

# Leyes de la Termodinámica, Fases de la Materia y Propiedades Estructurales.

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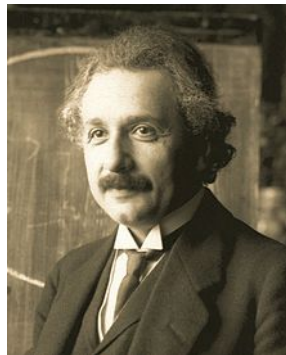
# Contenido

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  - Conceptos
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  - Primera Ley (Energía Interna y Ec. de Estado Calórica)
  - Segunda Ley (Entropía y Procesos Cíclicos)
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  - Fases Fuera de Equilibrio
- 3 **Propiedades Estructurales**
  - Mecanismo de cajas para un sistema de discos duros
  - Dinámica



## A. Einstein

*“Una teoría es mas impresionante cuanto mayor sea la **simplicidad** de sus postulados, el número de cosas que relacione y la extensión de su campo de aplicación. De aquí la impresión tan profunda que me ha causado la termodinámica. Es la única teoría física de contenido **universal** de la cual estoy convencido que, por lo que respecta al campo de aplicación de sus conceptos básicos, nunca será destituida. Por sólo esas razones, es una parte muy importante en la educación de un físico.”*



# Conceptos

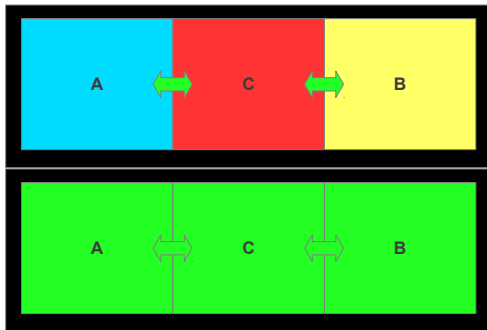
- **Sistema Termodinámico:** *Está constituido por alguna porción del universo físico que nosotros consideramos para su estudio.*
- **Fronteras:** *El mecanismo que lo separa del resto del universo.*
- **Alrededores:** *La interacción entre el sistema y sus alrededores estará caracterizada por los intercambios mutuos de energía, en sus diversas formas. El grado de interacción con sus alrededores dependerá obviamente de la naturaleza de sus fronteras.*





# Equilibrio Térmico

$$f_1(P_A, P_C, V_A, V_C) = 0, f_2(P_B, P_C, V_B, V_C) = 0$$



*"Si tres o más cuerpos se encuentran en contacto térmico, uno a uno, por medio de paredes diatérmicas y se encuentran en equilibrio todos juntos, entonces dos cualesquiera tomados separadamente se encuentran en equilibrio uno con el otro."*

$$\text{Existe: } f_3(P_A, P_B, V_A, V_B) = 0$$

*Equilibrio Térmico*



# Equilibrio Térmico

$$f_1(P_A, P_C, V_A, V_C) = 0$$

$$f_2(P_B, P_C, V_B, V_C) = 0$$

$$P_C = g_1(P_A, V_A, V_C)$$

$$P_C = g_2(P_B, V_B, V_C)$$

$$g_1(P_A, V_A, V_C) = g_2(P_B, V_B, V_C)$$

$$f_3(P_A, P_B, V_A, V_B) = 0$$

Estas última son expresiones que describen la misma situación física. Proponemos una función tal que se elimine  $V_C$

$$g_1 = \phi_1(P_A, V_A)\eta(V_C) + \xi(V_C)$$

$$g_2 = \phi_2(P_B, V_B)\eta(V_C) + \xi(V_C)$$

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B)$$

Analogamente:

$$\phi_2(P_B, V_B) = \phi_3(P_C, V_C)$$







# Ecuación de Estado Térmica

$$P = P(V, T)$$

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

$$\frac{dP}{P} = -\frac{1}{PV\kappa_T} dV + \frac{\beta}{P\kappa_T} dT$$

Compresibilidad Isotérmica

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \approx \frac{1}{P}$$

Coef. de Expansión Térmico

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \approx \frac{1}{T}$$

$$\frac{dP}{P} = -\frac{1}{V} dV + \frac{1}{T} dT$$

$$\ln P = -\ln V + \ln T + \ln C$$

$$\ln P = \ln CT/V$$

$$PV = CT; \text{ Gas Ideal}$$

Observaciones experimentales:

- Ley Charles, 1780

(o Gay-Lussac, 1802)

$$P = \text{cte (Isobáricas): } V \propto T$$

- Ley de Boyle-Mariotte, 1660

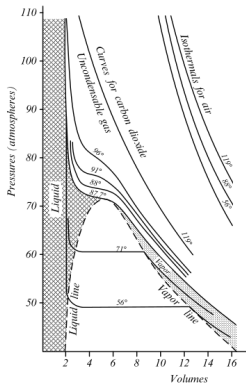
$$T = \text{cte (Isotermas): } P \propto \frac{1}{V}$$



# Ecuación de Estado Térmica

Experimentos de Thomas Andrews, 1861-1869

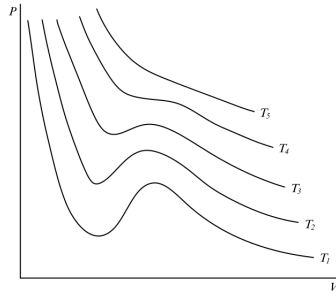
The Bakerian Lecture for 1869: "The continuity of the gaseous and liquid states of matter"



La Tesis de Johannes Diderik van der Waals 1873, "The continuity of the gaseous and liquid states of matter" posiblemente en respuesta a los experimentos de Andrews

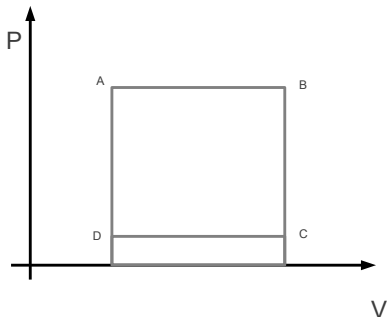
(Nobel 1910).

$$P = \frac{NKT}{(V-Nb)} - a\left(\frac{N}{V}\right)^2$$



# Diferenciales inexactas, variables de estado

$A \rightarrow C$



A diferencia de las variables termodinámicas como  $P$ ,  $V$ ,  $T$ ,  $U$ , El trabajo  $W$  y el calor  $Q$  no son variables de estado por lo que sus diferenciales son inexactas.

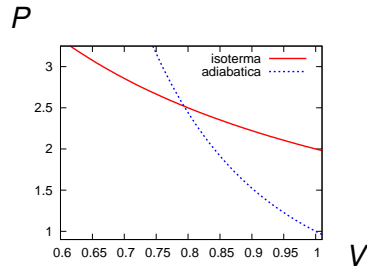
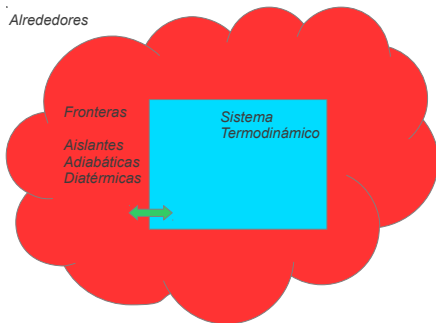
$$\delta W = \int P dV$$
$$\int_{A \rightarrow B \rightarrow C} P dV \neq \int_{A \rightarrow D \rightarrow C} P dV$$

$$dU = \delta Q - \delta W$$
$$dU = \delta Q - p dV$$



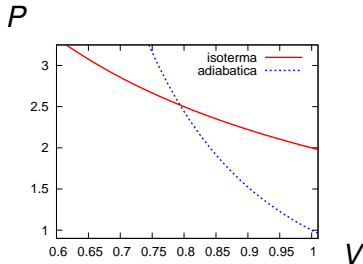
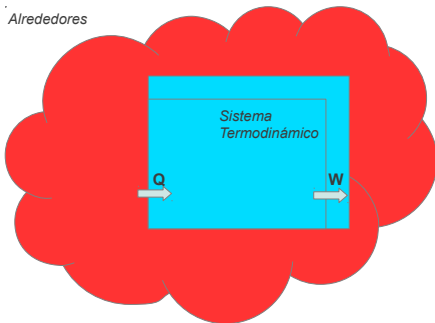
# Procesos Isotérmicos y adiabáticos

Presión ( $P$ ), Volumen ( $V$ ), Temperatura ( $T$ ),  
Energía ( $U_i \rightarrow U_f$ )



# Procesos Isotérmicos y adiabáticos

Presión ( $P$ ), Volumen ( $V$ ), Temperatura ( $T$ ),  
Energía ( $U_i \rightarrow U_f$ )

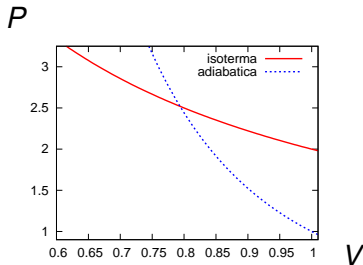
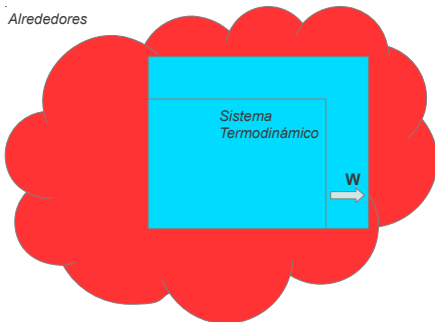


$$dU = \delta Q - \delta W$$



# Procesos Isotérmicos y adiabáticos

Presión ( $P$ ), Volumen ( $V$ ), Temperatura ( $T$ ),  
Energía ( $U_i \rightarrow U_f$ )

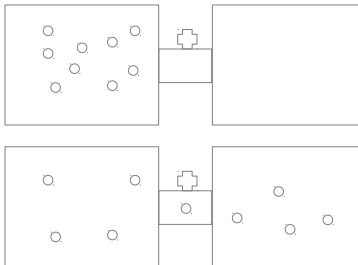


$$dU = -\delta W_{ad}$$



# Experimento de Kelvin (Ecuación Calórica)

$$dU = \delta Q - \delta W = 0$$



$$U_i(V_i, T_i) = U_f(V_f, T_f)$$

$$T_i = T_f;$$

$$V_i \neq V_f$$

$$U(T)$$

$$C_V = \frac{\delta Q}{dT} = \frac{dU}{dT}$$

$$U(T) = U(T_0) + \int_{T_0}^T C_V dT$$

$$U(T) = U(T_0) + C_V(T - T_0)$$

$$U(T) = C_V T$$

Ecuación de estado  
Calórica.

$$\delta Q = 0$$

$$\delta W = 0$$



# Entropía

Ley Cero:  $T$

$$PV = NkT \text{ (térmica)}$$

Primera Ley:  $U$

$$U(T) = U_0 + C_V T, \text{ (calórica)}$$

$$dU = \delta Q - \delta W$$

$$\delta Q = dU + \delta W$$

$$\delta Q = C_V dT + pdV$$

$$\frac{\delta Q}{T} = C_V \frac{dT}{T} + p \frac{dV}{T}$$

$$\frac{\delta Q}{T} = C_V \frac{dT}{T} + Nk \frac{dV}{V}$$

$$= C_V d(\ln(T)) + Nk d(\ln(V))$$

$$= d(\ln(T^{C_V} V^{Nk})) = dS$$

$$\frac{\delta Q}{T} = dS$$

$$\delta Q = TdS$$

Por lo que:

$$dU = TdS - pdV$$

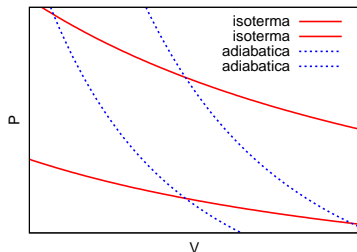
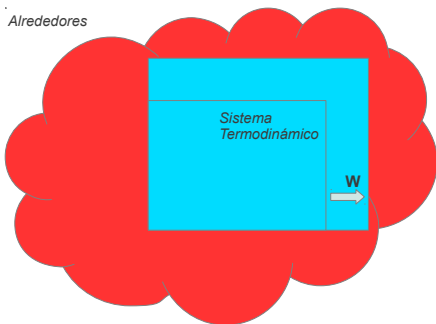
¡¡Para procesos reversibles!!





# Ciclo de Carnot

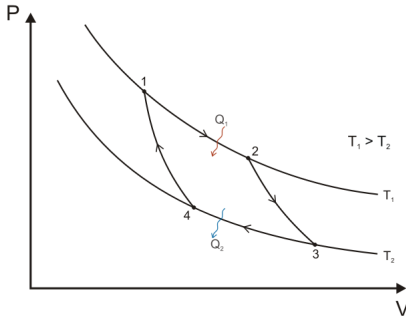
Presión ( $P$ ), Volumen ( $V$ ), Temperatura ( $T$ ),  
Energía ( $U_i \rightarrow U_f$ )



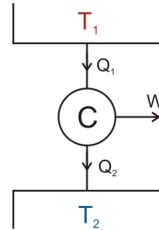
$$\oint dU = 0$$



# Ciclo de Carnot



$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$
$$\eta = 1 - \frac{T_2 \Delta S}{T_1 \Delta S}$$



$$\eta = 1 - \frac{T_2}{T_1}$$

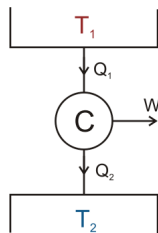


## Teorema y corolario de Carnot

*"Ninguna máquina térmica, operando en ciclos entre dos fuentes de temperaturas fijas, tiene una eficiencia mayor que la de una máquina reversible operando entre las mismas dos fuentes"*

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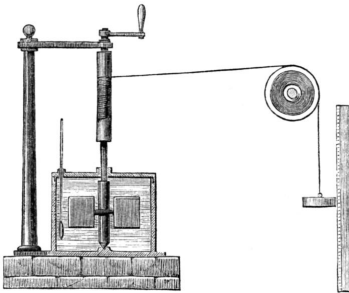
*"Todas las máquinas reversibles (e.g. máquinas de Carnot con cualquier sustancia) operando entre dos recipientes térmicos a temperaturas dadas, tienen la misma eficiencia"*



$$\eta = 1 - \frac{T_2}{T_1}$$



## Segunda ley: Procesos irreversibles



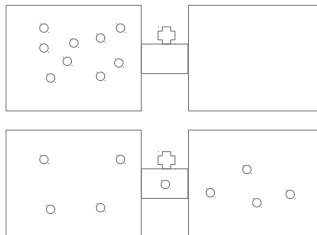
Experimento de Joule



Pelota rebotando



# Segunda ley: Procesos irreversibles

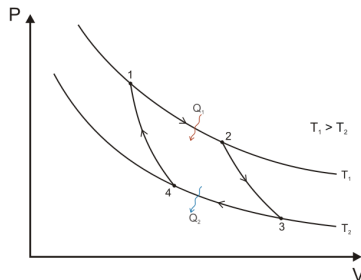


Experimento de Kelvin

$$\delta Q \neq TdS$$

Producción de entropía

$$Q_1 = 0$$

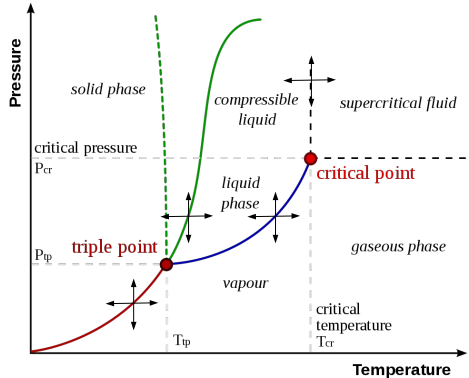
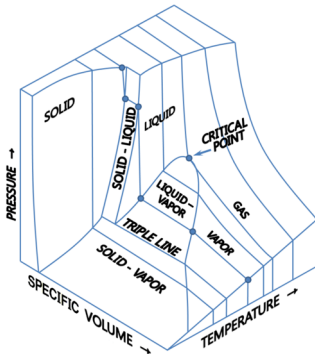


$$S_1 \rightarrow S_2$$

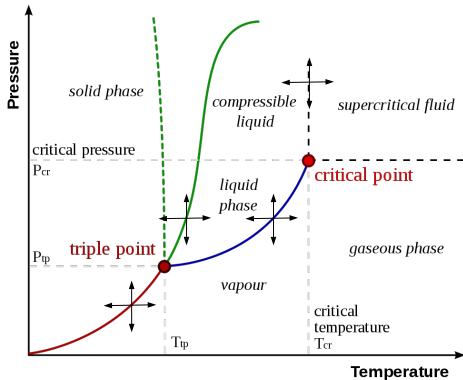
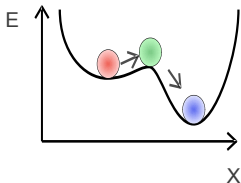
isotérmico pero irreversible



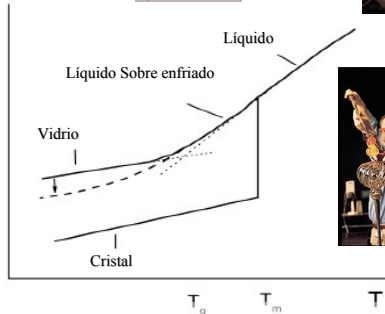
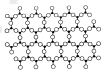
# Transiciones de Fase en Equilibrio



# Analogía con un Sist. Mecánico



## Motivación Solidificación



- *Dinámica Lenta*
- *Tiempos de relajación cambian aproximadamente 14 ordenes de magnitud.*

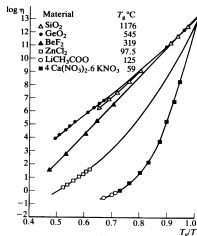
\* *S.R. Elliot, Physics of Amorphous Materials, (Wiley, NY, 1998).*





**Motivación**  
**Solidificación**

$$\eta = A \exp(E/kT)$$



**ASU** ARIZONA STATE UNIVERSITY

$$\eta = A \exp[B/(T - T_0)]$$

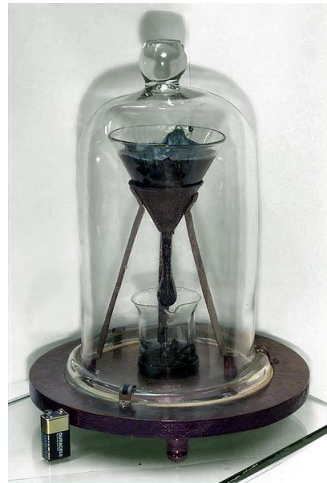
*Clasificación de vidrios fuertes y frágiles de Angell*

\*C.A. Angell, et al., *J. Non-Cryst. Solids*, **102**, 205 (1998) <http://www.public.asu.edu/~caangell/>



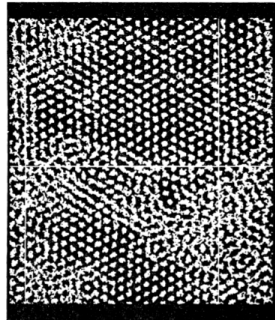
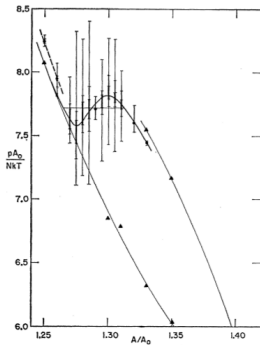
# The Pitch Drop Experiment

The experiment taking place at University of Queensland in Brisbane, Australia, is a long-term experiment which measures the flow of a piece of pitch. The experiment began in 1927 when Professor Thomas Parnell set it up. Demonstrating that pitch has a viscosity approximately  $10^{11}$  times that of water.



# History of Freezing Transition (FT)

FT was first seen in the computer simulation studies of 870 hard disks by Alder and Wainwright approx. 50 years ago:

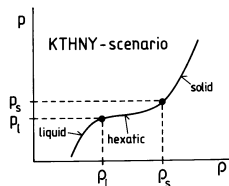
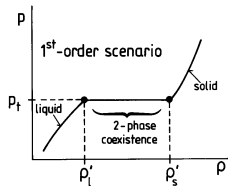


Equation of state and traces

B.J. Alder and T.E. Wainwright, *Phys. Rev.* **127**, 359 (1962)

# KTHNY

Although the system of 2D HD is one of the simplest models of a fluid it exhibits a rich behaviour, e.g. still is not clear if this transformation is...



"KTHNY theory predicts that the crystal undergoes a continuous melting transition into a possibly metastable hexatic phase. Hexatic phase: have short range translational order and long-range orientational order. Of course, the KTHNY scenario does not rule out the possibility of a first-order transition occurring by another mechanism."

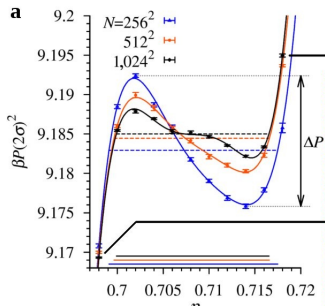
Trusket et al, *PRE*, **58**, 3083 (1998)

K. Binder, et al, *J. Phys.:* CM 14 (2002) 2323–2333



# KTHNY

Different Scenario



<http://www.lps.ens.fr/~krauth/index.php/>

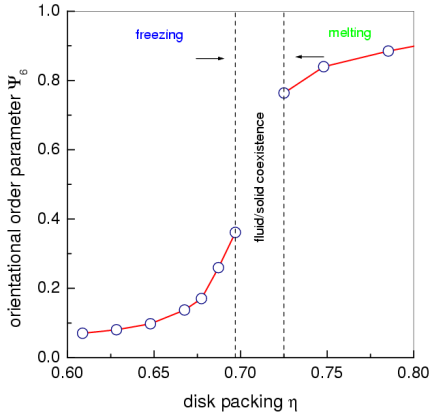
Bernard\_Krauth\_2011

A different possibility: Using large-scale simulations with event-chain Monte Carlo algorithm Bernad and Krauth have report "a first-order scenario between a liquid and a solid, and the KTHNY scenario with an intermediate hexatic phase separated by continuous transitions from liquid and the solid."

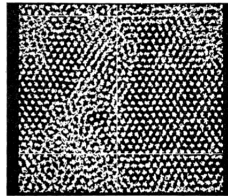


# Orientalational order parameter

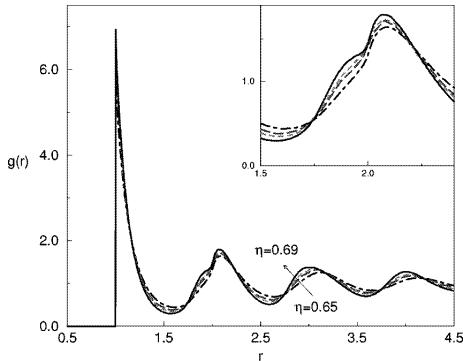
$$\eta_f = 0.69, \eta_m = 0.716$$



$$\psi_6 = \left| \frac{1}{N_{nn}} \sum_{jk} e^{i6\theta_{jk}} \right|$$



# Structural Precursor of Order



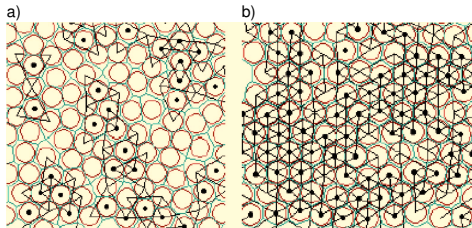
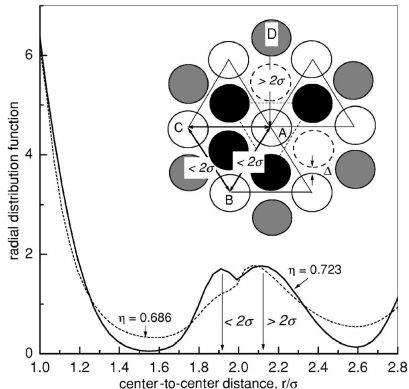
Truskett et al, *PRE*, **58**, 3083 (1998)

*"...As the dense fluid approaches the freezing transition, the ordered arrangements form large embryonic domains, commensurate with those seen in the crystal at the melting point. Contrary to the notion that the split second peak is a signature of the amorphous solid."*



# Caging Mechanism

$$\eta_f = 0.69, \eta_m = 0.716$$



From the Voronoi hexagonal cells.  
Select the three alternating nearest neighbors with distance  $< 2\sigma$ .

- a) Near freezing more single triangular caged
- b) Near melting more double triangular caged

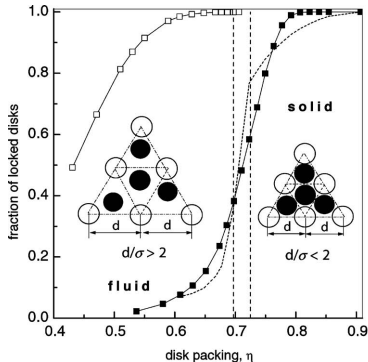
A. Huerta, A. Trokhymchuck, D. Henderson *PRE* **74**, 061106 (2006)





# Caging Mechanism

$$\eta_f = 0.69, \eta_m = 0.716, \psi_6 = \left| \frac{1}{N_{nn}} \sum_{jk} e^{i6\theta_{jk}} \right|$$



Fraction of caged disk follows two criteria:

- i) Voronoi hexagonal neighbors  $< 2\sigma$
- ii) Voronoi alternating hexagonal neighbors  $< 2\sigma$

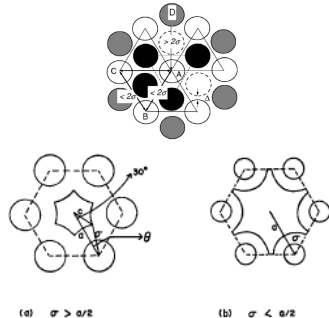
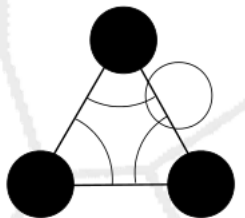


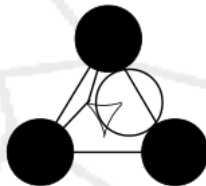
FIG. 3. Free areas in close packing. (a) The case of  $\sigma > a/2$ : the central hexagon shown by full curves is the free area in this case. (b) The case of  $\sigma < a/2$ : The hexagon shown by full curves is the free area.

Eyring J. Chem. Phys. 4, 283 (1936)





$$1 < d/\sigma < 2$$



$$d/\sigma > 2$$

$$\frac{a_f}{\sigma^2} = \frac{\sqrt{3}}{4}(d/\sigma)^2 - \frac{\pi}{2} + 3\cos^{-1}\left(\frac{d/\sigma}{2}\right) - \frac{3}{4}(d/\sigma)\sqrt{4 - (d/\sigma)^2}$$



# Equation of State

$$\frac{a_f}{\sigma^2} = \frac{\sqrt{3}}{4} \left(\frac{d}{\sigma}\right)^2 - \frac{\pi}{2} + 3\arccos\left(\frac{d}{2\sigma}\right) - \frac{3}{4}\sqrt{4\left(\frac{d}{\sigma}\right)^2 - \left(\frac{d}{\sigma}\right)^4} \quad (1)$$

If  $d < 2\sigma$ . If  $d > 2$  only first two terms.

Change the variable  $x = \left(\frac{d}{\sigma}\right)^2$ .

$$\frac{a_f}{\sigma^2} = \frac{\sqrt{3}}{4}x - \frac{\pi}{2} + 3\arccos\left(\frac{\sqrt{x}}{2}\right) - \frac{3}{4}\sqrt{4x - x^2} \quad (2)$$

The pressure can be obtained from

$$F = -kT \ln Z = -kT \ln a_f^N \quad (3)$$

$$F = -NkT \ln a_f \quad (4)$$

$$P = -\frac{\partial F}{\partial A} = NkT \frac{\partial \ln a_f}{\partial A} = kT \frac{\partial \ln a_f}{\partial A/N} = kT \frac{\partial \ln a_f}{\partial a} \quad (5)$$

$$\frac{Pa}{kT} = a \frac{\partial \ln a_f}{\partial a} = \frac{a}{a_f} \frac{\partial a_f}{\partial a}, \quad (6)$$

where  $a = A/N = 1/\rho$  is the area per one particle. Using the relation  $a = \frac{\sqrt{3}}{6}d^2 = \frac{\sqrt{3}}{6}x\sigma^2$ ,



# Equation of State

$$\frac{Pa}{kT} = \frac{x}{a_f} \frac{\partial a_f}{\partial x}, \quad (7)$$

and the derivative  $\partial a_f / \partial x$

$$\frac{\partial a_f}{\partial x} = \left( \frac{\sqrt{3}}{4} - \frac{3/2}{\sqrt{x}\sqrt{1-x/4}} + \frac{3\sqrt{x}/8}{\sqrt{1-x/4}} \right) \sigma^2 \quad (8)$$

substituting returning to the original variables

$$\frac{Pa}{kT} = \frac{d^2}{a_f} \left( \frac{\sqrt{3}}{4} - \frac{3\sigma/2d}{\sqrt{1-\frac{d^2}{4\sigma^2}}} + \frac{3d/8\sigma}{\sqrt{1-\frac{d^2}{4\sigma^2}}} \right) \quad (9)$$

$$\frac{Pa}{kT} = \frac{d^2}{a_f} \left( \frac{\sqrt{3}}{4} + \frac{3d/8\sigma - 3\sigma/2d}{\sqrt{1-\frac{d^2}{4\sigma^2}}} \right) \quad (10)$$

If  $d < 2\sigma$  If  $d > 2\sigma$  only the first term.



# Caging Mechanism

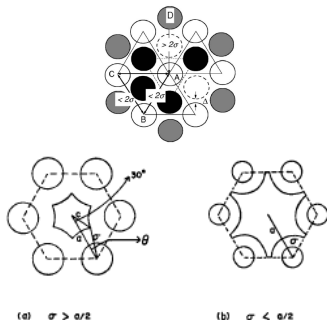
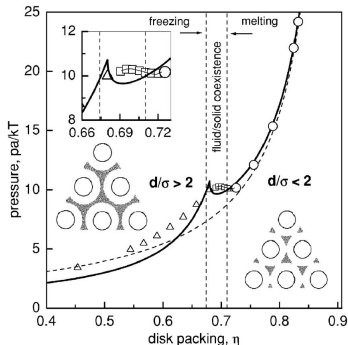


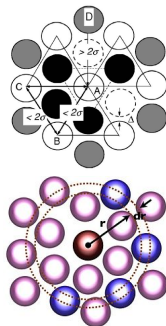
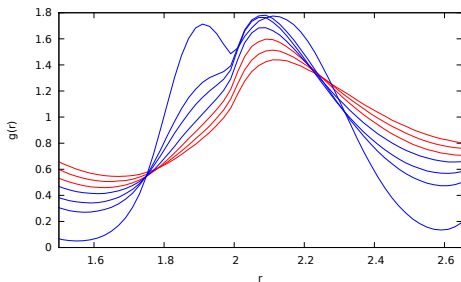
FIG. 3. Free areas in close packing. (a) The case of  $\sigma > a/2$ : the central hexagon shown by full curves is the free area in this case. (b) The case of  $\sigma < a/2$ : The hexagon shown by full curves is the free area.

Eyring J. Chem. Phys. 4, 283 (1936)



A. Huerta, A. Trokhymchuck, D. Henderson *PRE* 74, 061106 (2006)

# The Pair Distribution Function



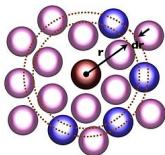
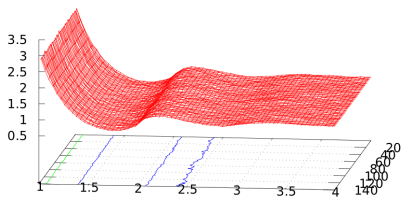
Second oscillation of the pair distribution function. For  $\eta = 0.600, 0.620, 0.640$  in red and  $\eta = 0.660, 0.680, 0.690, 0.723$  in blue.

A. Huerta, A. Trokhymchuck, D. Henderson *PRE* **74**, 061106 (2006)

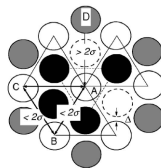
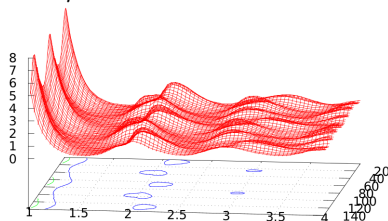


# $g(r, \theta)$ for HD $\eta_f = 0.69, \eta_m = 0.716$

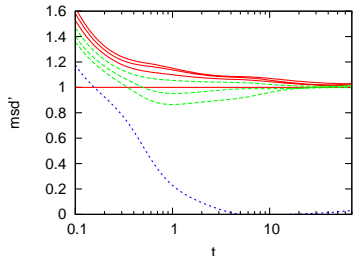
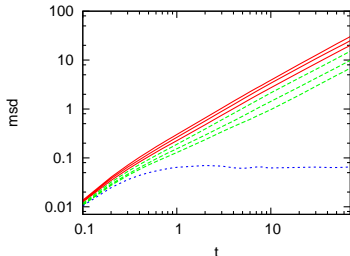
$\eta = 0.500$



$\eta = 0.686$



# The mean square displacement.

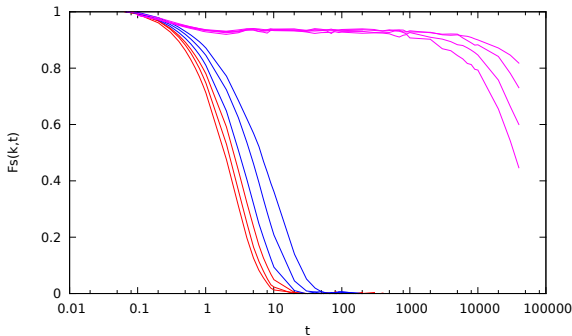


**Figure:** The mean square displacement. for  $\eta = 0.600, 0.620, 0.640$  in red and  $\eta = 0.660, 0.680, 0.690, 0.723$ . The behaviour at  $\eta = 0.723$  near melting are included for comparison proposes also a line with slope 1 is included to compare with diffusive behaviour.





# The intermediate self-scattering function.



**Figure:** The intermediate self-scattering function. All for  $\eta = 0.600, 0.620, 0.640$  in red and  $\eta = 0.660, 0.680, 0.690, 0.723$ .



# The intermediate self-scattering function.

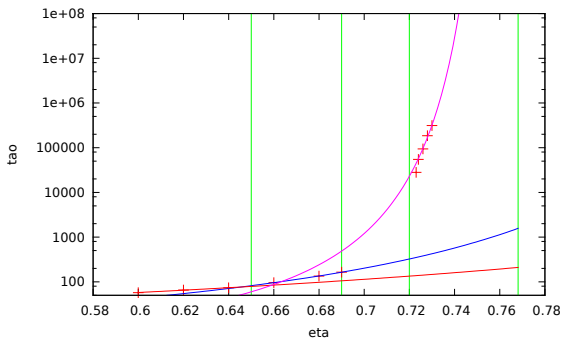
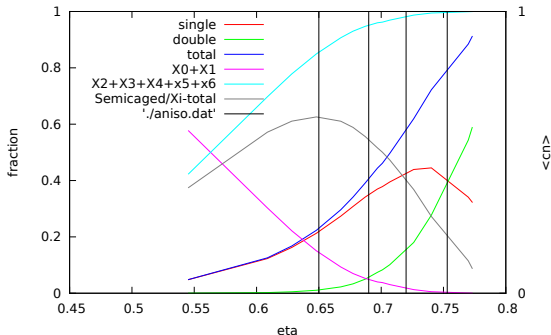


Figure: Vogel fulcher fit



# Fraction Semi-Caged Particles

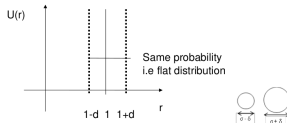
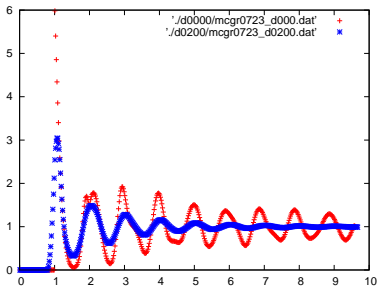


**Figure:** Fraction of single and double caged particles, the sum (particles with at least one cage. Fraction of particles with one and zero constraints, the fraction of particles with 2 and more constraints. And finally the fraction of semi-caged particles.



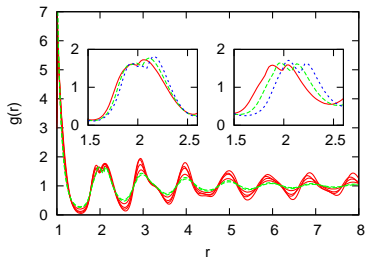
# Thesis Josefina Vicente Santiago UV

## Frustration of the caging mechanism using Polydispersity

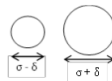


# Thesis Virginia Carrasco Fadanelli UV

## Frustration of the caging mechanism using Bidispersity



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Universidad Veracruzana

## *A frustration study of the freezing mechanism*

*Virginia Carrasco Fadanelli, fadanellive@gmail.com, Facultad de Física e I.A. Depto. Física, Universidad Veracruzana; Adrián Arturo Huerta Hernández, adrian.huerta@gmail.com, Facultad de Física e I.A. Depto. Física, Universidad Veracruzana*

### **ABSTRACT**

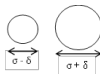
In the present work we report a systematic study of the frustration mechanism originally proposed in Huerta et al, Phys. Rev. E, 061106 (2006). The later was carried out by tuning the diameter ratio of a bidisperse system. We make an interpretation of the thermodynamic, structural and dynamic properties in terms of its energy landscape. The later helps us to give an interpretation of the glassy behavior due to the frustration of the originally proposed freezing mechanism.



# Frustración del mecanismo de cajas

## I. MODEL

In this work we use an equimolar mixture of hard disks of diameters  $\sigma \pm \delta$ . where  $\delta$  helps us to tunned the ratio of the diameters mixture. The  $\delta=0$  corresponds to the monodisperse case, the increase of the  $\delta$  values increases the hard disks asymmetry of the mixture.



## II. METHODOLOGY

We employed Monte Carlo Metropolis simulations to study the thermodynamics and structural behavior of different diameter ratios of hard disks mixture. To study the dynamical behavior we use even driven molecular dynamics simulations. To plot the  $F_{self}$  we use the wave vector  $k=2.14$  for all the reported packing fractions. We employed 400 hard disks and a rectangular simulation cell which sides have a square root of 3 ratio and we use periodic boundary conditions.





# Frustración del mecanismo de cajas

## III. THERMODYNAMICS

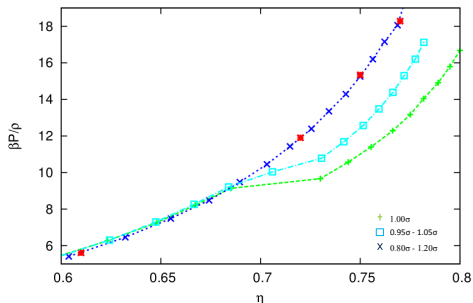


Figure 1: The phase diagram for: (green line) monodisperse hard disks system with radius  $1.00\sigma$ ; (light blue) bidisperse hard disks radius  $0.95\sigma - 1.05\sigma$  and (blue) bidisperse hard disks radius  $0.80\sigma - 1.20\sigma$ . The red asterisks indicates the first four msd plotted in figure 2.



# Frustración del mecanismo de cajas

## IV. DYNAMICS

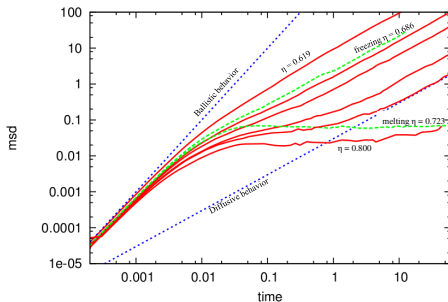


Figure 2: The mean square displacement (msd) as a function of time for the densities indicated in figure 1 in red, for the system with radius  $0.8\sigma$ - $1.20\sigma$ , the last two lines in red corresponds to  $\eta=0.782, 0.800$ , non shown in the phase diagram. We compare with the msd of the monodisperse system at freezing and melting points (lines in green).

The blue lines with slope two and one respectively are shown to guide the eye at ballistic and diffusive regimes, indicating a sub-diffusive regime between them. In all cases the density increase from top left to bottom right.



# Frustración del mecanismo de cajas

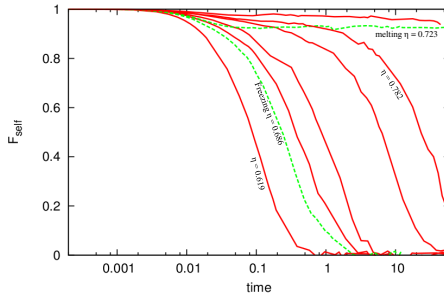


Figure 3: The self intermediate scattering function ( $F_{self}$ ) for the same situation described in figure 2.



# Frustración del mecanismo de cajas

## V. STRUCTURE

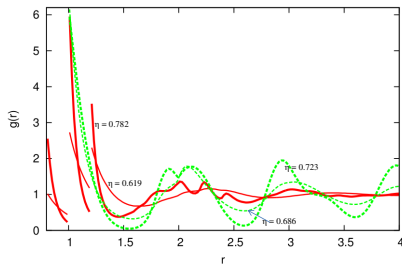


Figure 4: Radial distribution function of the bidisperse system at  $\eta = 0.619$  and  $0.782$ , thin and thick red lines respectively; and monodisperse system  $\eta = 0.686$  and  $0.723$  thin and thick green lines, respectively.



# Frustración del mecanismo de cajas

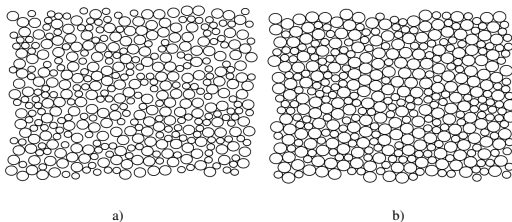


Figure 5: Snapshot of the final configurations of the bidisperse system at a)  $\eta=0.619$  and b)  $\eta=0.782$ .



# Frustración del mecanismo de cajas

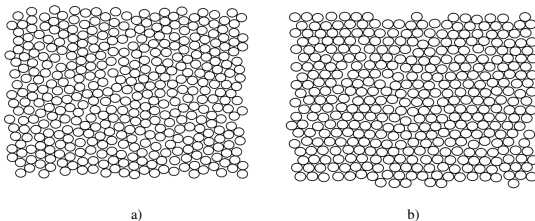


Figure 6: Snapshot of the final configurations of the monodisperse system at a)  $\eta=0.686$  and b)  $\eta=0.723$ .

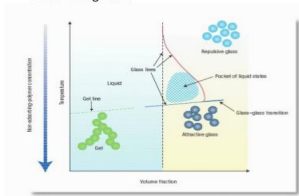


# Frustración del mecanismo de cajas

## VI. CONCLUSIONS

In this work we have evaluated the thermodynamics, dynamics and structural properties of a hard disks mixture for several hard disks ratios. For a large enough ratios we observe the avoidance of the crystalline phase driven the system to a high density liquidlike phase similar to the liquid pockets

What is a glass?



References:

- Freezing of two-dimensional hard disks a Huerta et al. Phys.Rev. E 2006.
- One liquid two glasses, F. Sciortino Nature Materials, November 2002.

