

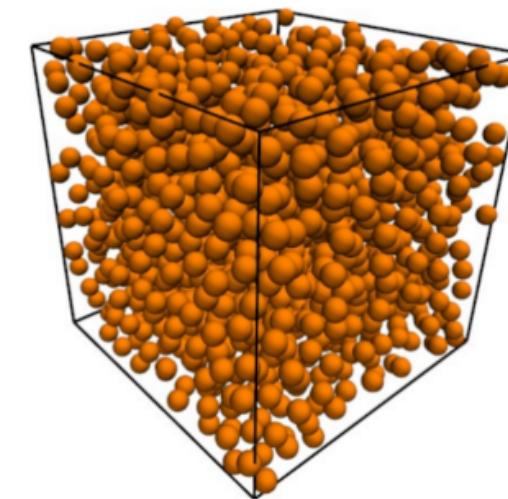
Diagrammi di fase dei materiali softici

1. Colloidi duri

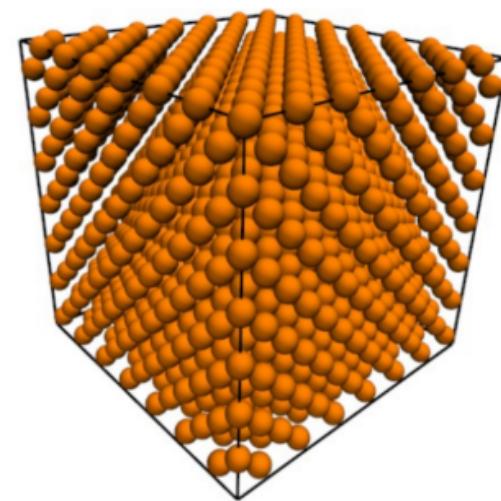
$$HS: u(r) = \begin{cases} \infty & r \leq r \\ 0 & r > r \end{cases} \quad \exp(-\beta U) = \begin{cases} 0 & \text{overlap} \\ 1 & \text{no overlap} \end{cases}$$

$$\text{Frazione di volume: } \phi = \frac{V_0}{V} = \frac{N \frac{4}{3} \pi (\sigma/2)^3}{V} = \frac{\pi}{6} \rho \sigma^3$$

FLUIDO



FCC



Phase Transition for a Hard Sphere System

B. J. ALDER AND T. E. WAINWRIGHT

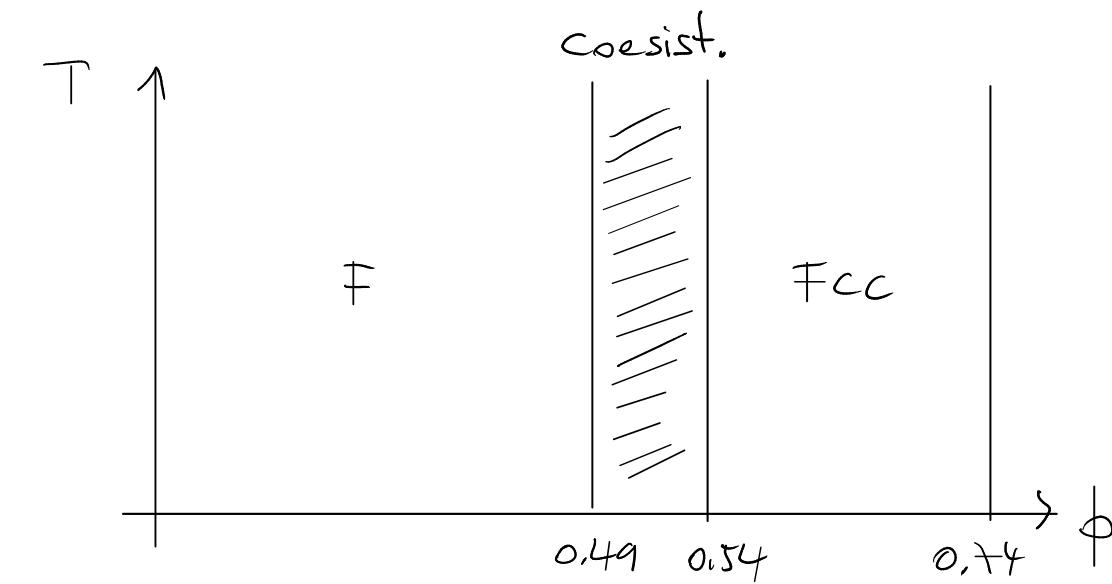
University of California Radiation Laboratory, Livermore, California

(Received August 12, 1957)

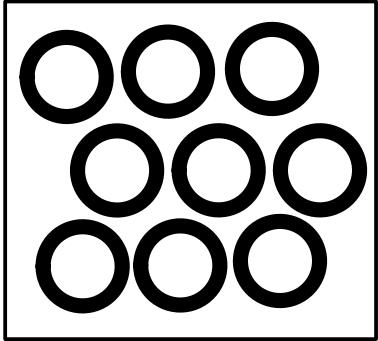
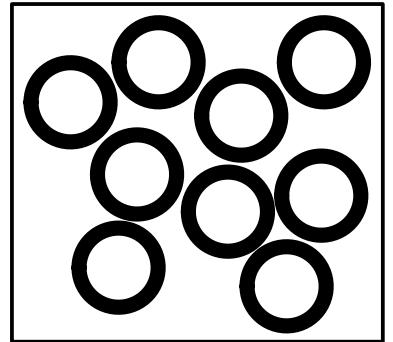
A CALCULATION of molecular dynamic motion has been designed principally to study the relaxations accompanying various nonequilibrium phenomena. The method consists of solving exactly (to the number of significant figures carried) the simultaneous classical equations of motion of several hundred particles by means of fast electronic computers. Some of the



Alder



V, T



$$F = E - TS = -TS$$

↑
HS

$\phi > 0.54$:

$S_{FCC} > S_{FLUIDO}$!!

↓
+ volume libero!

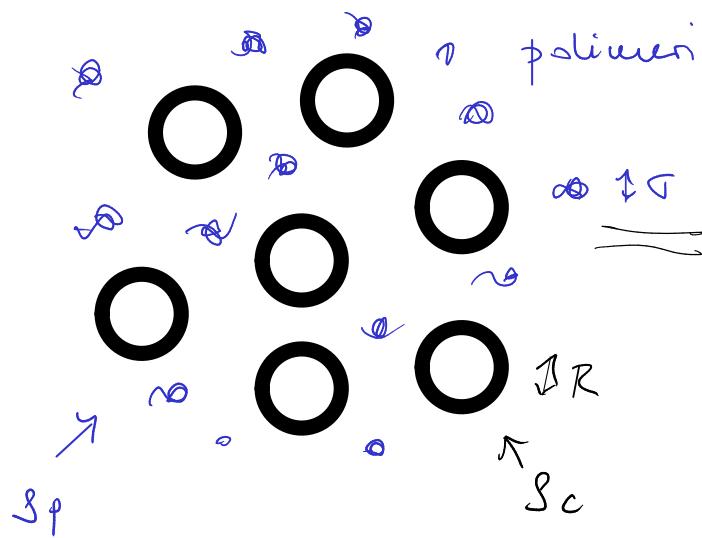
Pusey Van Megen Science 1986



Colloidi duri: \approx HS

- PMMA : $0.305 \pm 0.01 \mu\text{m}$
- stabilizzazione strica : $\sim 10 - 20 \text{ nm}$
- index matching

2. Colloidi attrattivi ; colloidii + polimeri \rightarrow deplezione



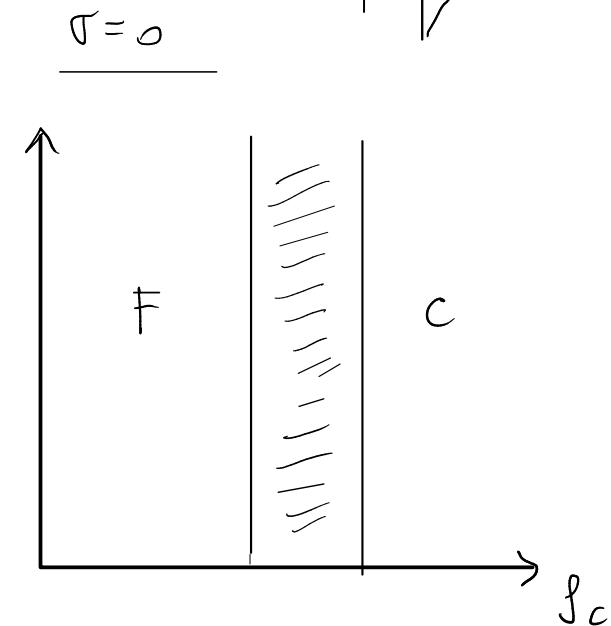
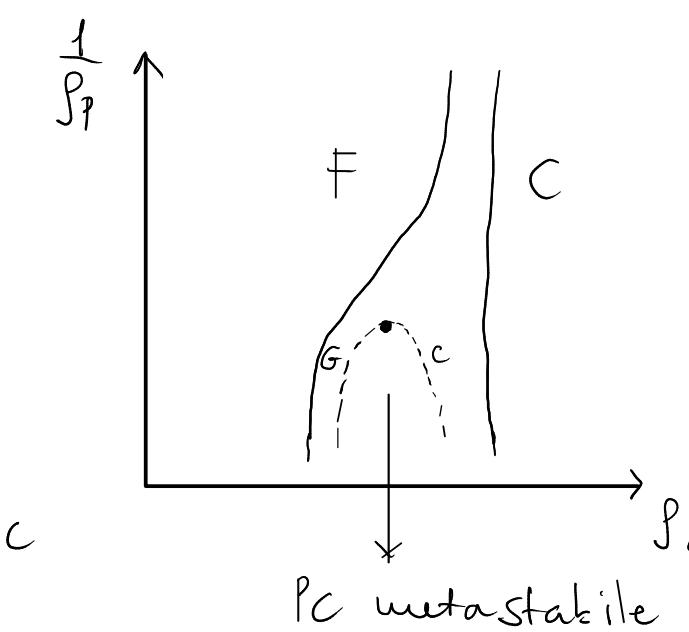
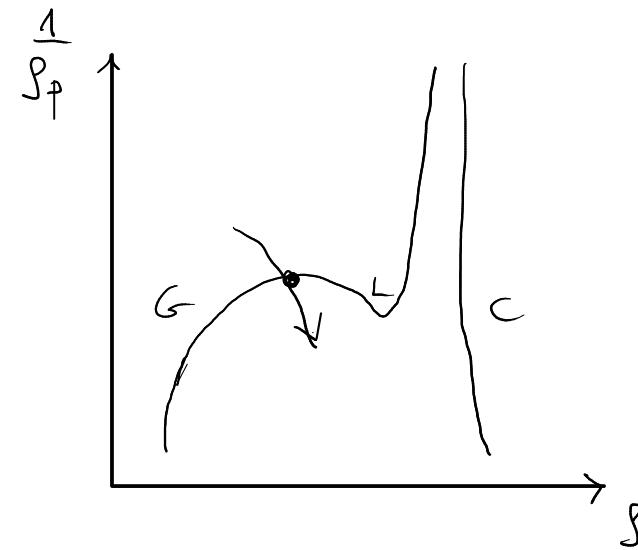
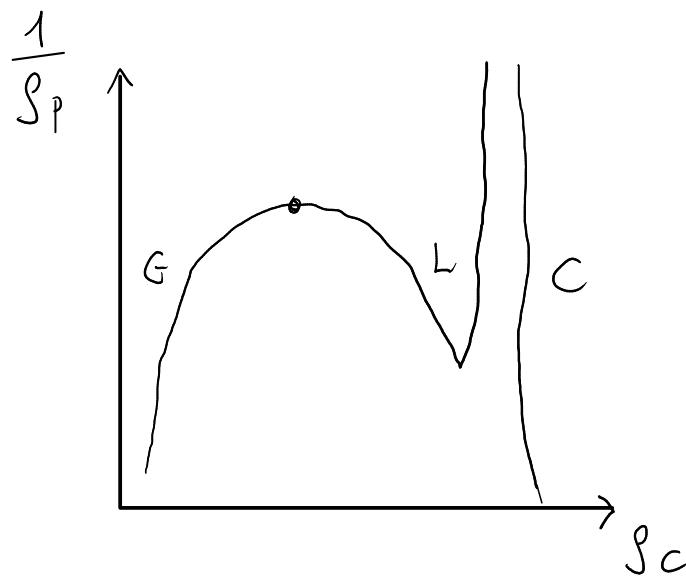
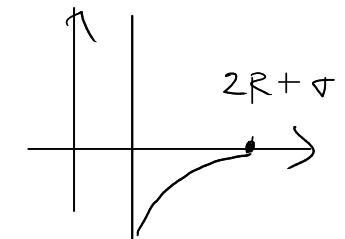
{ colloid - colloid : HS
 polymer - polymer : gas non interagente

$$D = 2R + \sigma$$

$$U_{\text{eff}}(r) = u_{\text{HS}}(r) + u_{\text{AO}}(r) = \begin{cases} \infty & r \leq 2R \\ -k_B T \cdot g_p f(r/D) & r > 2R \end{cases}$$

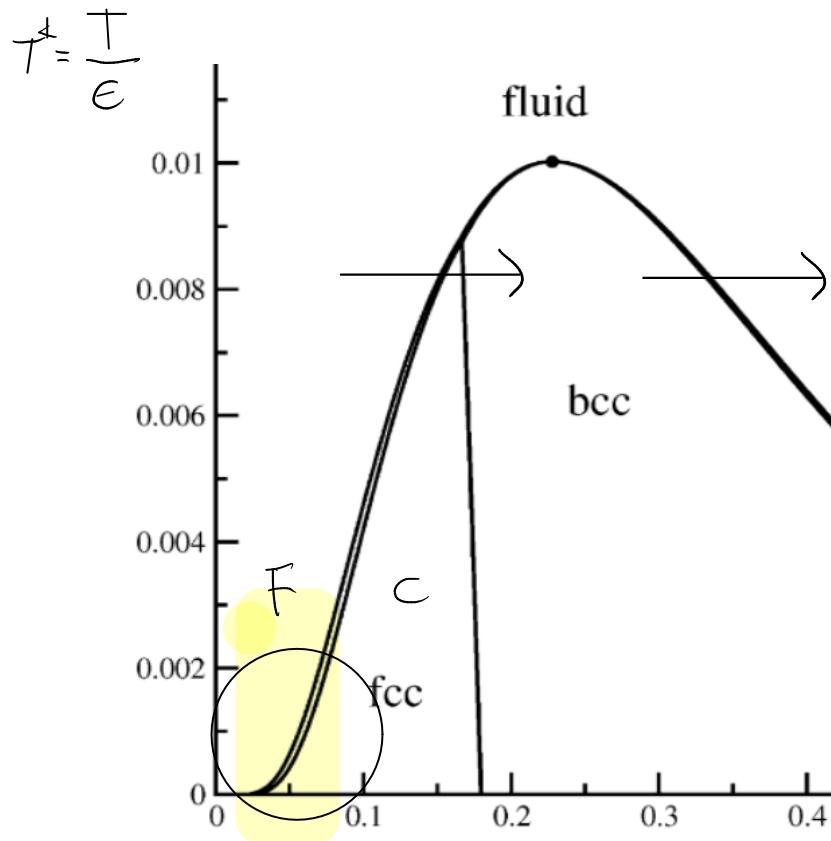
$$e^{-\frac{1}{k_B T} (-k_B T) g_p \sum \dots} \sim e^{-\frac{1}{1/g_p} (\dots)} \rightarrow \text{indipendente da } T$$

$$\begin{array}{ll} r \leq 2R \\ r > 2R \end{array}$$



3. Colloidi ultrasoftici

$u(0) = \text{cost}$ \rightarrow GCM: modello core gaussiano



$$u(r) = \epsilon \exp\left[-\left(\frac{r}{r_f}\right)^2\right] \quad [\epsilon \sim k_B T] \quad \epsilon = \text{cost}$$

TFO: Stillinger \rightsquigarrow poi Likos et al.

reentrant melting

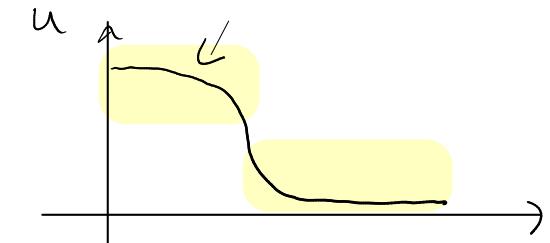
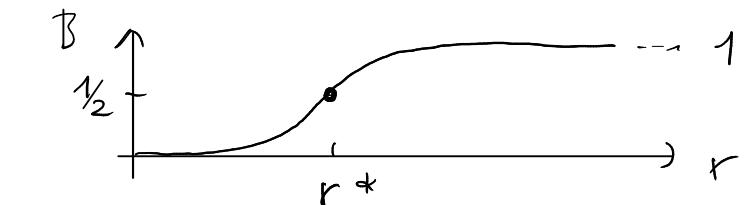


Diagramma di fase a bassa T e β

$$\beta \sigma^3 = \beta^*$$

$$\beta(r, \beta) = \exp\left[-\beta \epsilon \exp\left[-\left(\frac{r}{r_f}\right)^2\right]\right]$$

$$\begin{cases} r \rightarrow \infty : \beta \rightarrow 1 \\ r \rightarrow 0 : \beta \rightarrow \exp(-\beta \epsilon) \end{cases} \quad \text{Se } T \rightarrow 0, \beta \rightarrow \infty \Rightarrow \beta \rightarrow 0$$



$$\beta(r^*, \beta) \approx \frac{1}{2}$$

$$-\ln 2 = -\beta \epsilon \exp\left[-\left(\frac{r^*}{r_f}\right)^2\right] \rightarrow \frac{-\ln 2}{\beta \epsilon} = \exp\left[-\left(\frac{r^*}{r_f}\right)^2\right] \rightarrow \ln\left[\frac{-\ln 2}{\beta \epsilon}\right] = -\left(\frac{r^*}{r_f}\right)^2$$

$$\sqrt{\ln\left[\frac{\beta\epsilon}{\mu^2}\right]} \cdot \sigma = r^*$$

$$\frac{d\beta}{dr} = \exp\left[-\beta\epsilon \underbrace{\exp\left[-(r/\sigma)^2\right]}\right] \cdot (-\beta\epsilon) \underbrace{\exp\left[-(r/\sigma)^2\right]} \left(-\frac{2r}{\sigma^2}\right)$$

$$\exp\left[-(r/\sigma)^2\right] = \exp\left[-\ln\left(\frac{\beta\epsilon}{\mu^2}\right)\right] = \frac{\mu^2}{\beta\epsilon}$$

$$\frac{d\beta}{dr}\Big|_{r^*} = \exp\left[-\beta\epsilon \frac{\mu^2}{\beta\epsilon}\right] \cdot \cancel{\beta\epsilon} \frac{\mu^2}{\cancel{\beta\epsilon}} \frac{2r^*}{\sigma^2} = \frac{1}{2} \mu^2 \cdot 2 \frac{r^*}{\sigma^2} = \mu^2 \cdot \frac{r^*}{\sigma^2}$$

$$T \rightarrow 0 \Rightarrow r^* \rightarrow \infty \Rightarrow \frac{d\beta}{dr}\Big|_{r^*} \rightarrow \infty$$

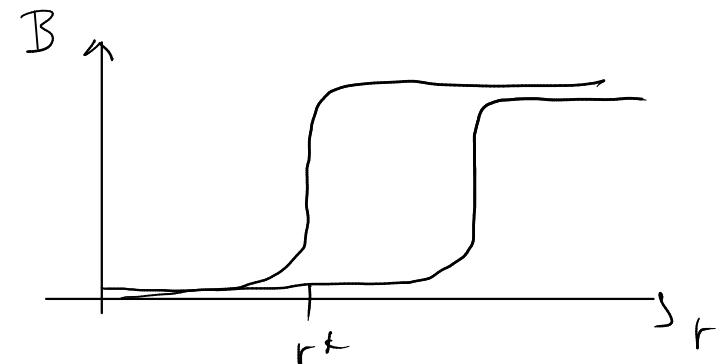
\rightarrow HS con diametro r^*

$$\gamma r^{*3} = 0.94$$

$$\phi_f = 0.49 \rightarrow \gamma_f = \frac{6}{\pi} \frac{1}{\sigma^3} \phi_f \rightarrow \gamma_f \sigma^3 = \phi_f \frac{6}{\pi} = 0.94$$

$$\gamma \left(\ln\left(\frac{\beta\epsilon}{\mu^2}\right)\right)^{3/2} \sigma^3 = 0.94$$

$$\left(\ln\left(\frac{\beta\epsilon}{\mu^2}\right)\right)^{3/2} = \frac{0.94}{\tilde{\gamma}} \Rightarrow \ln\left(\frac{\beta\epsilon}{\mu^2}\right) = \frac{0.96}{\tilde{\gamma}^{2/3}} \Rightarrow \frac{\beta\epsilon}{\mu^2} = \exp\left(\frac{0.96}{\tilde{\gamma}^{2/3}}\right) \Rightarrow T_f \sim \exp\left(-\frac{0.96}{\tilde{\gamma}^{2/3}}\right)$$



Generalized exponential model: $u(r) = e^{-\exp[-(r/\rho)^n]}$ $n \sim 3 \rightarrow$ dendrimer

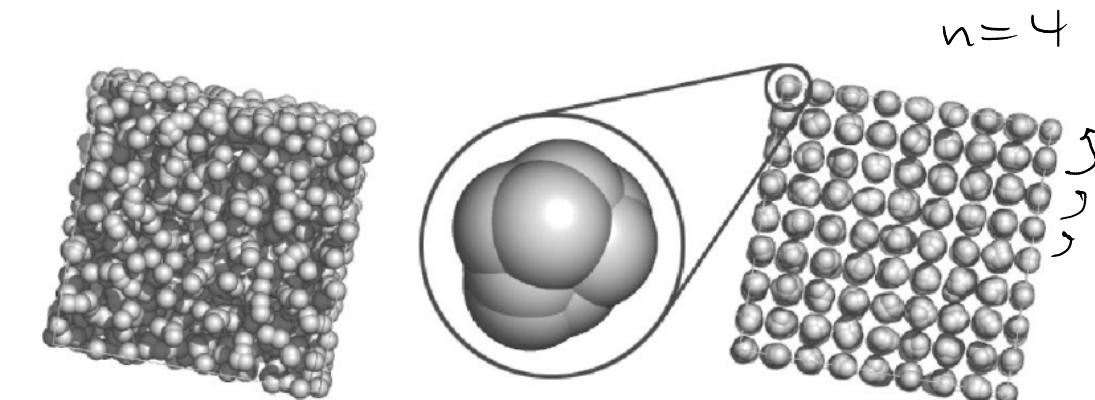
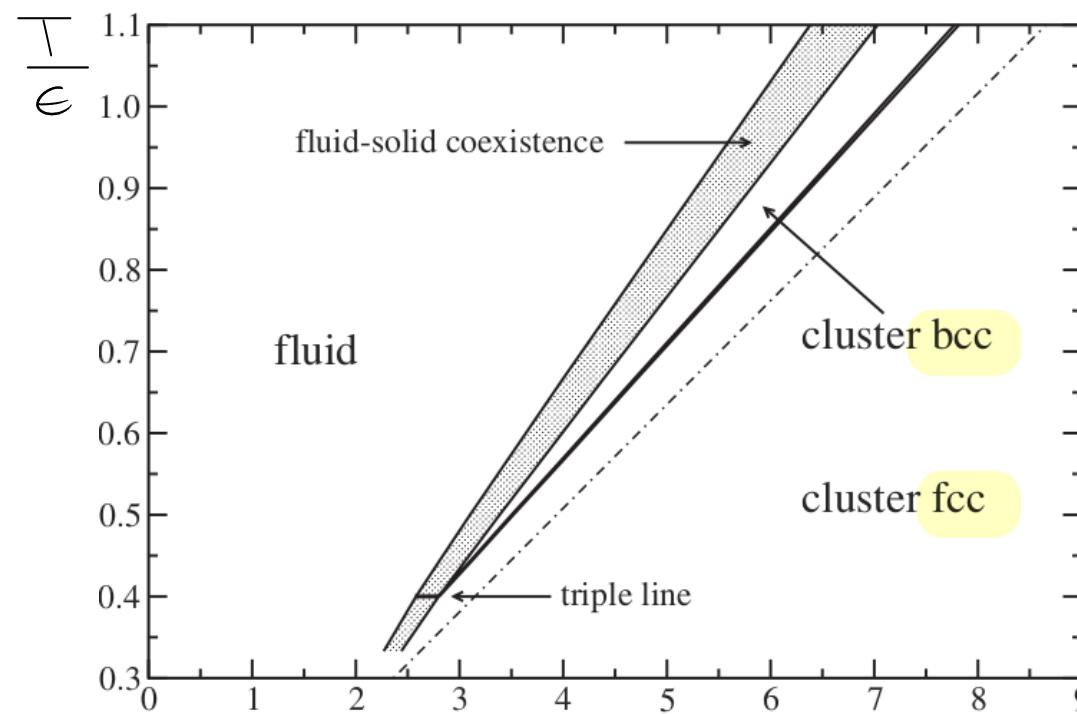
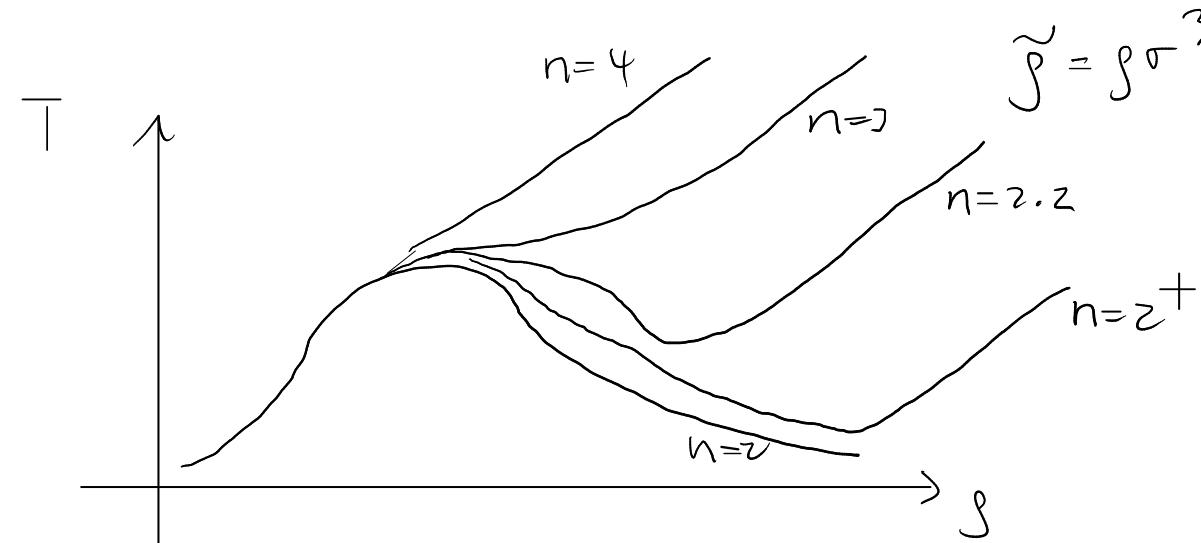


FIG. 2. Two simulation snapshots of a GEM-4 system for $T^* = 0.4$ and $\rho^* = 2.5$ and 7 (left and right). The middle panel shows a close-up of one cluster. Particle diameters are not drawn to scale but are chosen to optimize the visibility of the structures.

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$$\tilde{u}(k) \quad \exists k^* \rightarrow \tilde{u}(k^*) < 0$$

↓
cluster