

Geometrical

$\sigma_1, \sigma_2, \sigma_{12}$: diameters

$\gamma = \sigma_2/\sigma_1 < 1$: size ratio

$\tilde{\gamma} = \sigma_2^d/\sigma_1^d = \gamma^d < 1$: volume ratio

$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)(1 + \Delta)$, Δ : non-additivity parameter

Thermodynamic

$x_i = N_i/N$: mole fractions

$\rho = N/V$: number density

$\eta = \rho(x_1\sigma_1^d + x_2\sigma_2^d)v_d$: packing fraction

Volume of a sphere of unit diameter (v_d)

p : pressure $(k_B T = 1)$

g : Gibbs free energy per particle

High-dimensionality limit ($d \to \infty$)

The second virial approximation becomes exact

[Frisch, Rivier, and D. Wyler, PRL **54**, 2061 (1985); Carmesin, Frisch, and Percus, JSP **63**, 791 (1991)]

$$p \to \rho + B_2\rho^2, \qquad g \to g^{\text{ideal}} + 2B_2\rho$$

$$B_2 = v_d 2^{d-1}\left(x_1^2\sigma_1^d + x_2^2\sigma_2^d + 2x_1x_2\sigma_{12}^d\right)$$

Scaling

volume ratio: $\tilde{\gamma} = \sigma_2^d / \sigma_1^d = \gamma^d < 1 = \text{finite}$

scaled non-additivity parameter: $\widetilde{\Delta} = d^2 \Delta = \text{finite}$

scaled packing fraction: $\tilde{\eta} \;=\; (d^{-1} 2^d)\eta = \text{finite}$

$$\Rightarrow \eta \to 0$$

scaled pressure: $\tilde{p} \;=\; (v_d d^{-2} 2^{d-1}) p \sigma_1^d = \text{finite}$

$$\Rightarrow p\sigma_1^d \to \infty$$

Simple algebra yields the critical point

irrelevant → $g^{(0)}$, essential → $g^{(1)}$

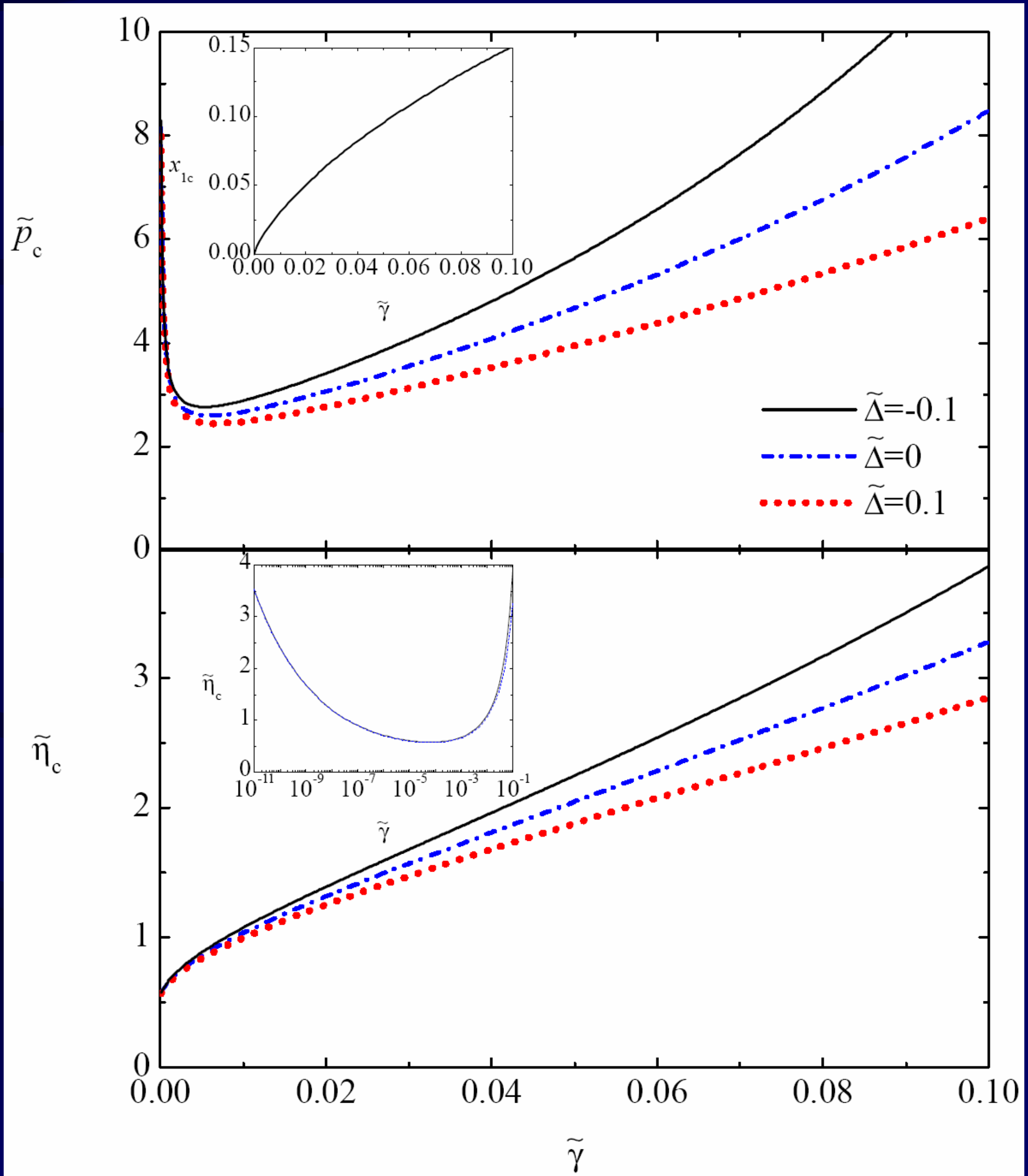
$$g = d\left[g^{(0)} + g^{(1)} d^{-1} + \cdots\right]$$

Critical point: $\left(\frac{\partial^2 g}{\partial x_1^2}\right)_p = \left(\frac{\partial^3 g}{\partial x_1^3}\right)_p = 0$

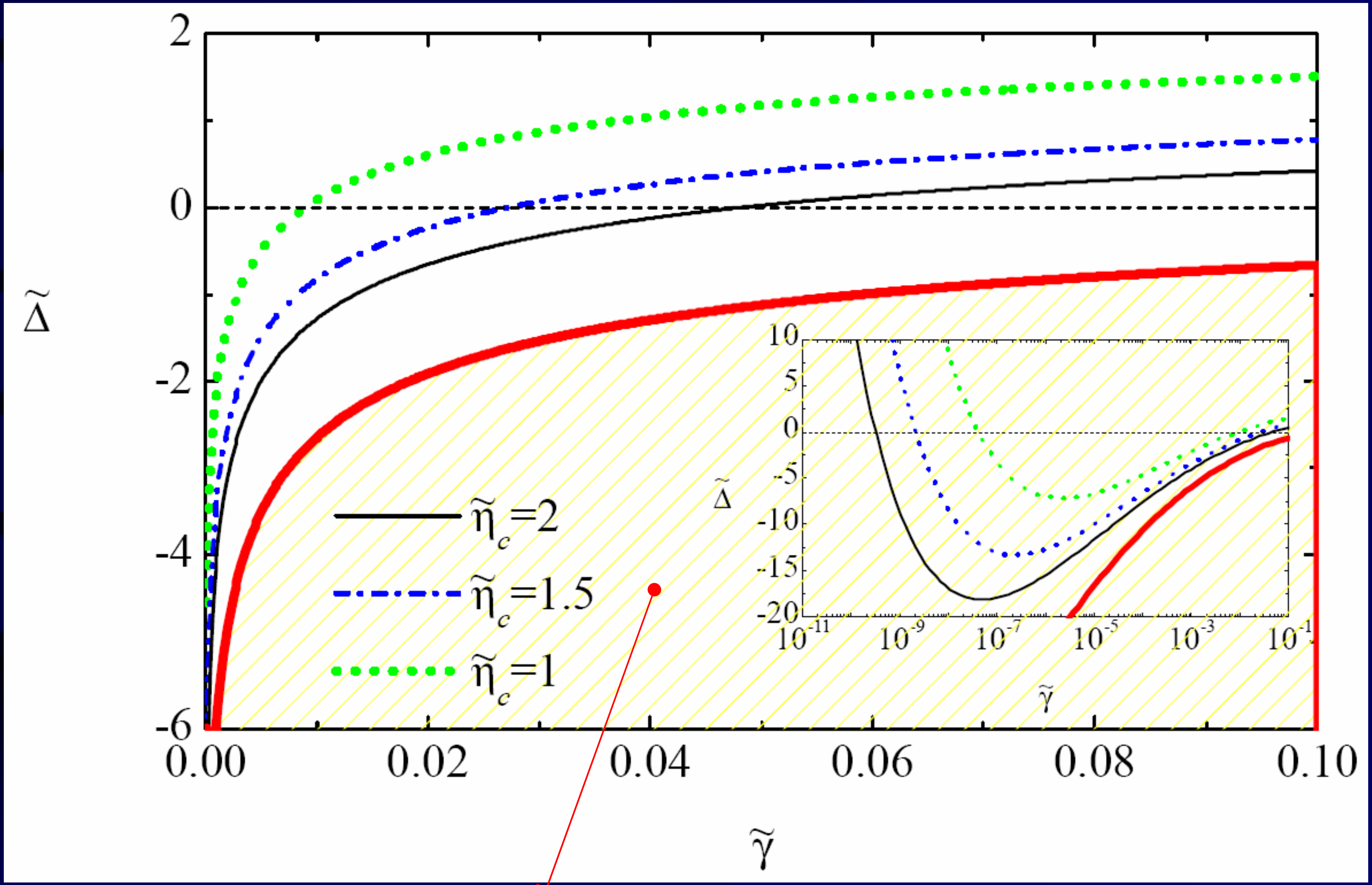
$$x_{1c} = \frac{\tilde{\gamma}^{3/4}}{1+\tilde{\gamma}^{3/4}}, \quad \tilde{\eta}_c = \frac{\left(\tilde{\gamma}^{1/8} + \tilde{\gamma}^{-1/8}\right)^2}{K}, \quad \tilde{p}_c = \frac{\left(1+\tilde{\gamma}^{1/4}\right)^4}{4\tilde{\gamma}K^2}$$

$$K \equiv \frac{1}{4}(\ln\tilde{\gamma})^2 + 2\widetilde{\Delta} = d^2\left[\frac{1}{4}(\ln\gamma)^2 + 2\Delta\right] > 0 \Rightarrow \boxed{\Delta > -\frac{1}{8}(\ln\gamma)^2}$$

Critical point as a function of the (scaled) size asymmetry and non-additivity parameters

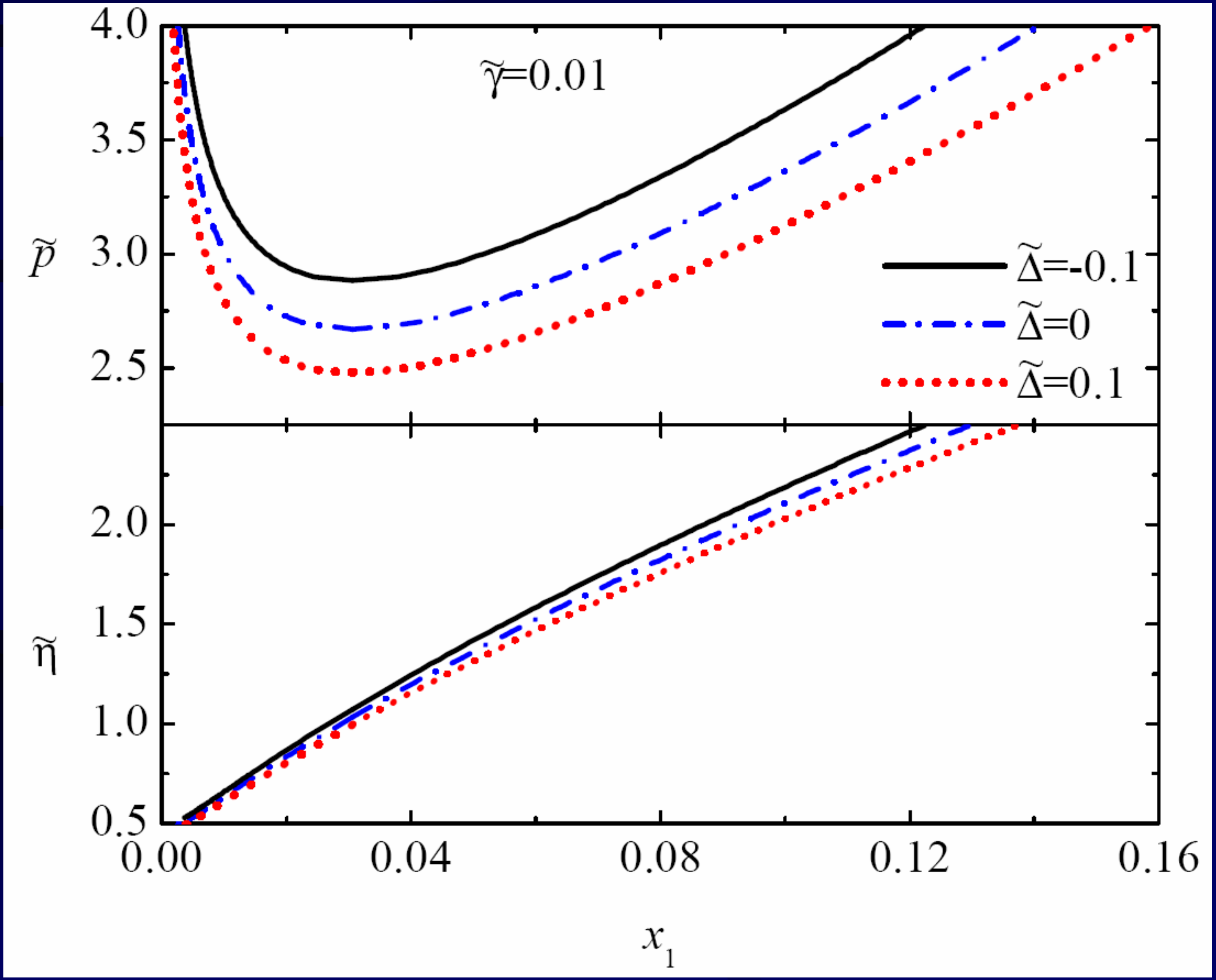


Threshold curve and loci $\tilde{\eta}_c = \text{const}$



No phase separation

Coexistence curves (binodals)



Are the densities consistent with the second-virial approximation?

- Yes:

$$\tilde{\eta} = \mathcal{O}(1) \Rightarrow \lim_{d\to\infty} \frac{B_3 \rho}{B_2} = 0$$

Does demixing occur within the stable fluid region?

- Possibly yes:

✓ Colot & Baus's conjecture (1986)

$(\eta_f/\eta_{cp})^{1/d} \to d$-independent

✓ Simple free volume theory for the solid

$$\widetilde{\eta}_f \sim 1\text{–}2$$

Conclusions (I)

- In the high-dimensionality limit, a binary hard-sphere mixture can phase separate, even for negative non-additivities, provided the non-additivity parameter Δ and the size ratio γ are such that

$$\Delta > -\frac{1}{8}(\ln\gamma)^2$$

- In the demixing region, the density and pressure scale as

$$\eta \sim 2^{-d}d, \quad p/\rho \sim d$$

Conclusions (II)

- It is plausible that the phase separation preempts the freezing transition.
- The main effects at work (competition between osmotic depletion and hetero-coordination) are also present in three-dimensional systems.
- The limit $d \to \infty$ allows one to derive exact results and get a caricature or toy model to highlight features already present in real systems.

Theory of asymmetric nonadditive binary hard-sphere mixtures

PHYSICAL REVIEW E, VOLUME 64,

R. Roth* and R. Evans A. A. Louis

Effective one-component fluid

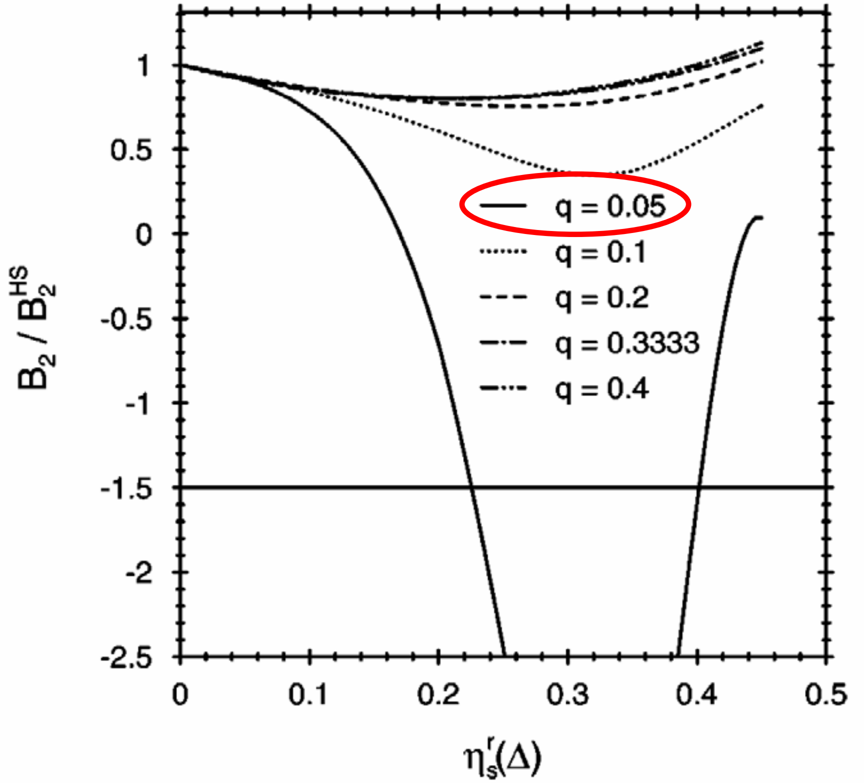
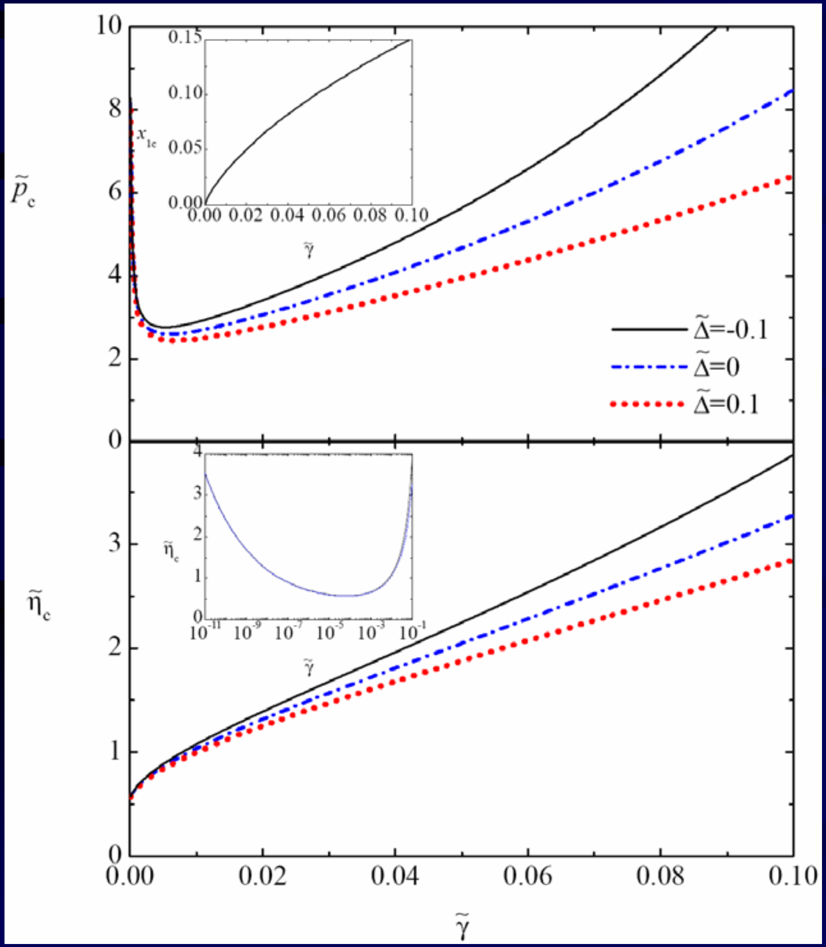


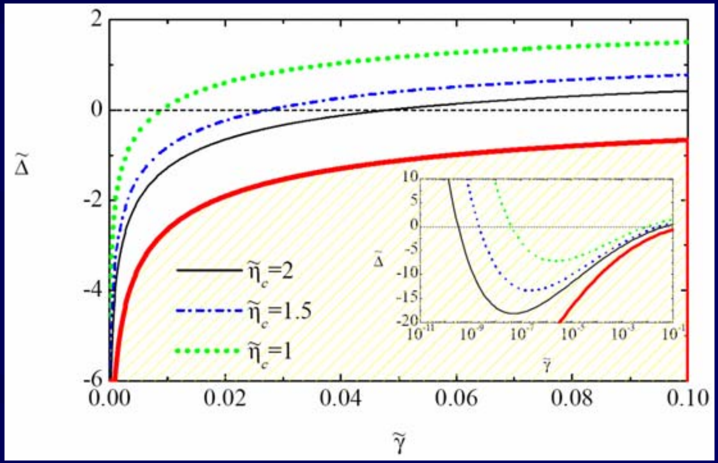
FIG. 10. The reduced second virial coefficient of the big spheres in hard-sphere mixtures with a small *negative* nonadditivity $\Delta = -q/20$ for various size ratios q versus $\eta_s^r(\Delta)$, the packing fraction of small spheres in the reservoir. Note that B_2/B_2^{HS} falls below -1.5 only for the smallest ratio, $q = 0.05$, considered here.

Only for very small q can the depletion potential in nonadditive mixtures with negative Δ generate sufficient net attraction to drive B_2 negative.

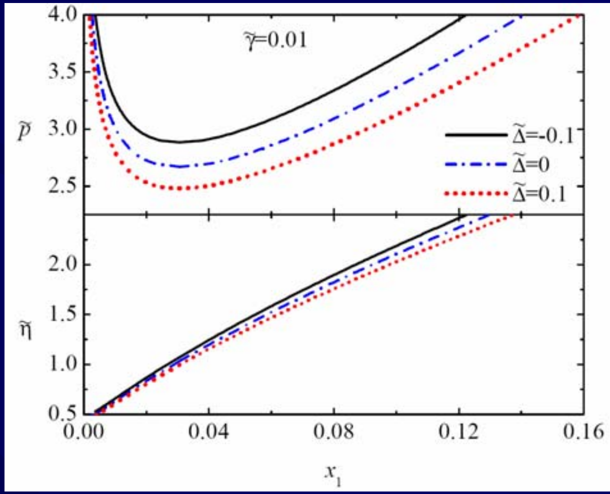
Thanks!



$\tilde{p}_c$
x_{1c}
$\tilde{\gamma}$
$\tilde{\Delta}$=-0.1
$\tilde{\Delta}$=0
$\tilde{\Delta}$=0.1
$\tilde{\eta}_c$



$\tilde{\Delta}$
$\tilde{\eta}_c$=2
$\tilde{\eta}_c$=1.5
$\tilde{\eta}_c$=1
$\tilde{\gamma}$



$\tilde{\gamma}$=0.01
$\tilde{p}$
$\tilde{\Delta}$=-0.1
$\tilde{\Delta}$=0
$\tilde{\Delta}$=0.1
$\tilde{\eta}$
x_1