Kinetic Theory of Soft Matter. The Penetrable-Sphere Model

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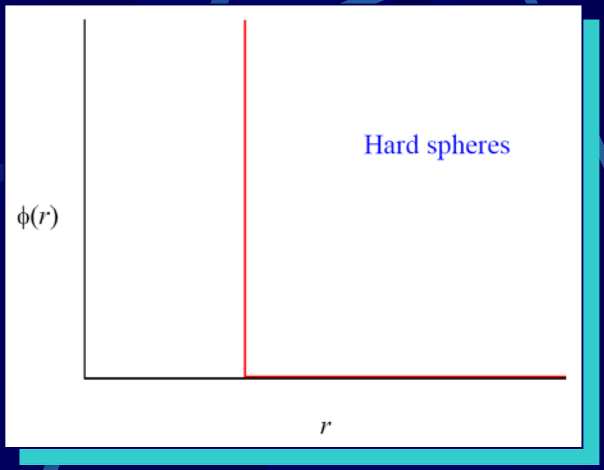
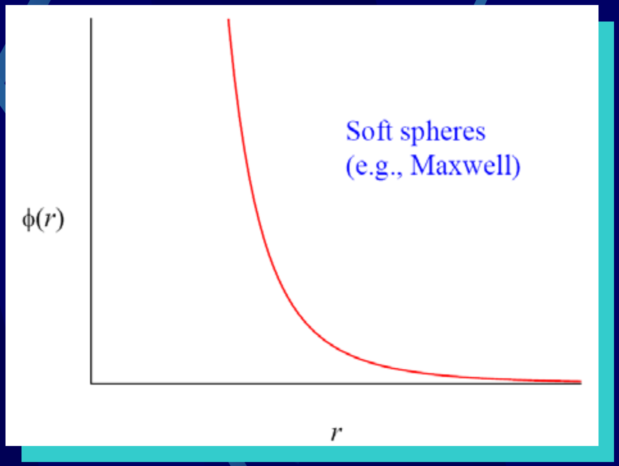
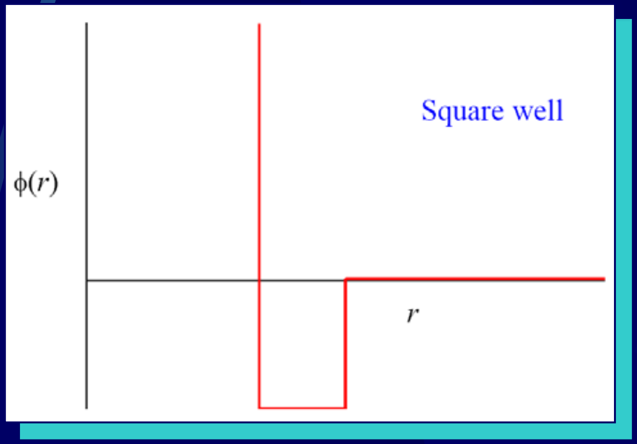
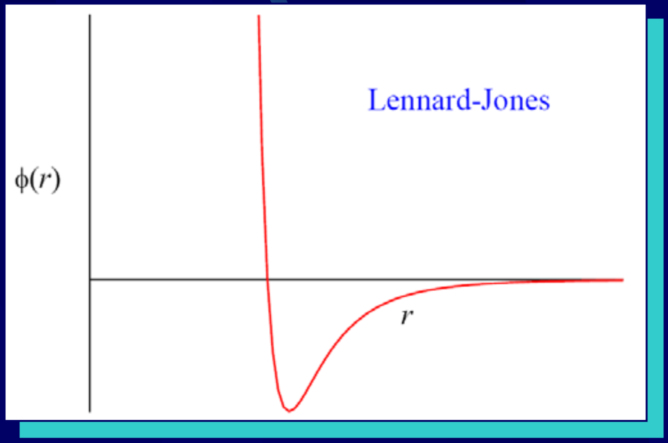
Traditionally, the kinetic theory of gases has been applied to particles interacting via *unbounded* potentials, e.g.,









Unbounded potentials are useful representations of the interactions in *atomic* systems, but not necessarily so in *colloidal* systems (soft matter).

Soft matter: Large class of materials composed of *mesoscopic* particles (i.e., particles with typical sizes 1 nm–1 μm) dispersed into a solvent whose molecules are much smaller in size (typically of atomic dimensions).

In addition, soft matter systems may contain other, smaller unities such as short polymeric chains, salt dissociated into ions, etc.

Dilute solution of *polymer chains* in a good solvent

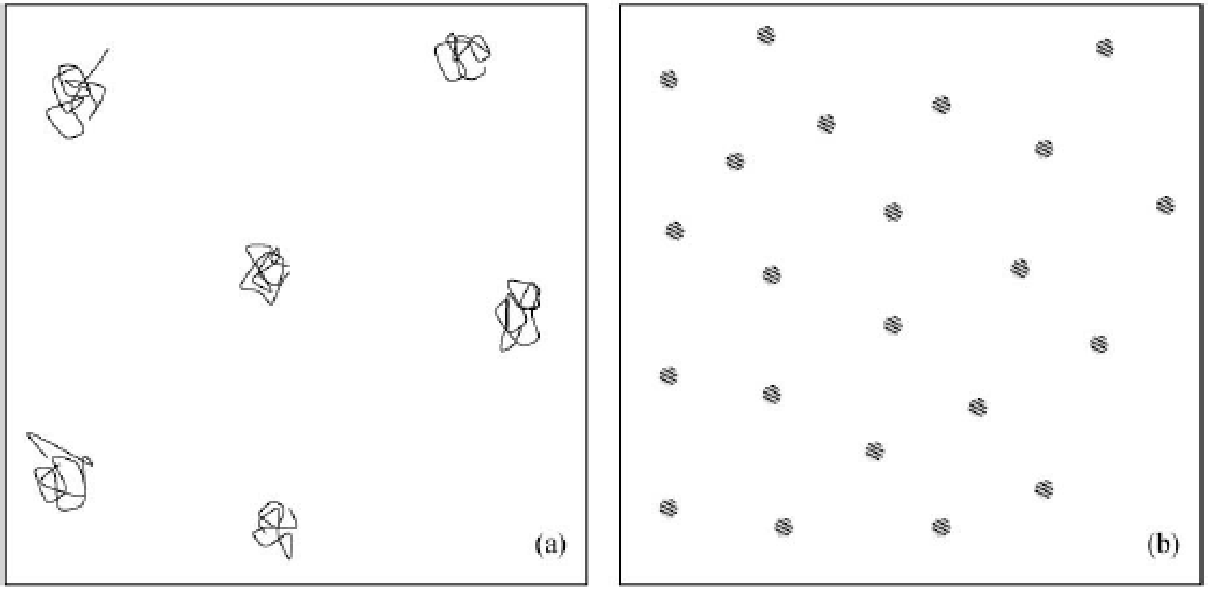


Fig. 13. A dilute polymer solution observed through two different microscopes. In (a) the microscope can resolve details above the monomer length whereas in (b) the microscope can only resolve details above the size of the chain. As a result, all length scales in (b) appear reduced with respect to those in (a) and the objects which appear as flexible chains in (a) show up as "point particles" in (b). Note that the field of view in (b) includes many more particles than in (a).

After C. Likos, *Phys. Rep*. **348**, 267–439 (2001)

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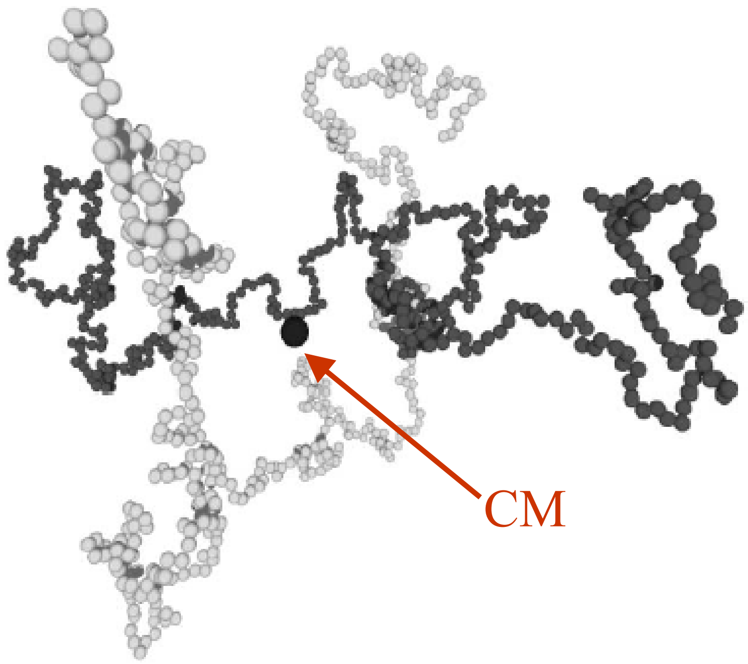

Fig. 14. A snapshot from a simulation involving two self-avoiding polymers. In this configuration, the centers of mass of the two chains (denoted by the big sphere) coincide, without violation of the excluded-volume conditions. (Courtesy of Arben Jusufi.)

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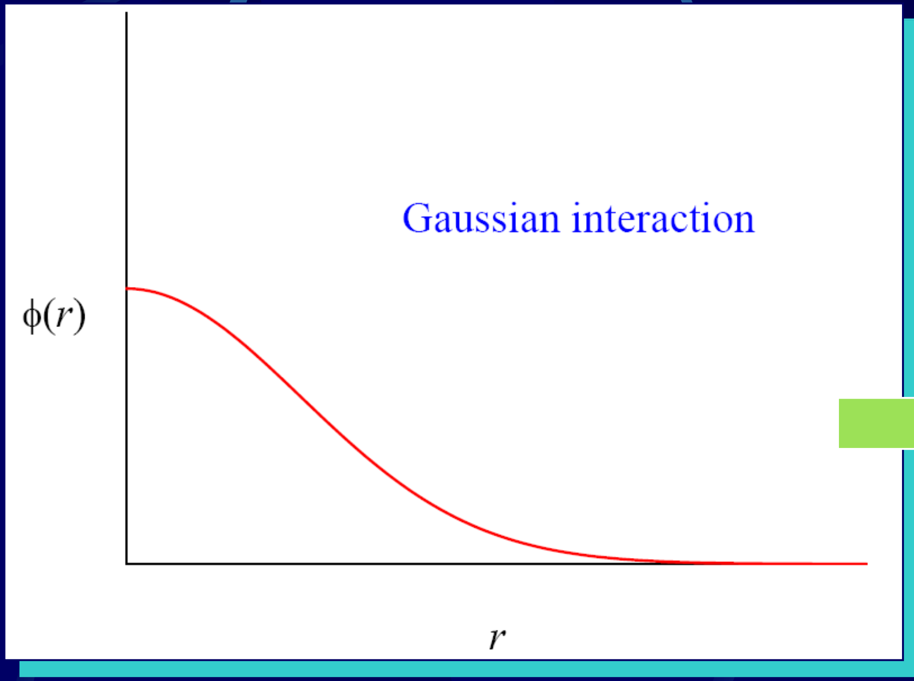
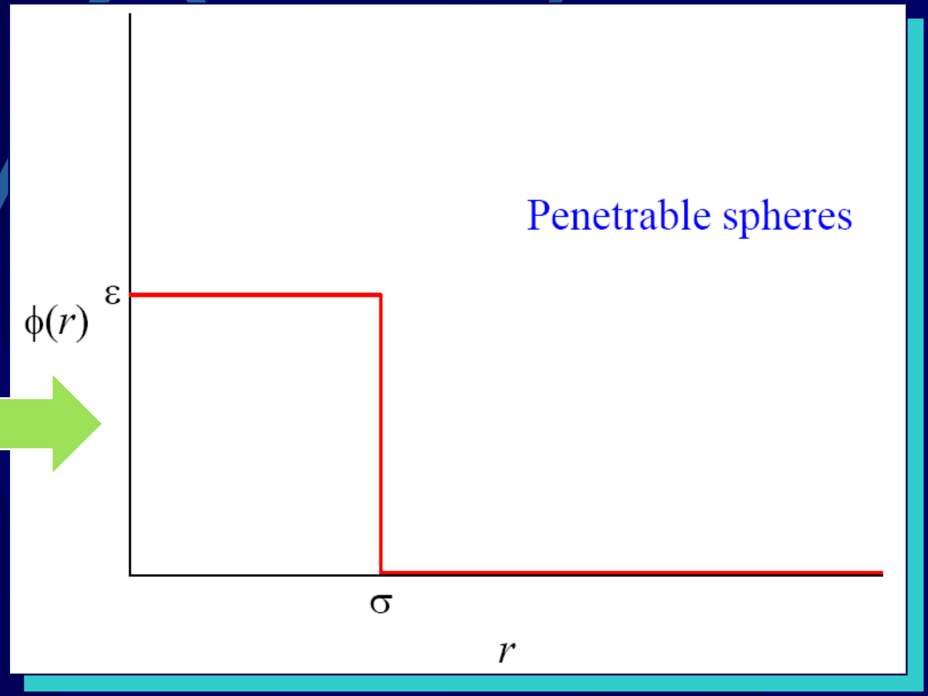
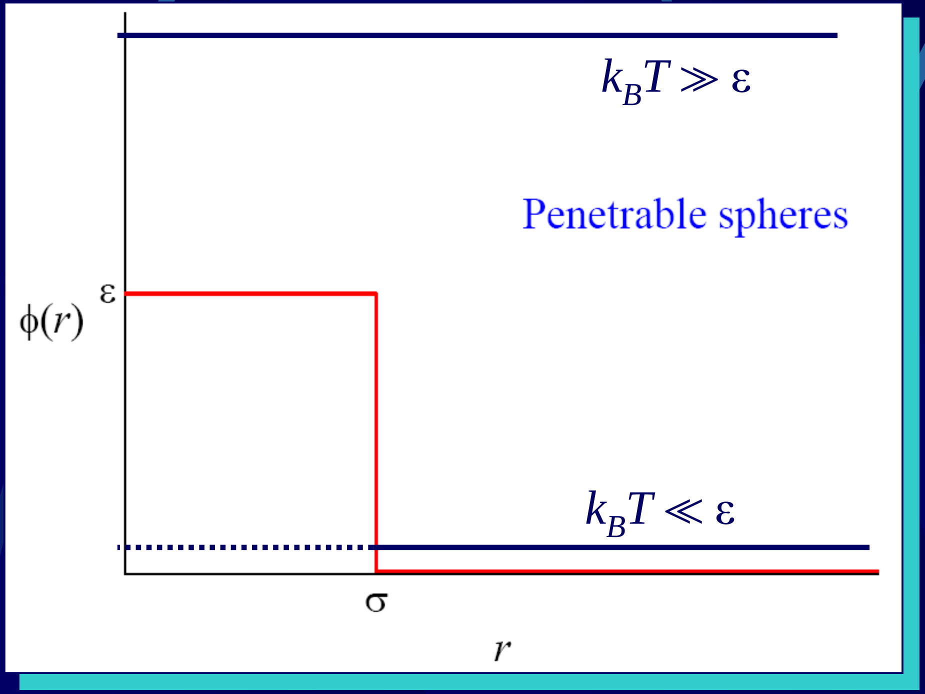
Dilute solution of *polymer chains* in a good solvent

Effective interaction between two polymer chains:





Goal: Evaluate the transport coefficients of a *dilute* gas of penetrable spheres

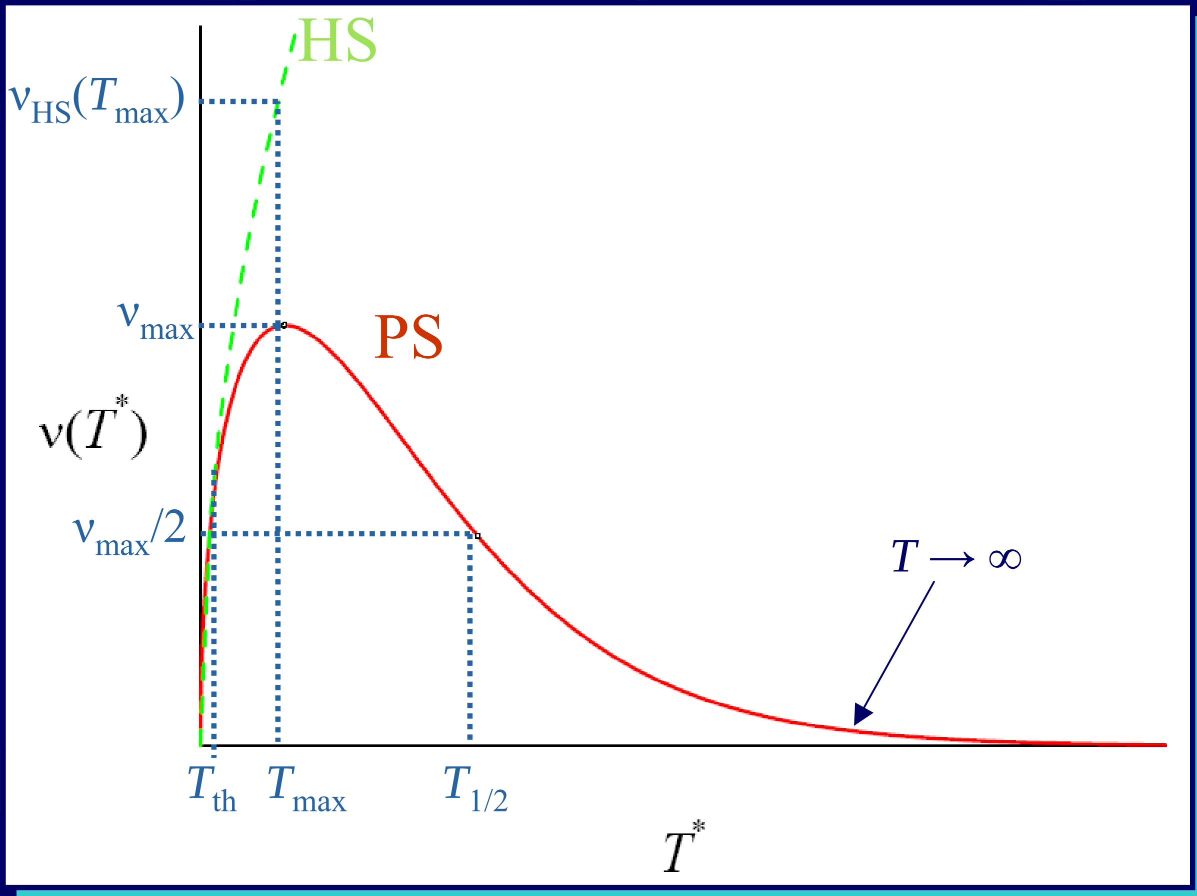


$T^* \equiv k_B T/\varepsilon$

$T^* \to \infty$: gas of collisionless particles

$T^* \to 0$: gas of hard spheres

Key quantity:
Effective collision frequency $\nu(T^*)$



T_{th}=?

T_{max}=?

$\nu_{HS}(T_{max})/\nu_{max}$=?

$T_{1/2}$=?

$\lim_{T\to\infty} \nu(T)$=?

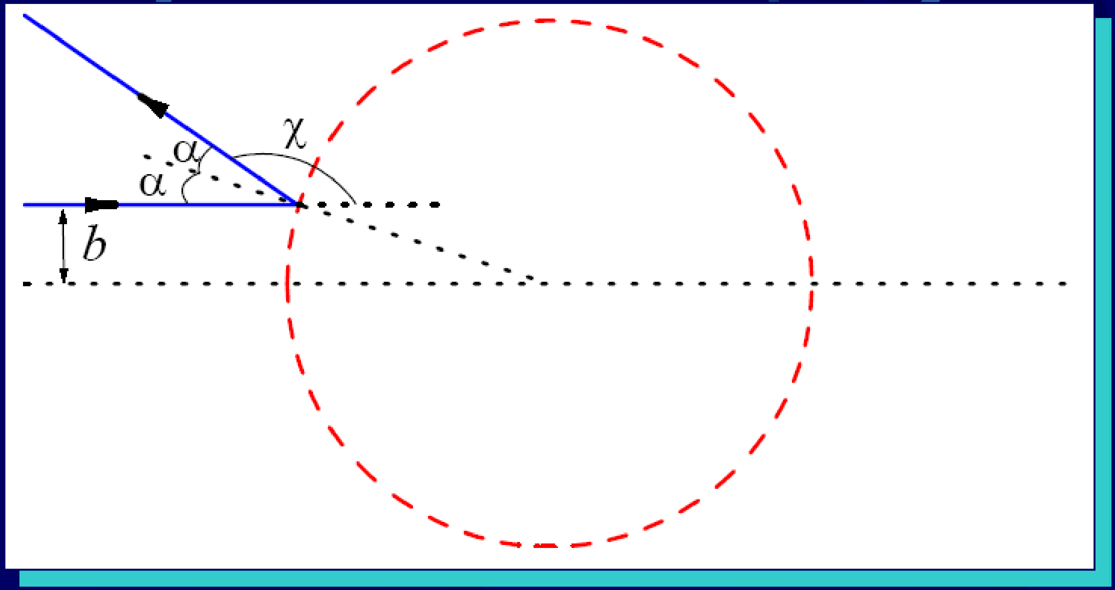
Collision event

Equivalent one-body problem ($\mu = m/2$, reduced mass):

$b^* = b/\sigma$ (dimensionless) impact parameter

$g^* = g/(2\varepsilon/\mu)^{1/2}$ (dimensionless) relative speed

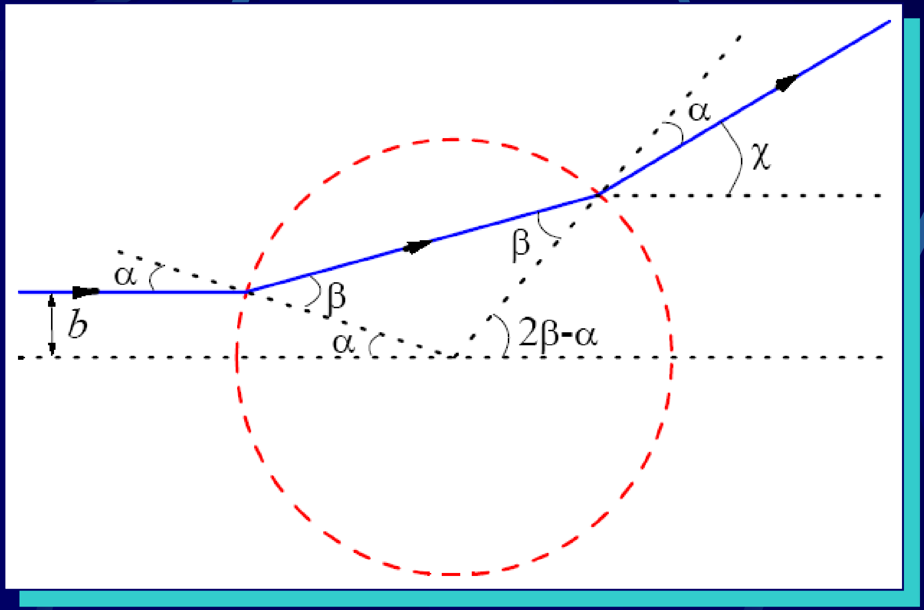
$\chi(b^*, g^*)$ scattering angle

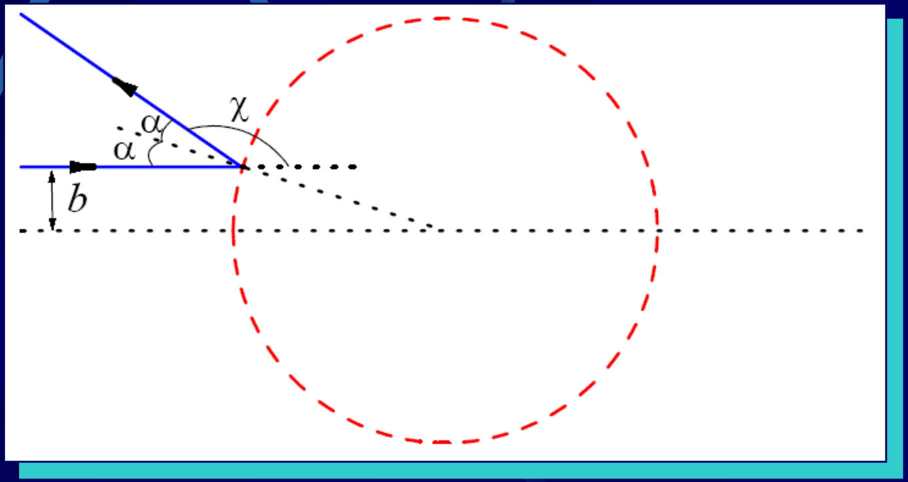


$g^* < 1$: Specular reflection

$\cos \chi(b^*, g^*) = 2b^{*2} - 1$

$g^{*}>1 \Rightarrow$ "Refraction index": $n(g^{*})=(1-1/g^{*2})^{1/2}$





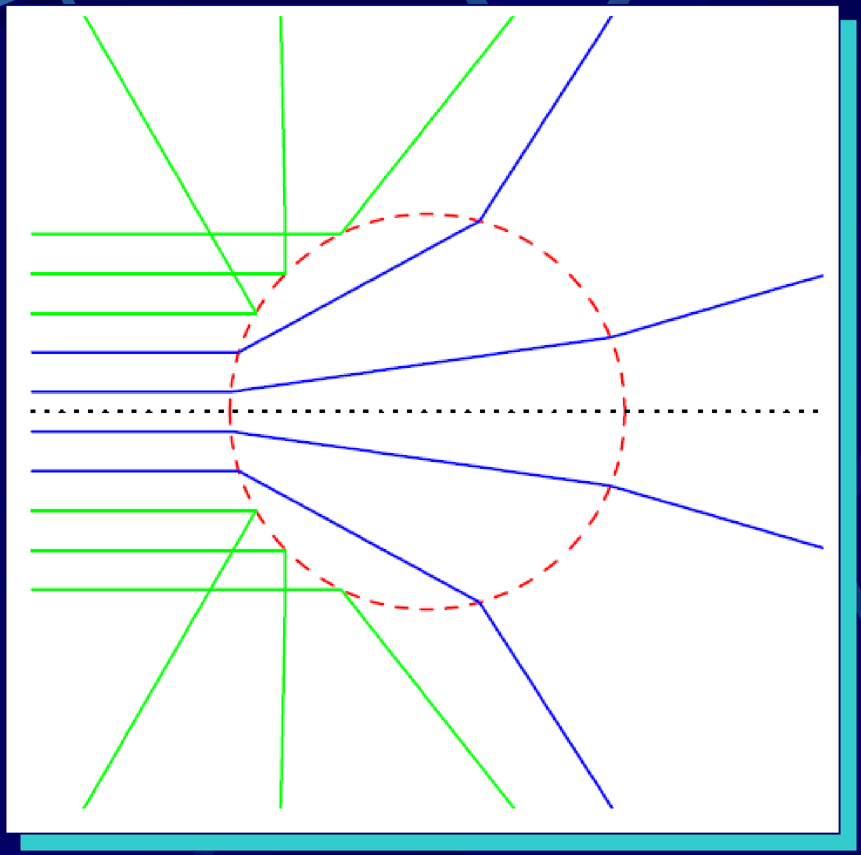
$0 \leq b^{*} \leq n(g^{*})$

Double refraction

$n(g^{*}) \leq b^{*} \leq 1$

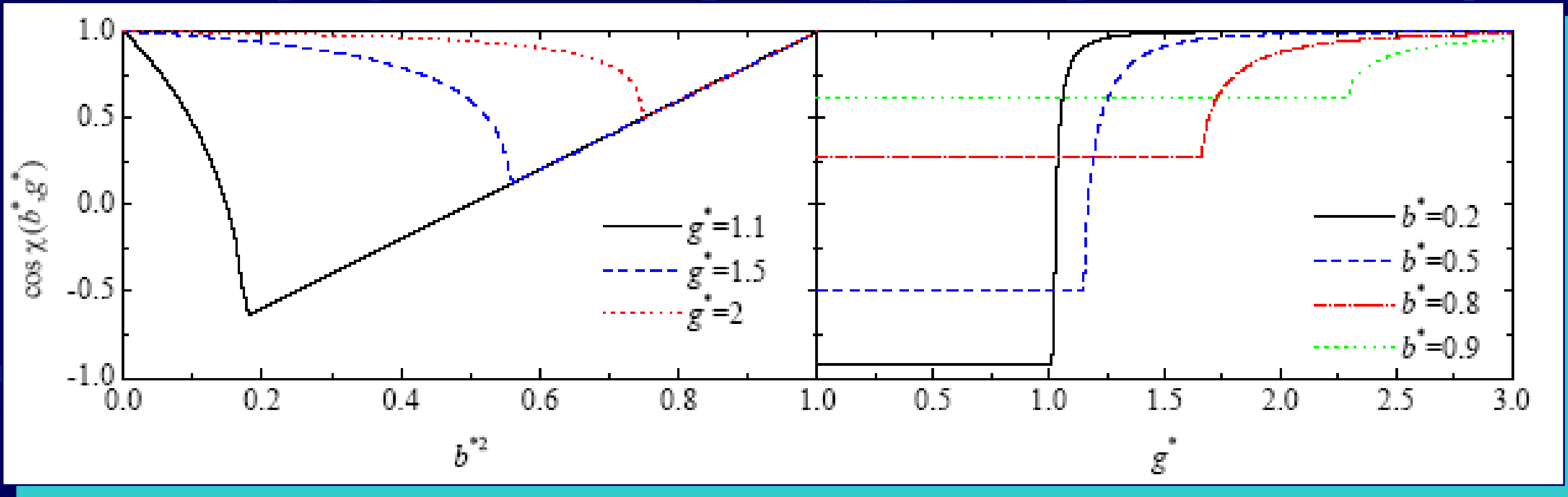
Total reflection

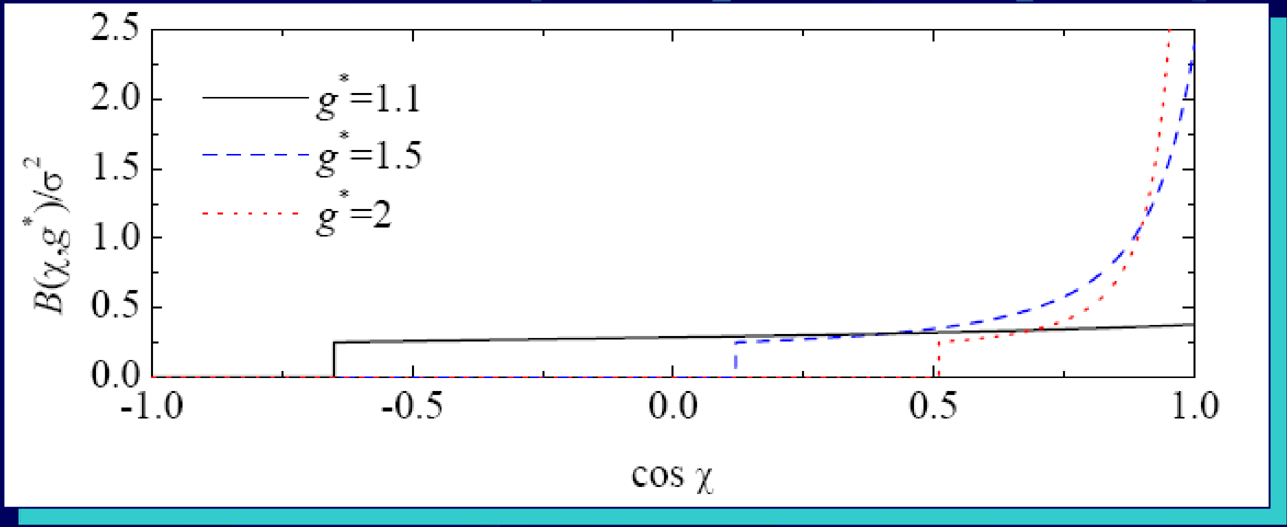
Examples of trajectories in the case $g^*=1.1$



χ is a non-monotonic function of b^*

Maximum value $\chi_{max}(g^*)=\cos^{-1}[2n^2(g^*)-1]$ at $b^*=n(g^*)$





Differential cross section. *Total* cross section = $\pi\ \sigma^2$

Transport coefficients

$$\eta(T) = \frac{5}{8}\frac{k_B T}{\Omega_{2,2}(T)}, \quad \kappa(T) = \frac{15}{4}\frac{k_B}{m}\eta(T), \quad D(T) = \frac{3}{8}\frac{k_B T}{mn\Omega_{1,1}(T)}$$

Shear viscosity — Thermal conductivity — Self-diffusion

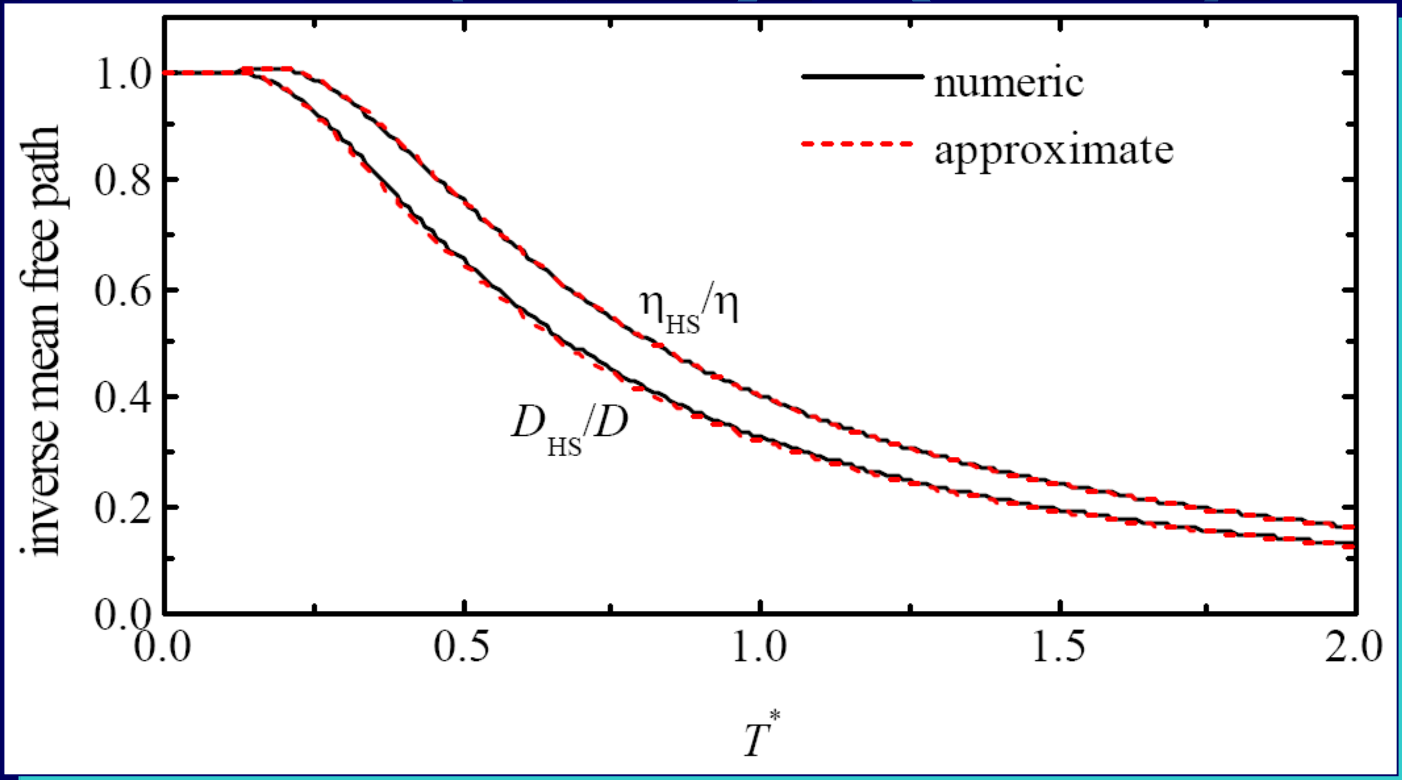
$$\Omega_{k,\ell}(T) = \sqrt{\frac{2\pi k_B T}{\mu}} \int_0^\infty dy\, e^{-y^2} y^{2k+3} \int_0^\infty db\, b \left[1 - \cos^\ell \chi(b, y\sqrt{2k_B T/\mu})\right]$$

Omega-integrals

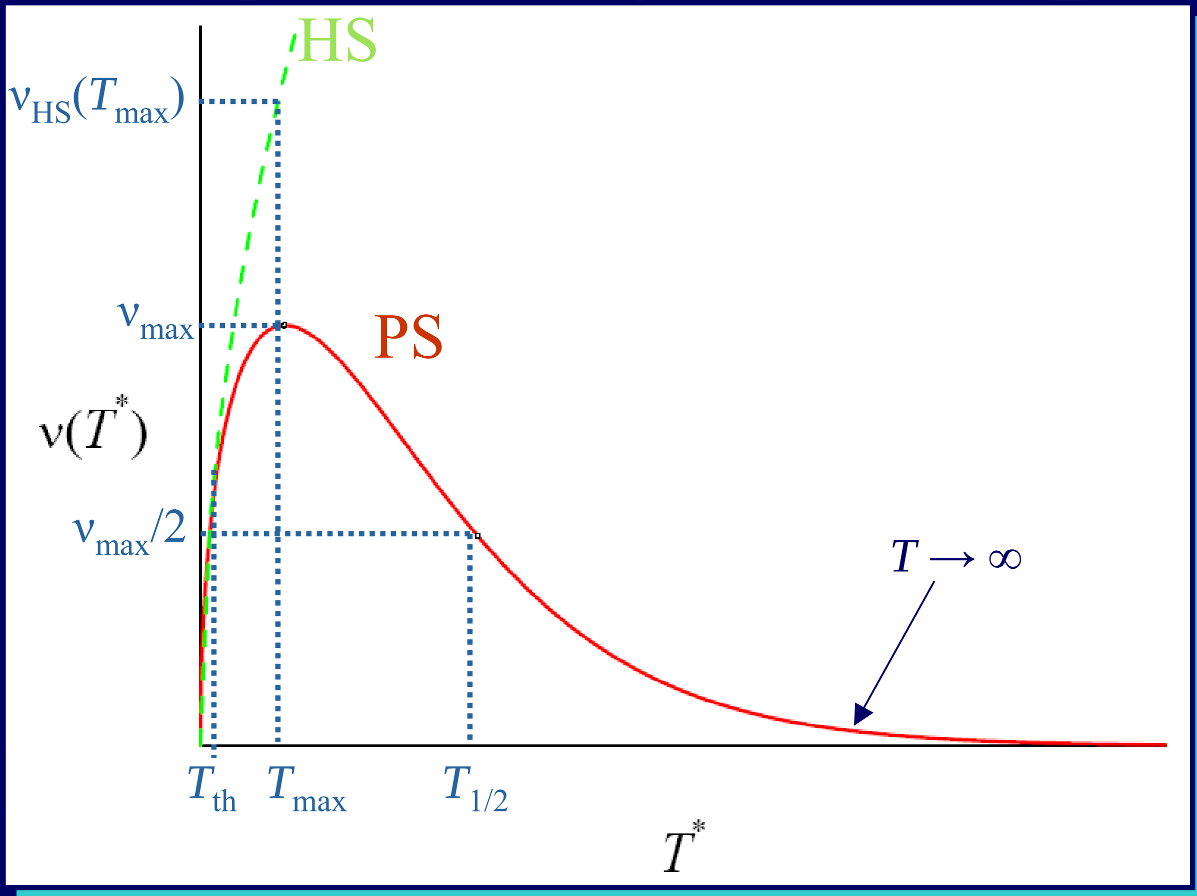
$$\frac{D_{HS}(T)}{D(T)} \approx 1 - e^{-1/T^*}\left(1 + \frac{1}{T^*}\right) - \frac{\mathrm{Ei}(-1/T^*)}{4{T^*}^2}$$

Exponential integral function

$$\frac{\eta_{HS}(T)}{\eta(T)} = \frac{\kappa_{HS}(T)}{\kappa(T)} \approx 1 - e^{-1/T^*}\left(1 + \frac{1}{T^*} - \frac{4\ln 2 - 1}{8{T^*}^2}\right) - \frac{\mathrm{Ei}(-1/T^*)}{4{T^*}^2}$$



Key quantity:
Effective collision frequency $\nu(T^*)$



T_{th}=?

T_{max}=?

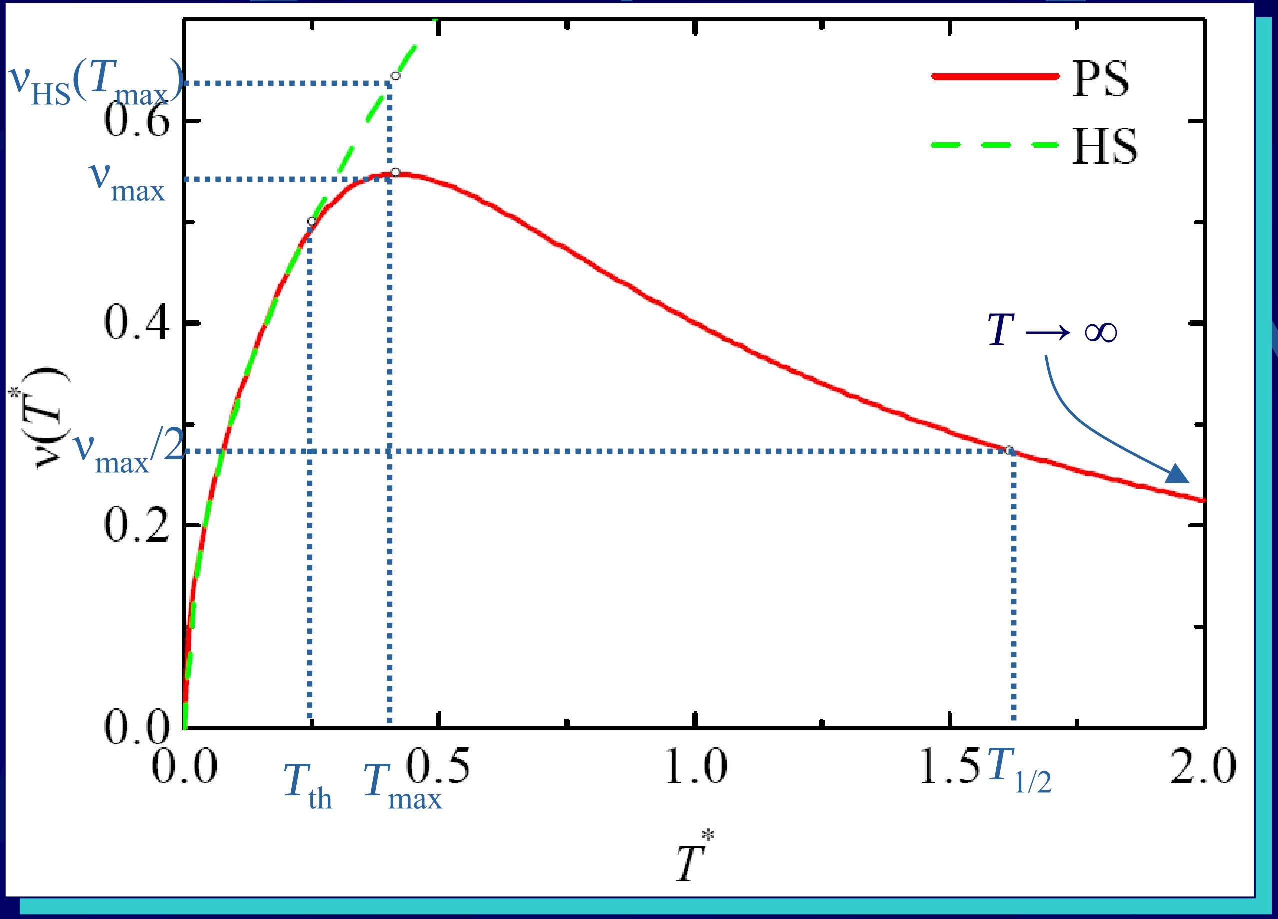
$\nu_{HS}(T_{max})/\ \nu_{max}$=?

$T_{1/2}$=?

$\lim_{T\to\infty} \nu(T)$=?

Effective collision frequency

$$\nu(T^*)=nk_BT/\eta(T)$$



$T^*_{th}=0.25$

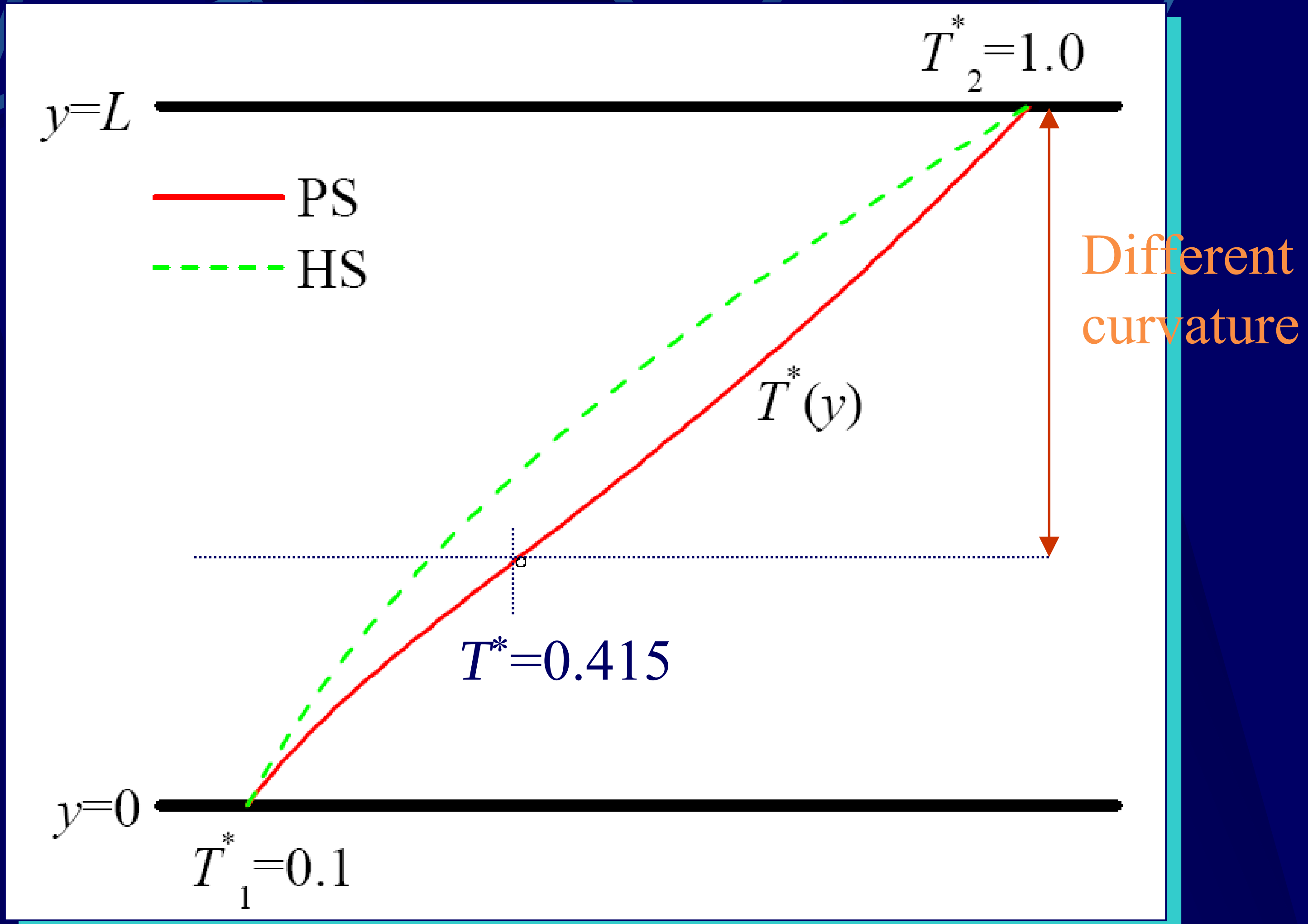
$T^*_{max}=0.415$

$\nu_{HS}(T_{max})/\ \nu_{max}=1.18$

$T^*_{1/2}=1.619$

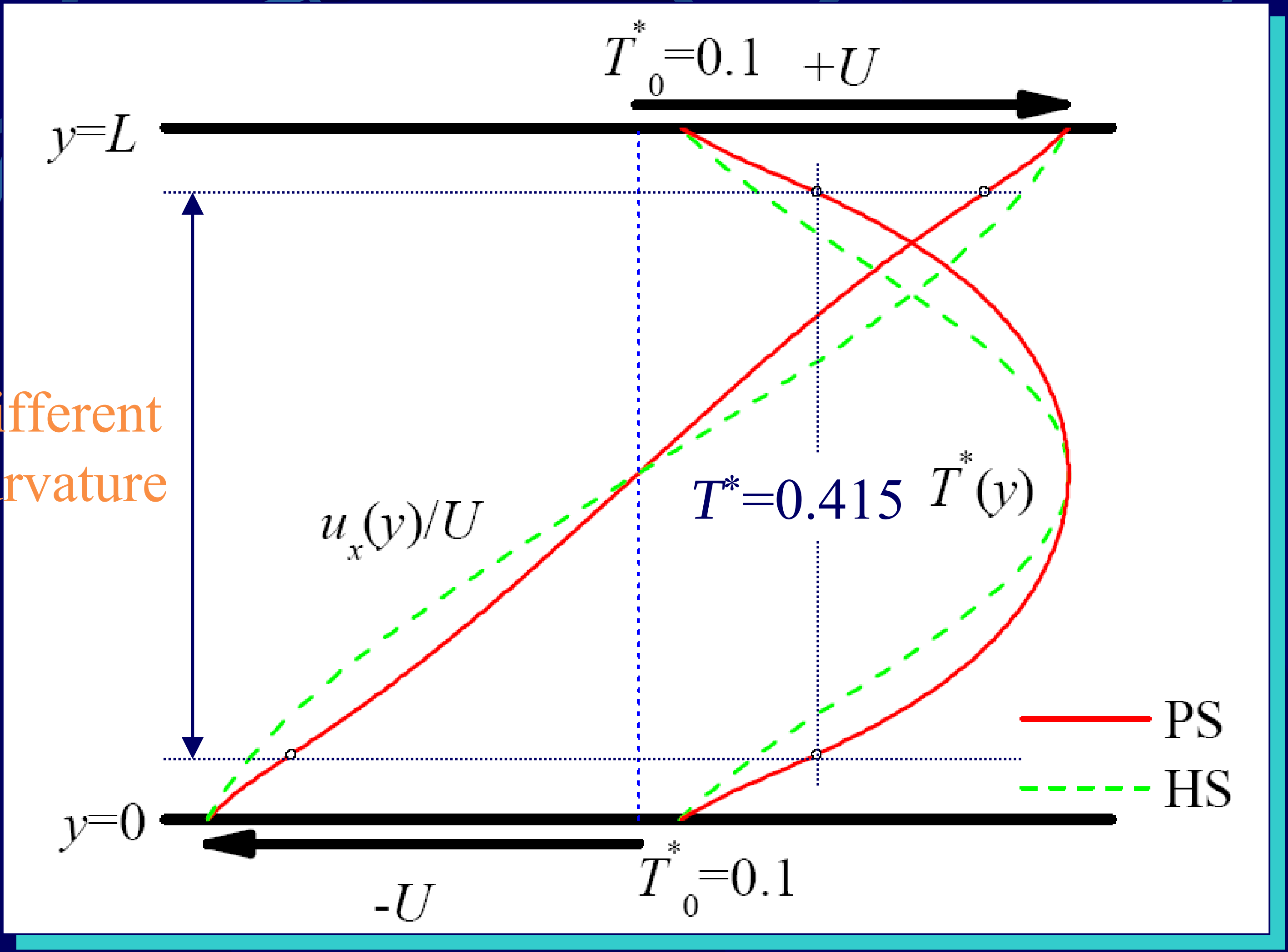
$\lim_{T\rightarrow\infty} \nu(T)= {}^1/_4\, T^{*-3/2} \ln T^*$

Application to Fourier flow



Application to Couette flow

Different curvature



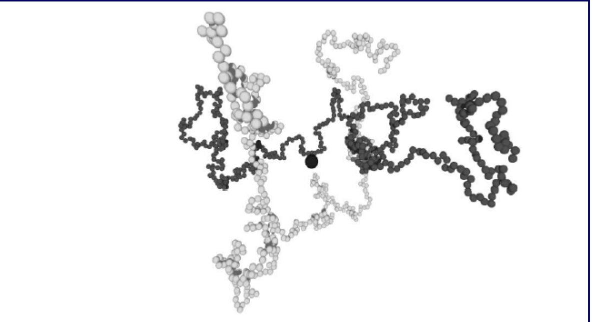
Final comments (I)

- Kinetic theory of particles interacting via *bounded* potentials exposes an intriguing and non-trivial influence of temperature.
- Apart from its practical interest as models of soft matter, bounded repulsive potentials are theoretically interesting: they represent a crossover between hard spheres (low temperatures) to collisionless particles (high temperatures).

Final comments (II)

- The penetrable-sphere (PS) model is the simplest bounded potential. However, its two-body collision process exhibits some interesting features.
- The (effective) collision frequency starts growing as $T^{*1/2}$ (up to $T^{*}\approx 0.25$), reaches a maximum at $T^{*}\approx 0.415$, and decays as $T^{*-3/2}\ln T^{*}$ for high remperatures.
- This non-monotonic behavior can give rise to hydrodynamic profiles qualitatively different from those of unbounded repulsive potentials.

THANKS!



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