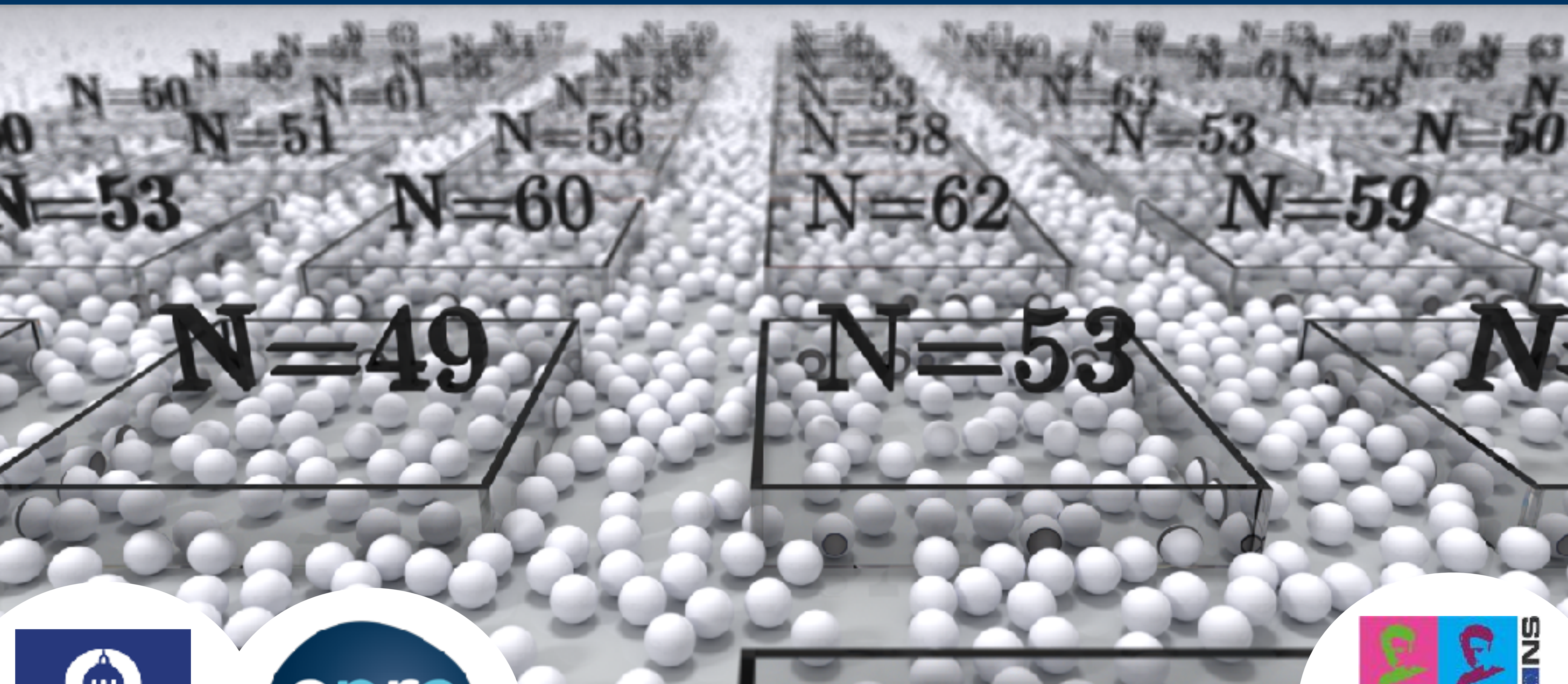
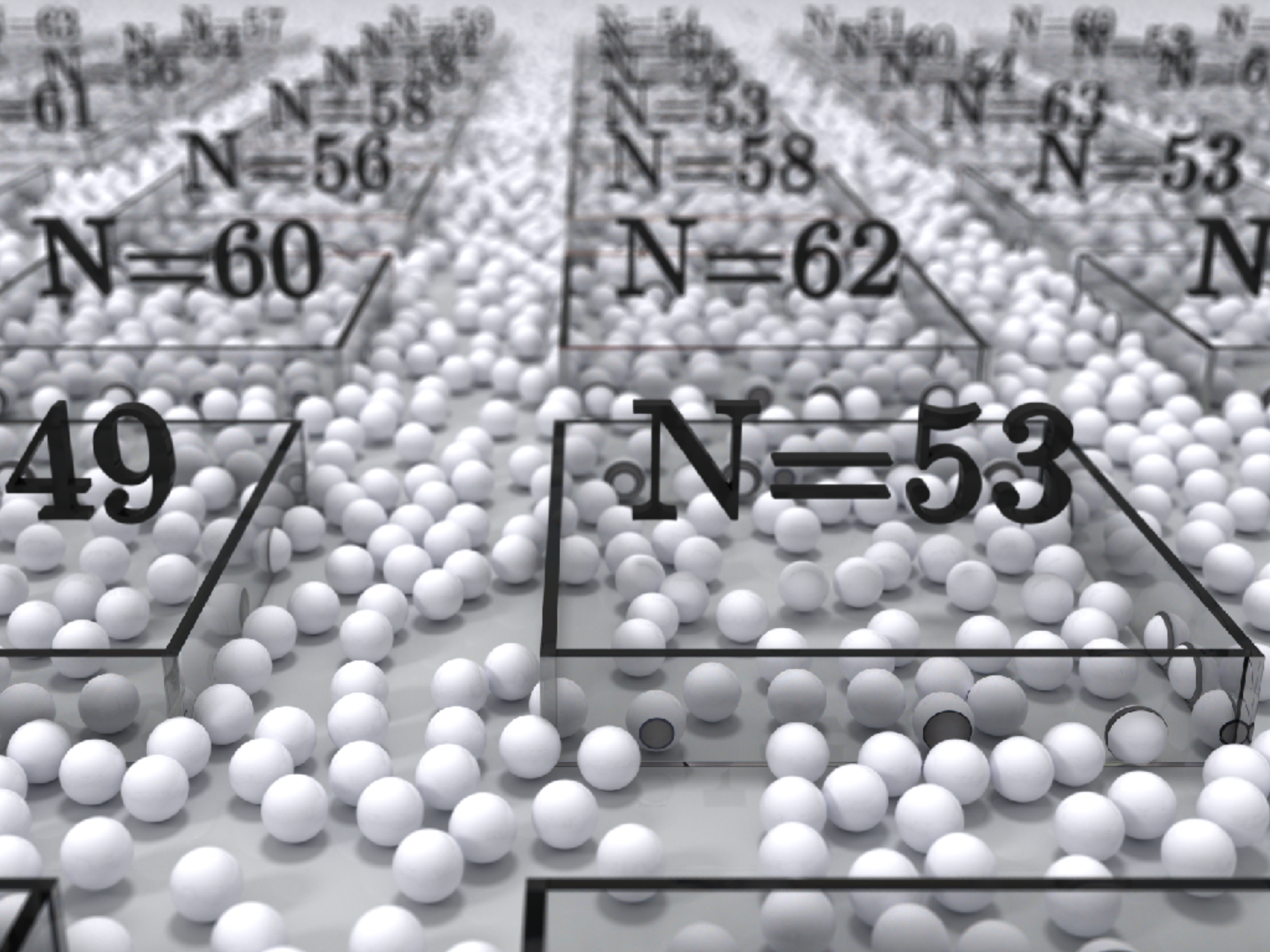
Fancy Counting

Dynamic fluctuations in finite volumes

Sophie Marbach

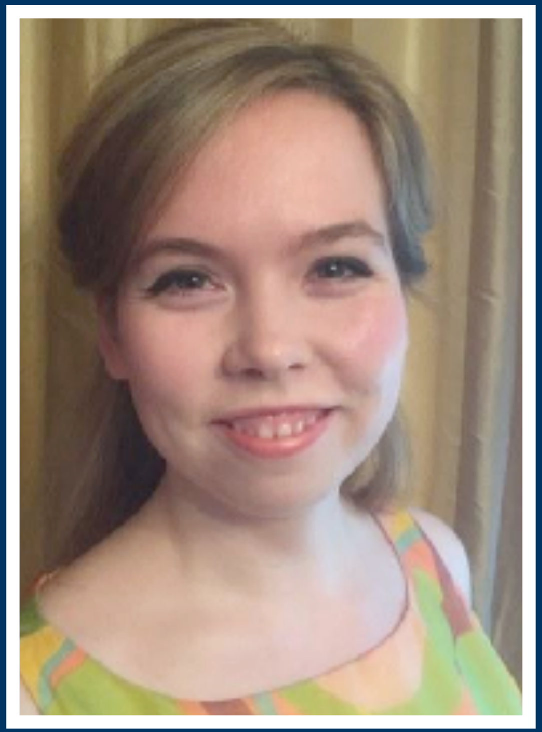


Sorbonne Université - Paris



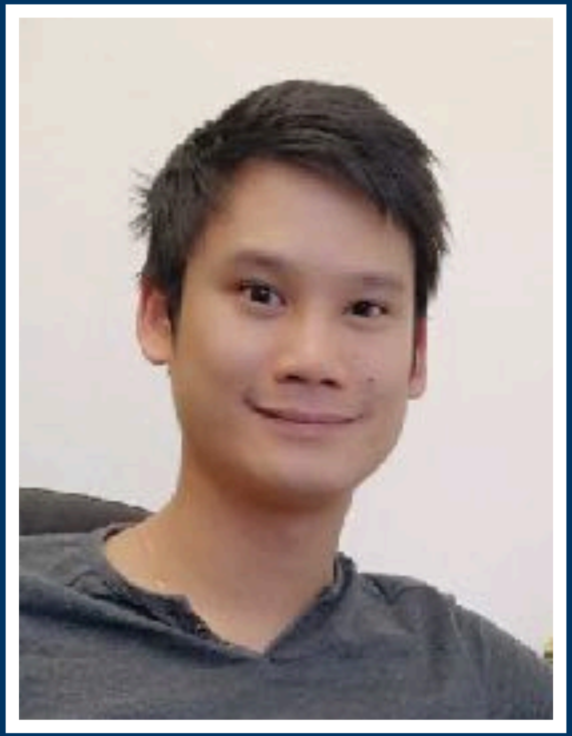
N=60
N=62
49
N=53
N=56
N=58
N=58
N=53
N=53
N=63

Brennan Sprinkle
(Colorado)



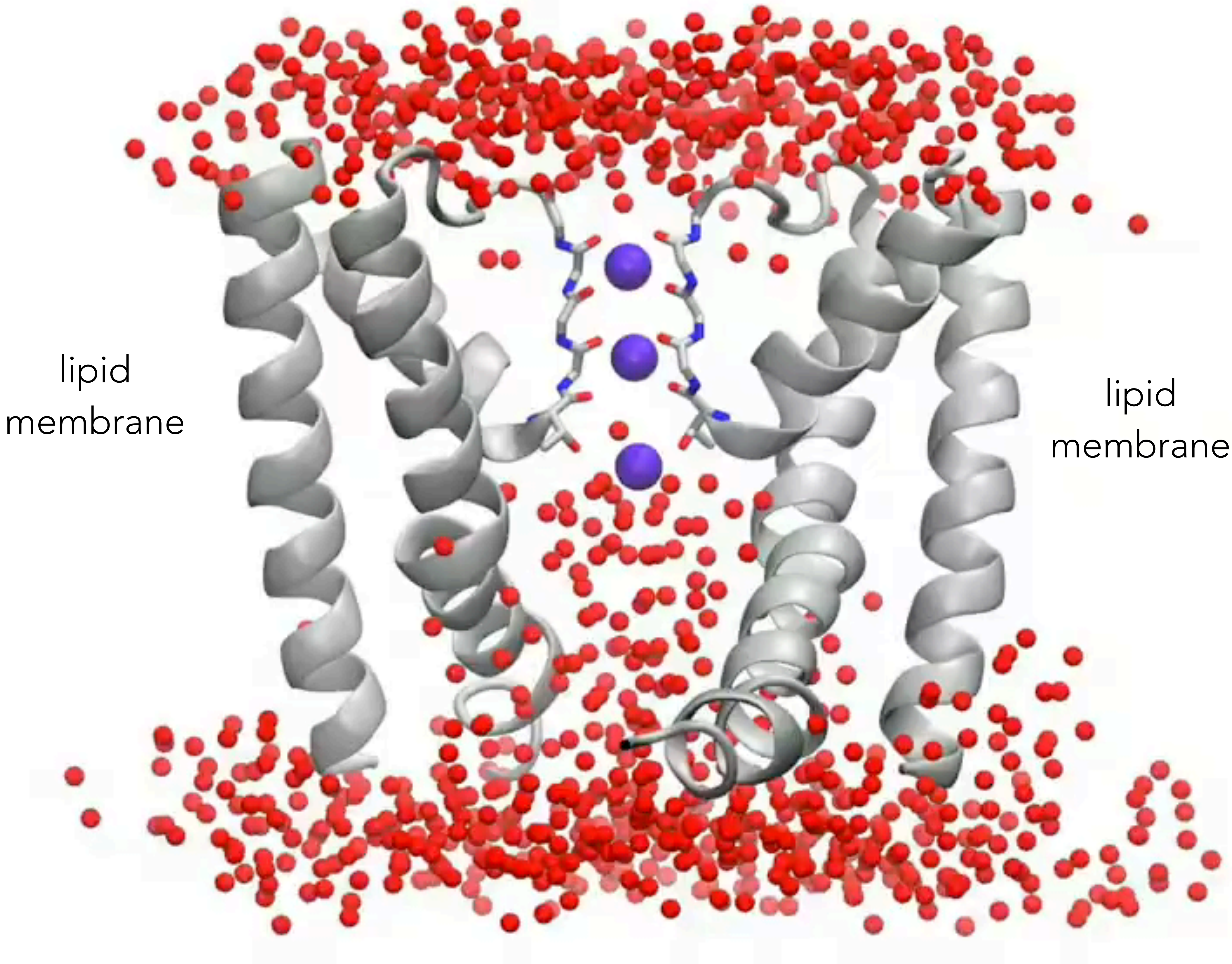
Alice Thorneywork
(Oxford)

Benjamin Rotenberg
(Paris)

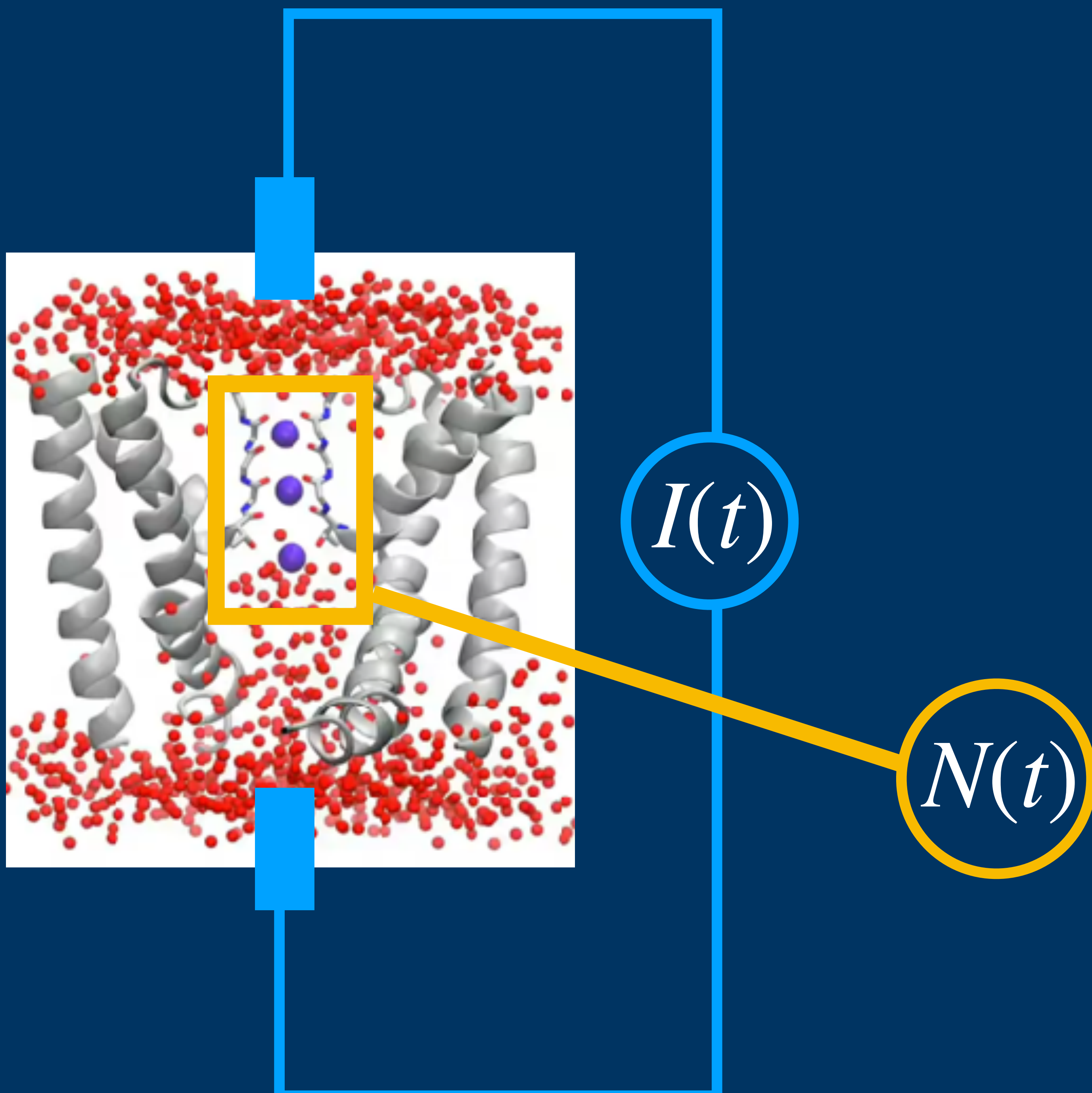


Minh Thé Hoang Ngoc
(Paris)

Potassium channel KcsA



(courtesy Wojciech Kopec)

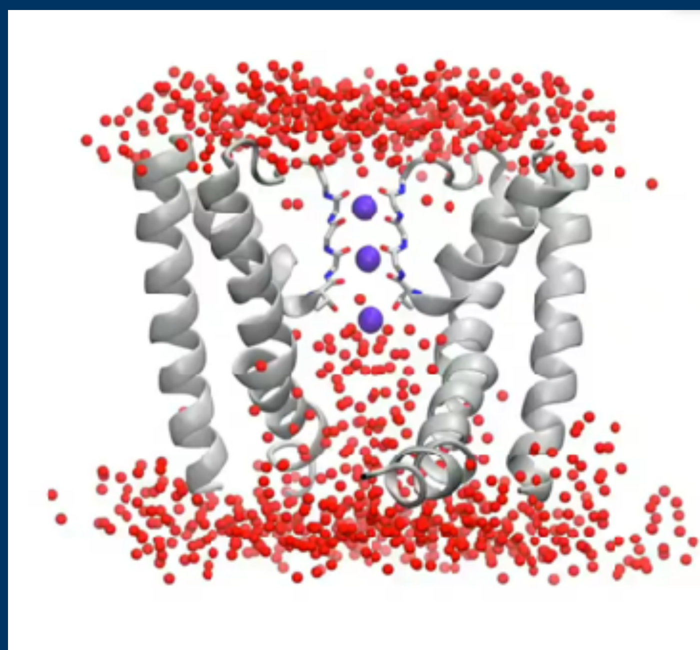


$$I(t) \propto \frac{\mathrm{d}N(t)}{\mathrm{d}t}$$

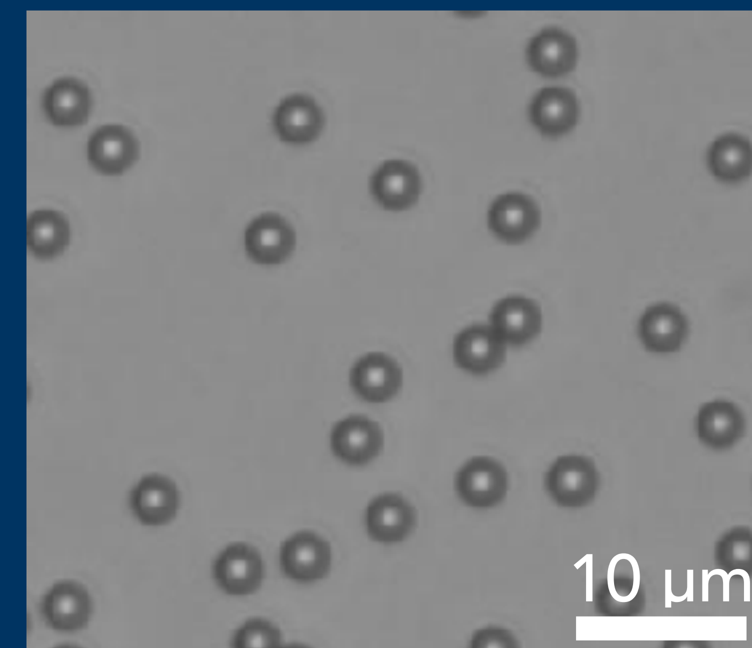
counting particles can inform us on function!

You always need to count…

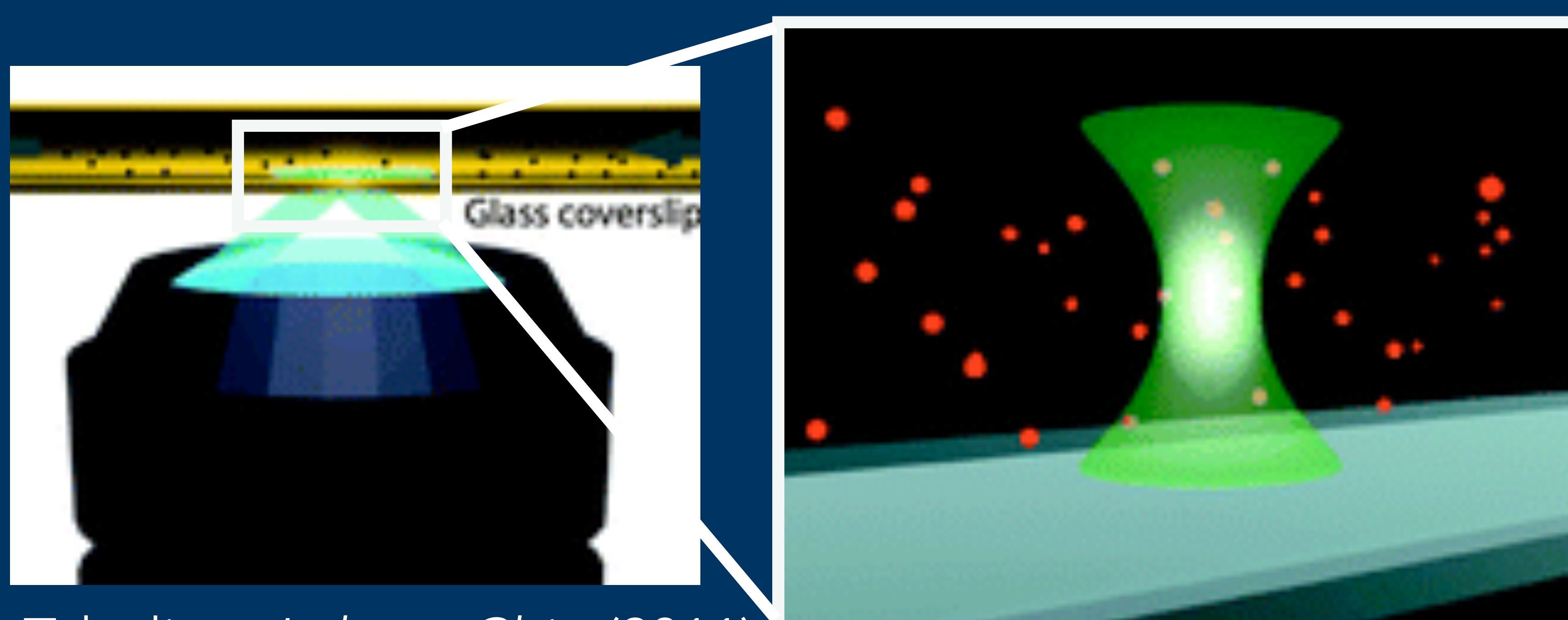
ion channels



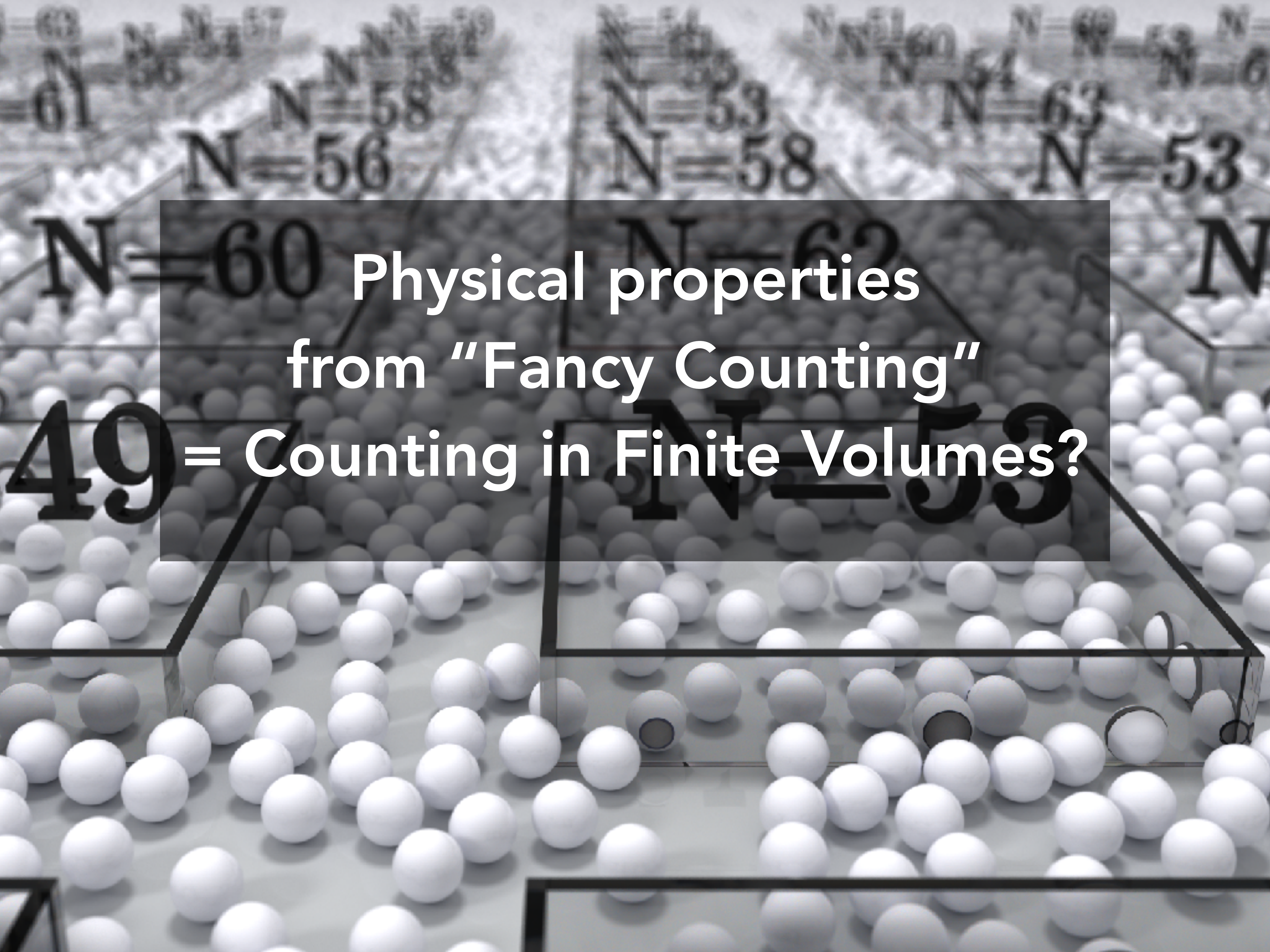
colloids in water (top view)

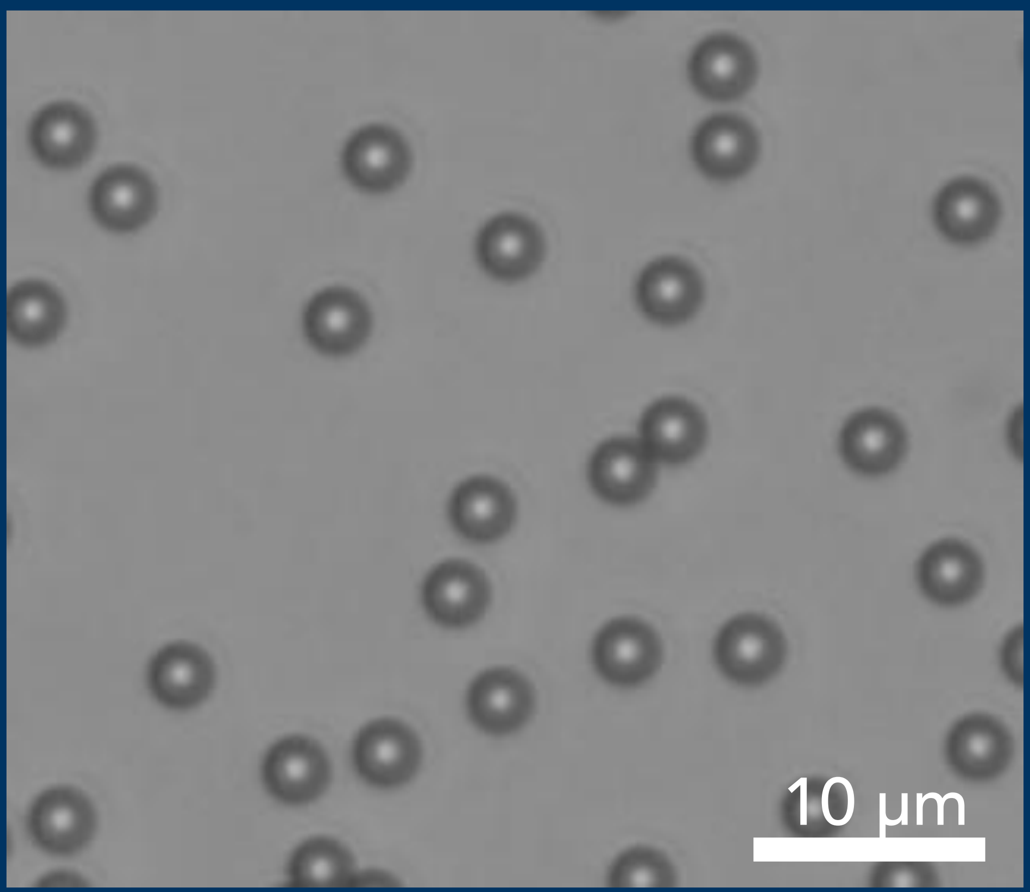


FCS = Fluorescence
Correlation Spectroscopy

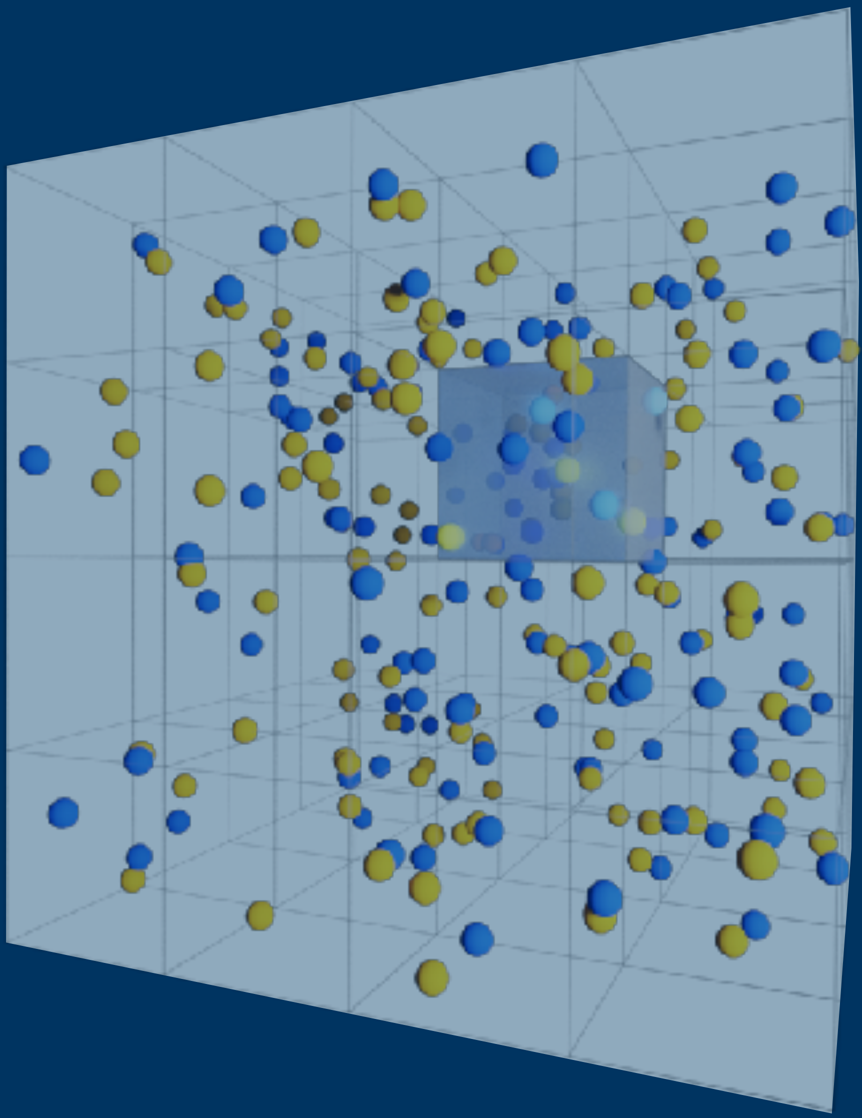


Nghe… Tabeling, *Lab on Chip* (2011)


Physical properties
from "Fancy Counting"
= Counting in Finite Volumes?

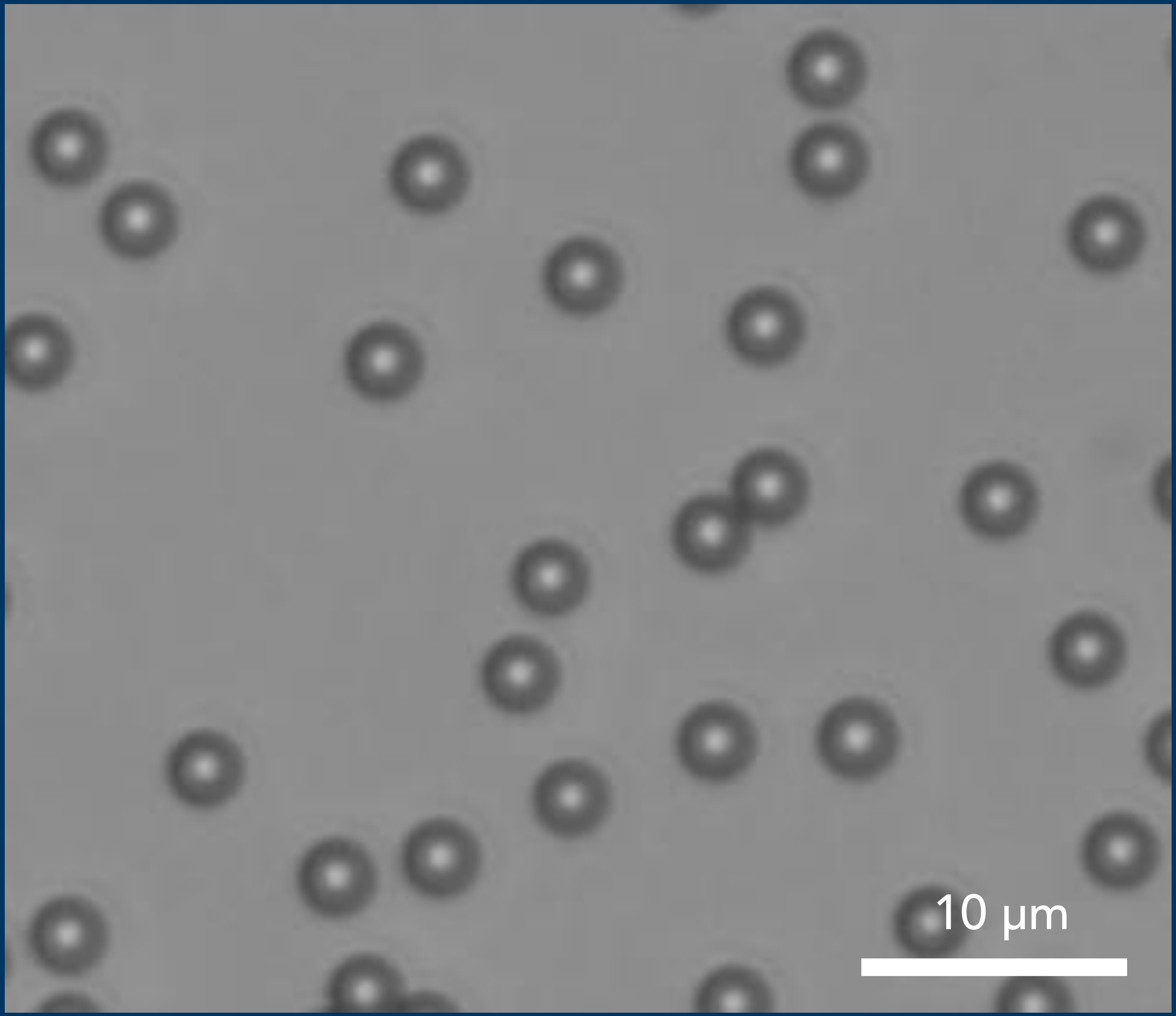


2D - short range interactions

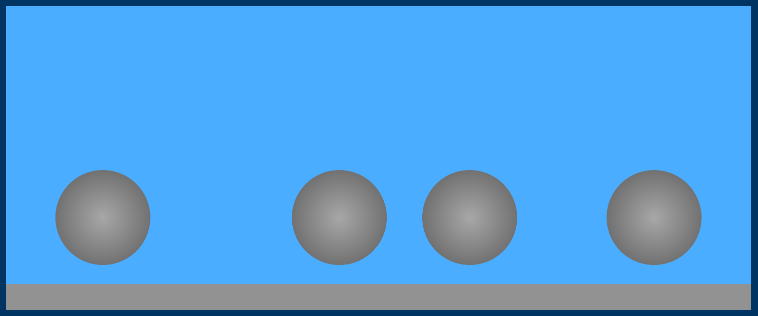


3D - long range interactions

Model experimental system

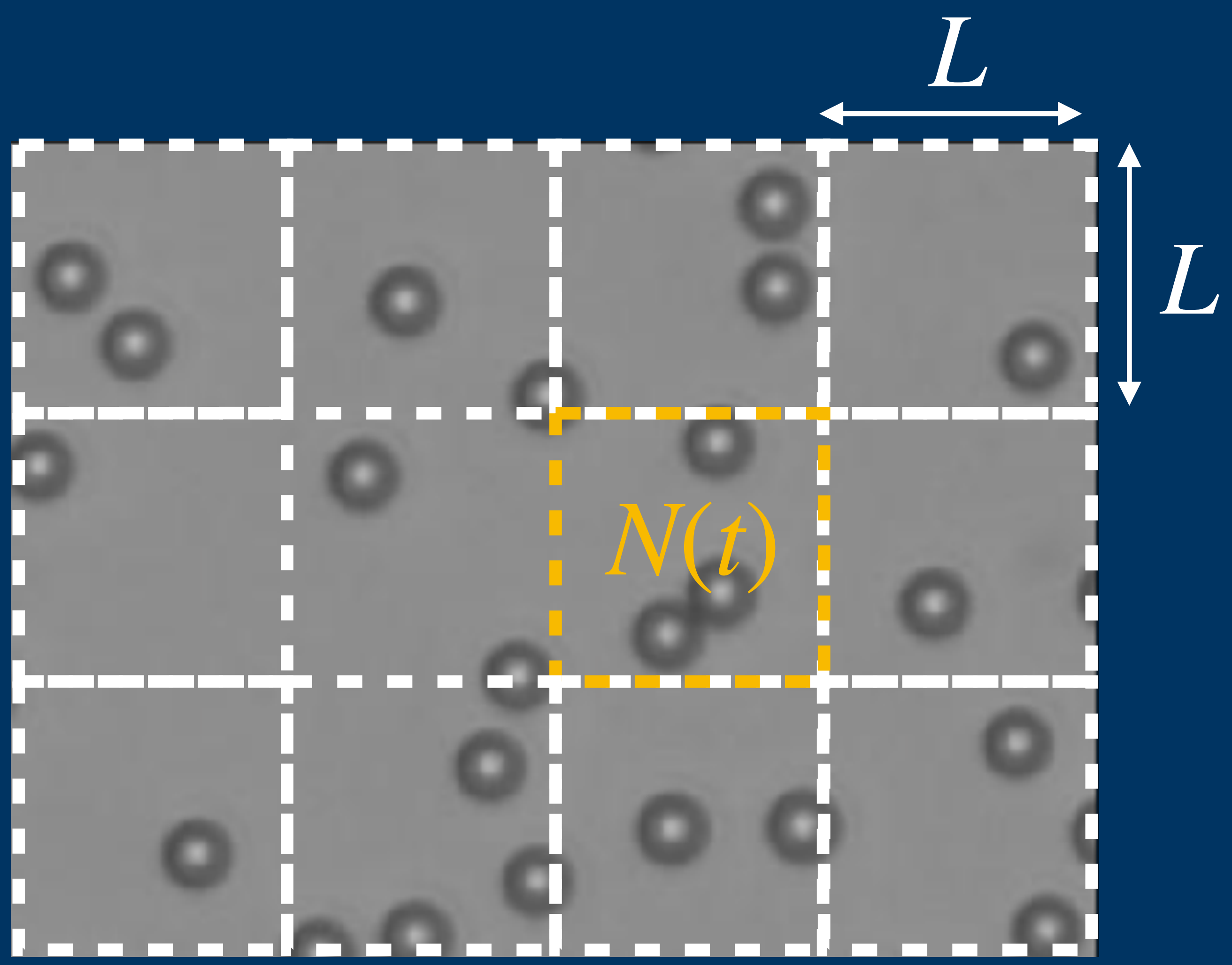


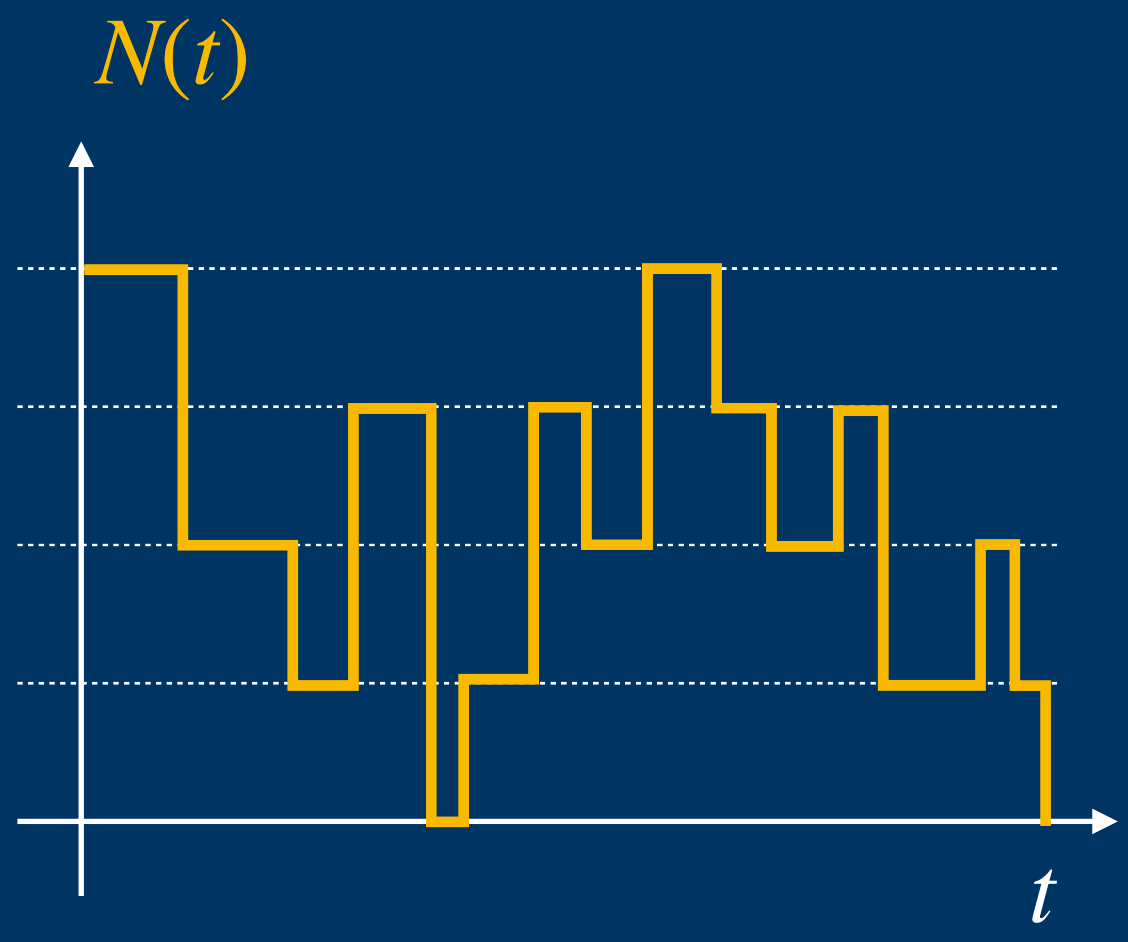
colloids in water (top view)



(side view)

“Fancy Counting”





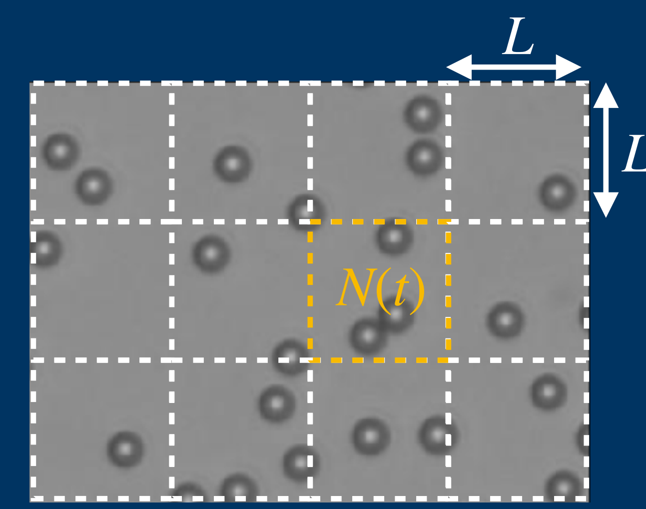
Physical Properties

from the dynamics of N(t) ?

@ Steady state => **Thermodynamic properties**

$$\langle N^2 \rangle - \langle N \rangle^2$$

"Kirkwood Buff integrals" = **Infinite** volumes



The Statistical Mechanical Theory of Solutions. I

John G. Kirkwood and Frank P. Buff*
Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California†

(Received March 26, 1951)

A general statistical mechanical theory of solutions is developed with the aid of the theory of composition fluctuations in the grand canonical ensemble. It is shown that the derivatives of the chemical potentials and osmotic pressure with respect to concentrations, the partial molar volumes, and compressibility may be expressed in terms of integrals of the radial distribution functions of the several types of molecular pairs present in the solution. Explicit coefficients of a q-fraction expansion of the thermodynamic variables are presented in a detailed treatment of the two-component system.

Thermodynamics and correlation functions of plasmas and electrolyte solutions

by H. VAN BEIJEREN and B. U. FELDERHOF
Institut für Theoretische Physik A,
Rheinisch-Westfälische Technische Hochschule Aachen,
5100 Aachen, Germany

(*Received* 21 *December* 1978)

The Charge Fluctuations in Classical Coulomb Systems

Ph. A. Martin[1] and T. Yalcin[1]

Received August 3, 1979

We study the asymptotic behavior of the charge fluctuations $\langle (Q_\Lambda - \langle Q_\Lambda \rangle)^2 \rangle$ in infinite classical systems of charged particles, and show, under certain clustering assumptions, that if the charge fluctuations are not extensive, then they are necessarily of the order of the surface $|\partial\Lambda|$. Moreover, when the canonical sum rules that are typical for equilibrium states of particles interacting with long-range forces hold true, we prove a central limit theorem for the normalized charge variable $|\partial\Lambda|^{-1/2}(Q_\Lambda - \langle Q_\Lambda \rangle)$ in two and three dimensions. In one dimension, the probability distribution of the charge itself converges. The latter case is illustrated by the example of the one-dimensional Coulomb gas.

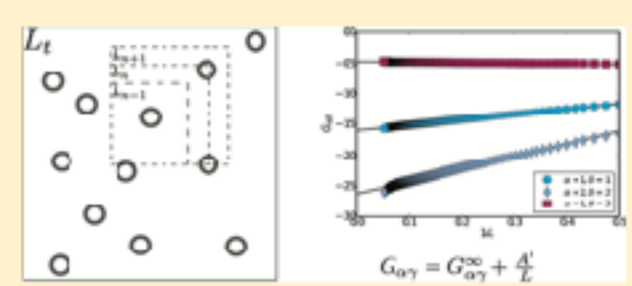
KEY WORDS: Classical Coulomb systems; long-range force; charge fluctuations; canonical sum rules; central limit theorem; one-dimensional Coulomb gas.

Calculating Thermodynamic Properties from Fluctuations at Small Scales

Sondre K. Schnell,[†] Xin Liu,[†,‡] Jean-Marc Simon,[§] André Bardow,[‡] Dick Bedeaux,[∥] Thijs J. H. Vlugt,[†] and Signe Kjelstrup*[,†,∥]

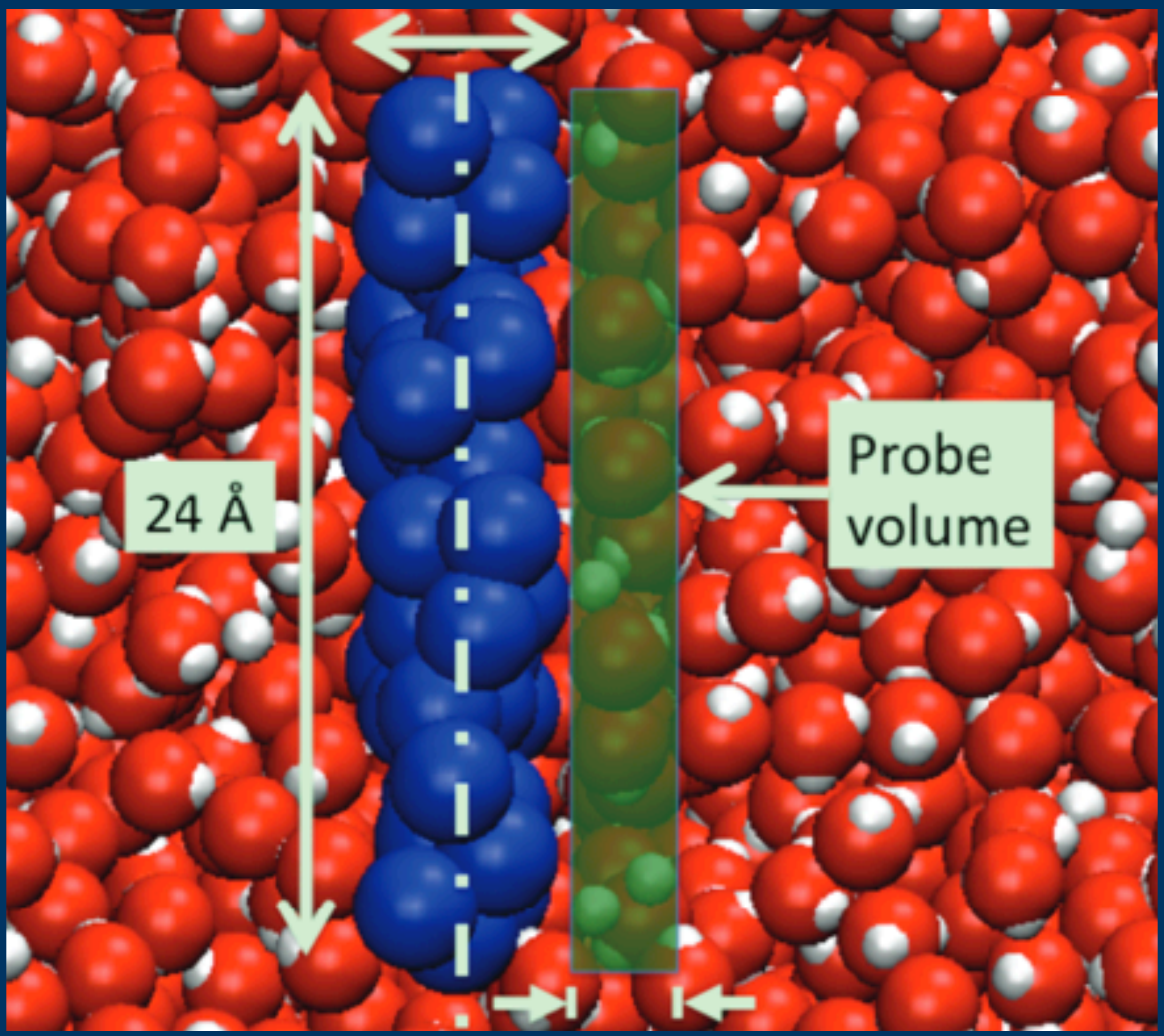
[†]Process and Energy Laboratory, Delft University of Technology, Leeghwaterstraat 44, 2628CA Delft, The Netherlands,
[‡]Lehrstuhl für Technische Thermodynamik, RWTH Aachen University, Schinkelstraße 8, 52062 Aachen, Germany
[§]Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, Dijon, France, and
[∥]Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway

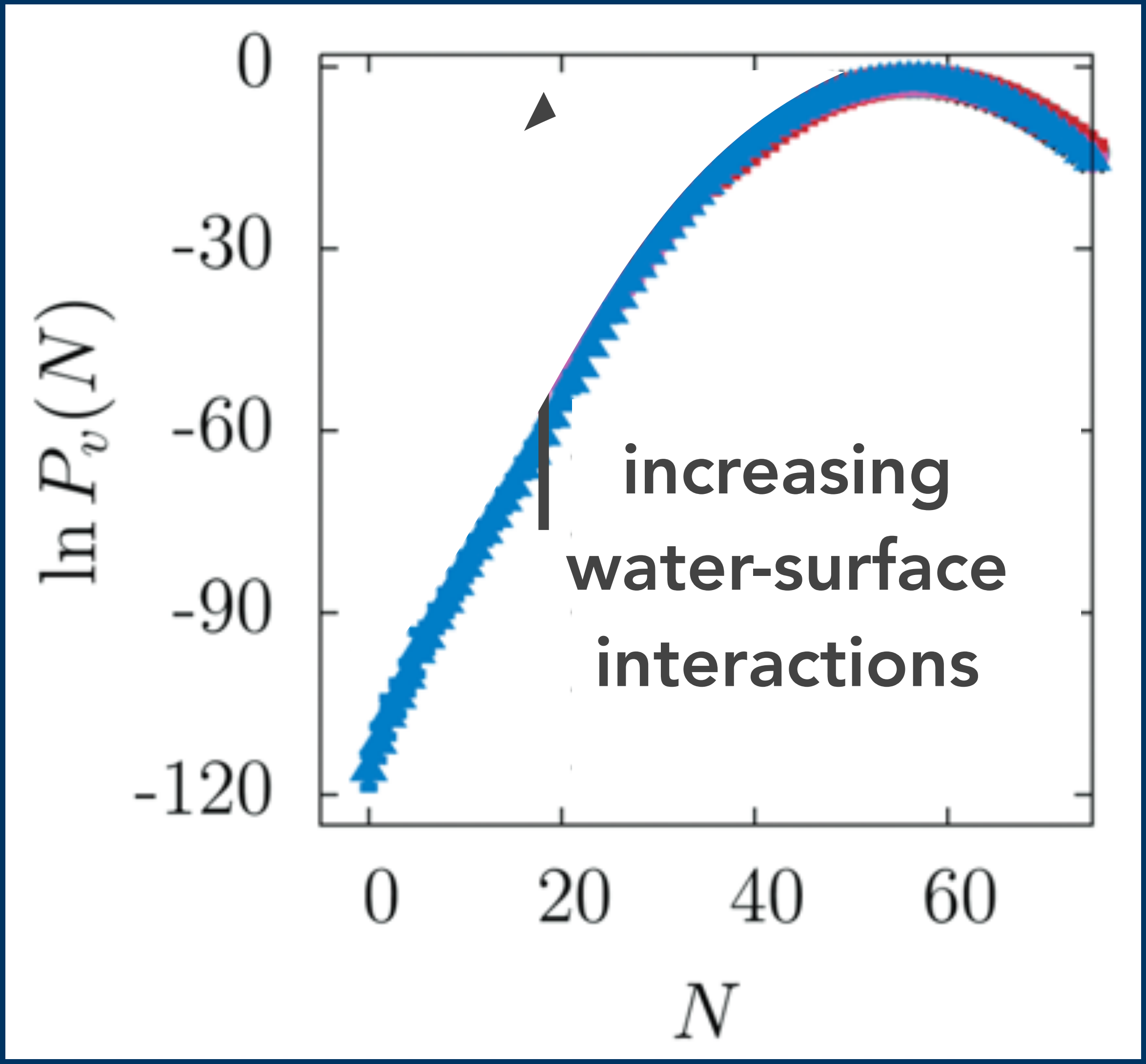
ABSTRACT:



@ Steady state => **Thermodynamic properties**

finite volumes?



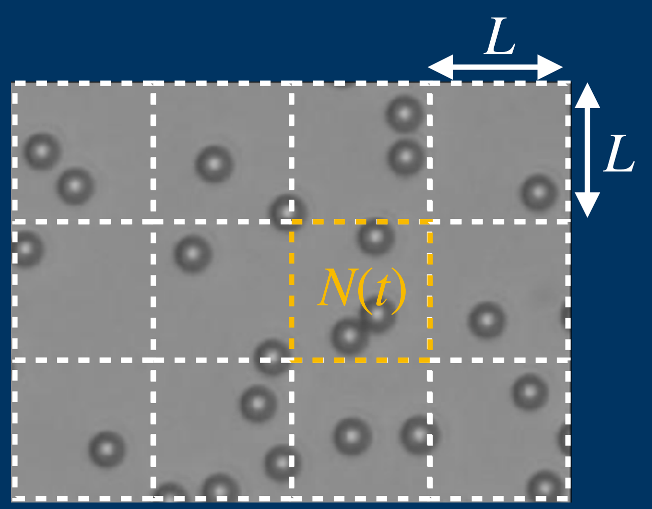


AJ Patel, P. Varilly, D. Chandler, *J. Phys. Chem. B* 2010

@ Steady state => **Thermodynamic properties**

$$\langle N^2 \rangle - \langle N \rangle^2$$

"Kirkwood Buff integrals"/Finite volumes

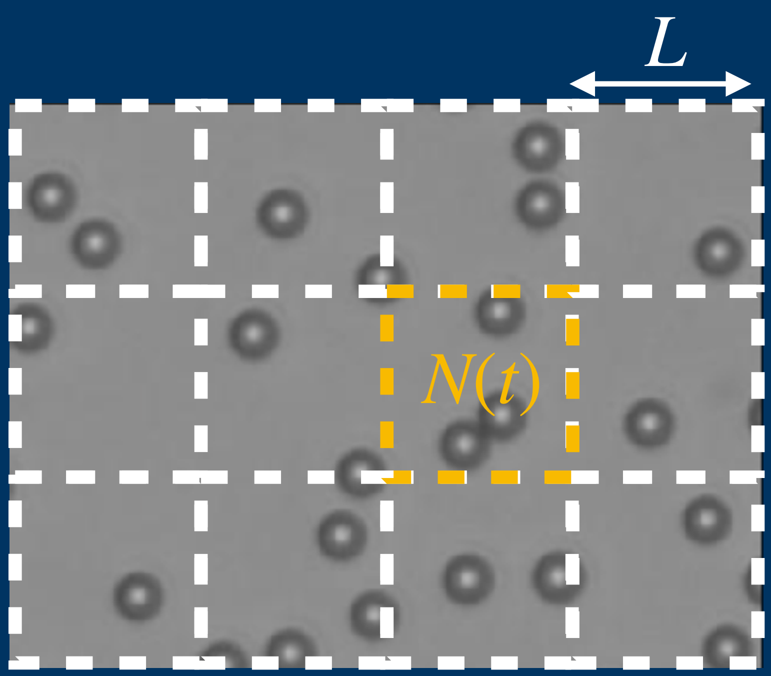


@ Outside steady state => **Dynamic properties!**

$$C_N(t) = \langle N(t)N(0) \rangle - \langle N \rangle^2$$

much to explore…

"Fancy Counting"



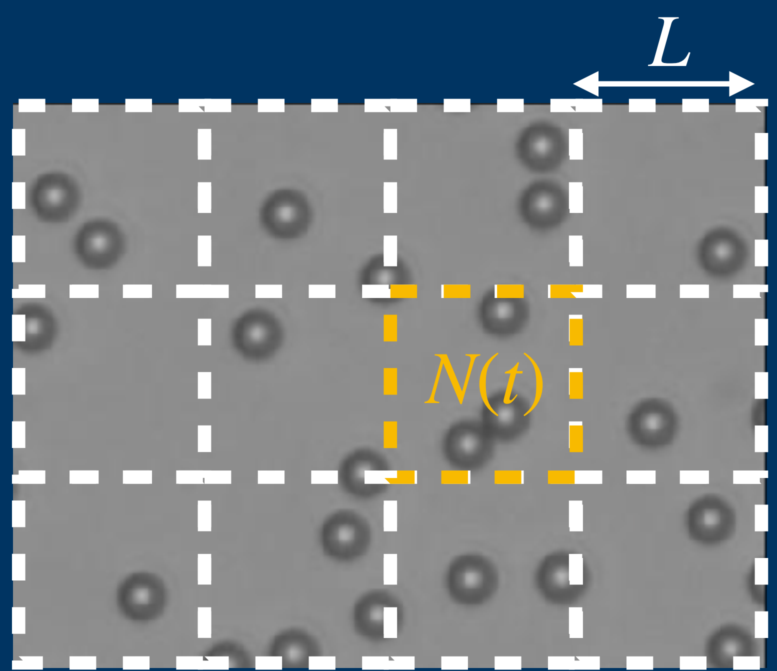
$$C_N(t) = \langle N(t)N(0)\rangle - \langle N\rangle^2$$

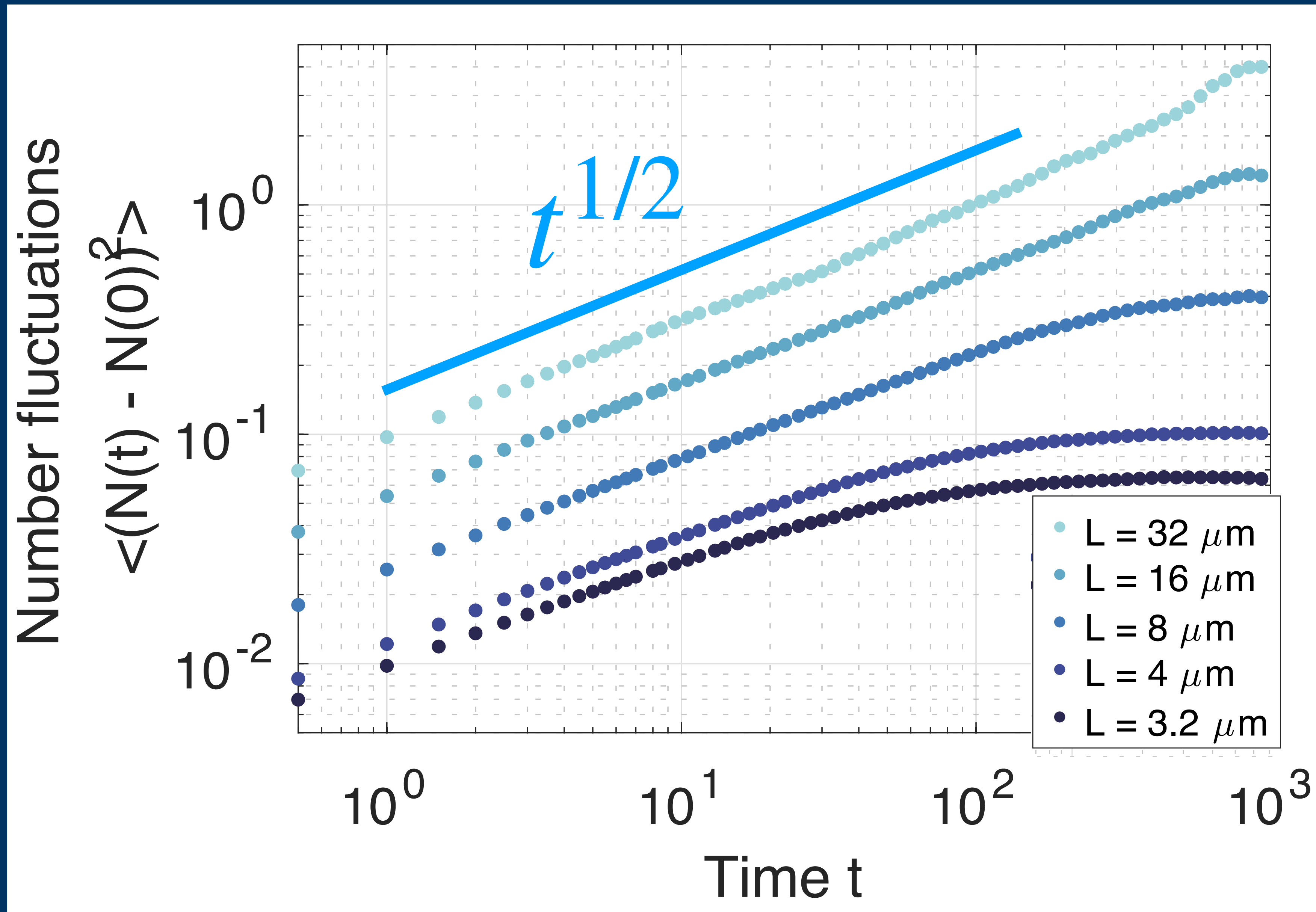
hard in practice…

$$\left\langle \big(N(t) - N(0)\big)^2 \right\rangle$$
$$= 2\left(\langle N^2\rangle - \langle N\rangle^2\right) - 2C_N(t)$$

"MSD of particle number"

“Fancy Counting”

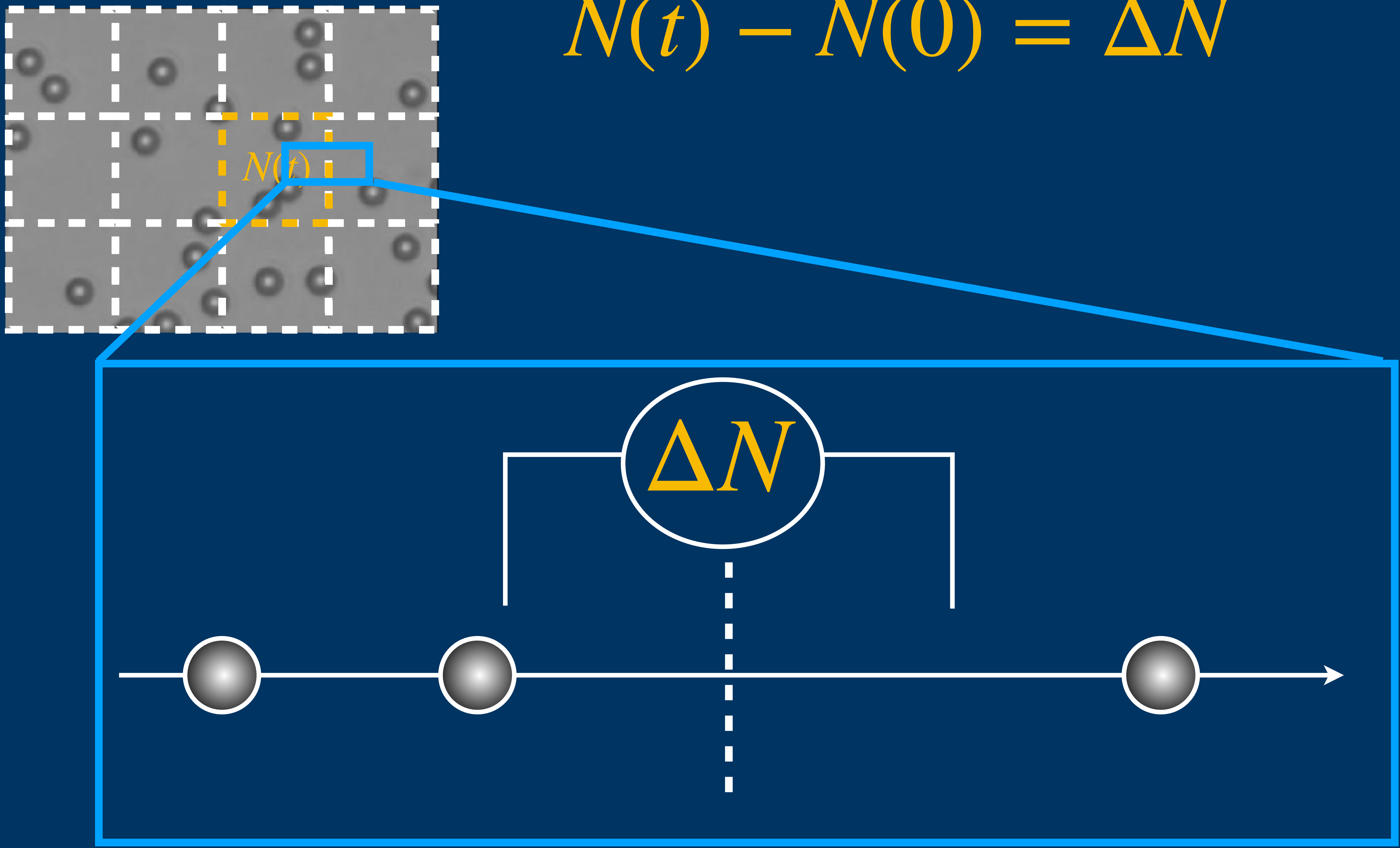


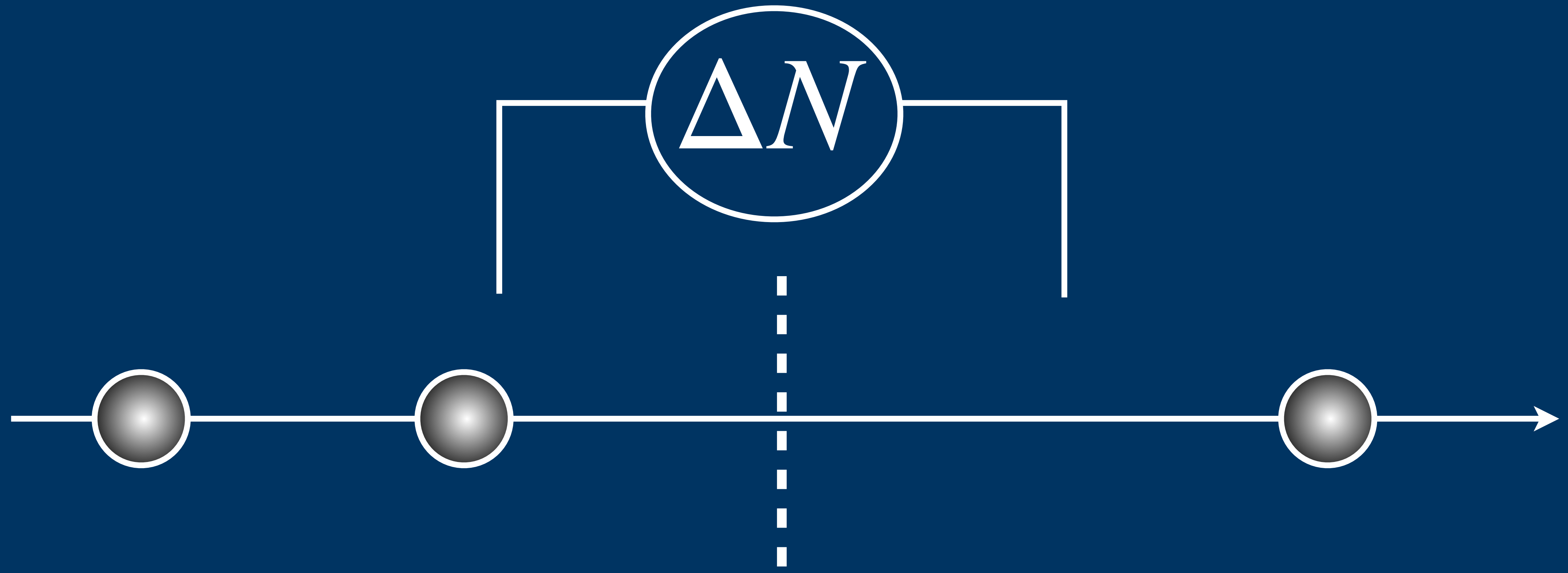


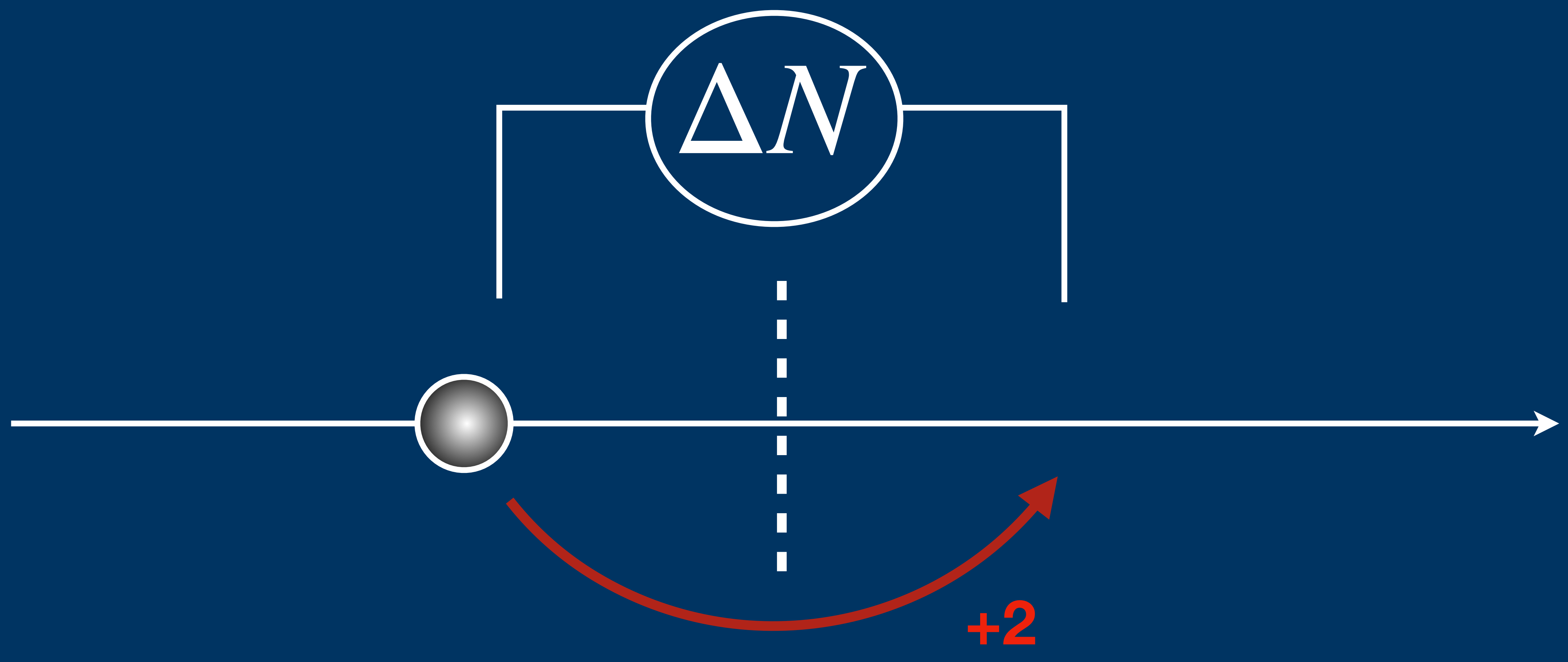
Subdiffusive behavior in a very simple system!

Boundary crossings

$$N(t) - N(0) = \Delta N$$




ΔN

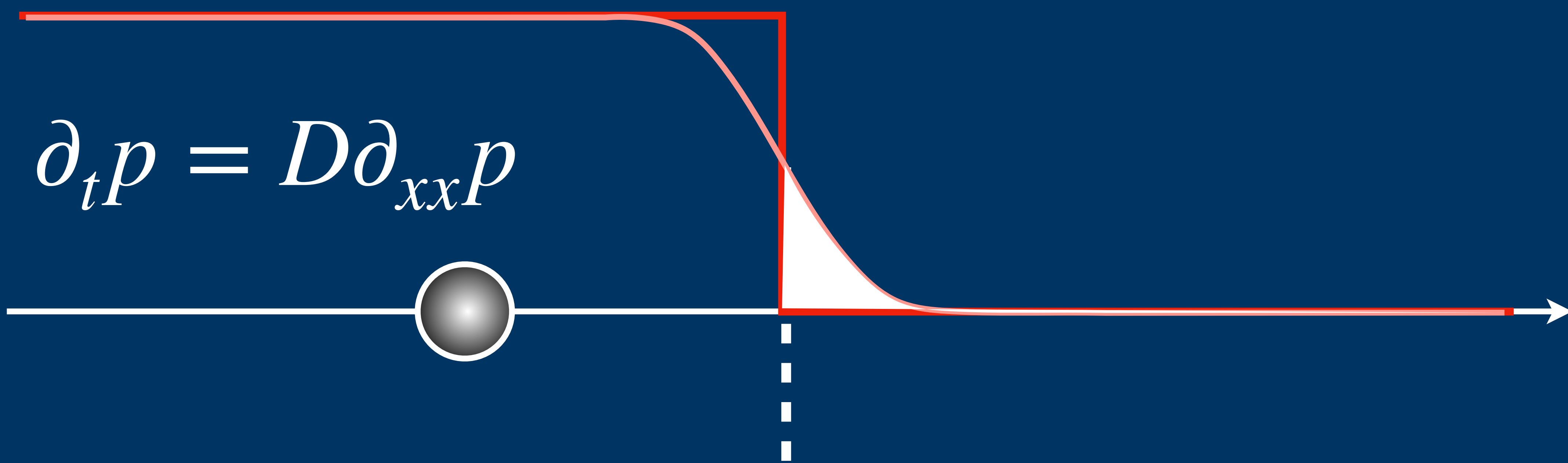


$$< \Delta N^2 > = \quad (2^2) \times p_{L\to R}(t)$$

$p_{L\to R}(t)$?

$$p(x, t=0) = c_0$$

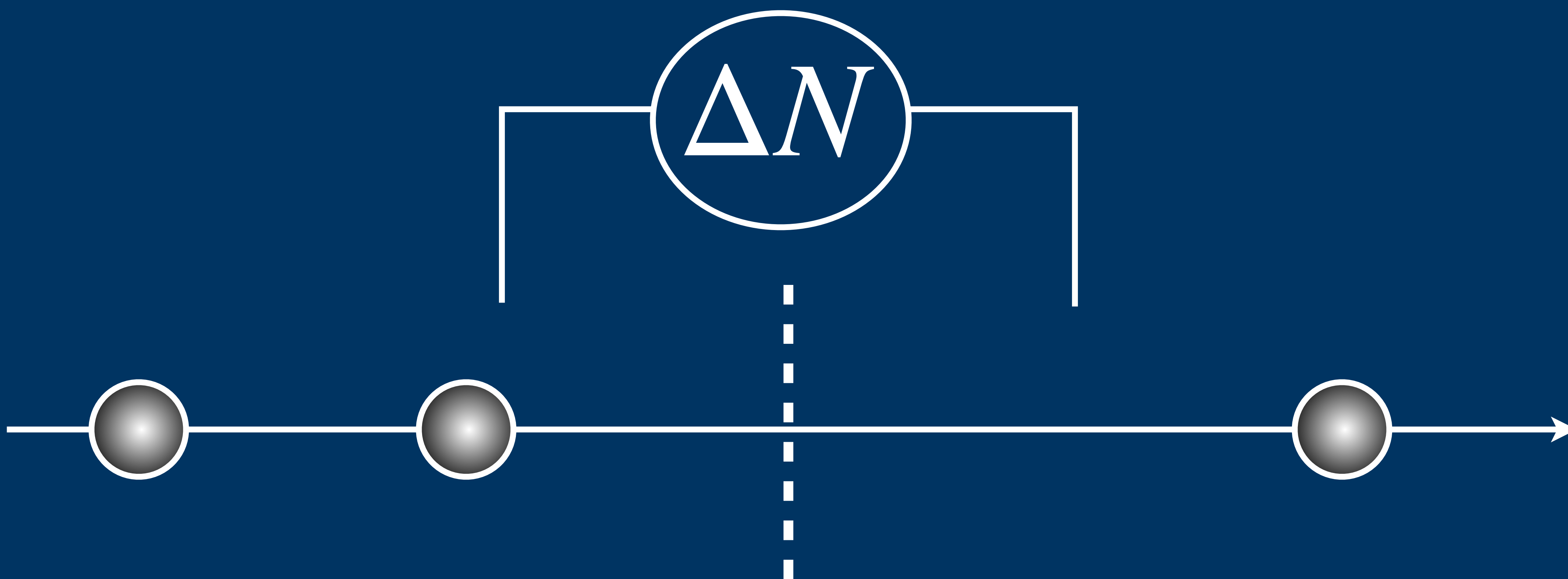
$$\partial_t p = D\partial_{xx} p$$



$$p(x,t) = c_0 \mathrm{erfc}\left[\frac{x}{\sqrt{4Dt}}\right]$$

$$p_{L\to R}(t) = \int_0^{+\infty} p(x,t)\,dx \;\sim \sqrt{t}$$

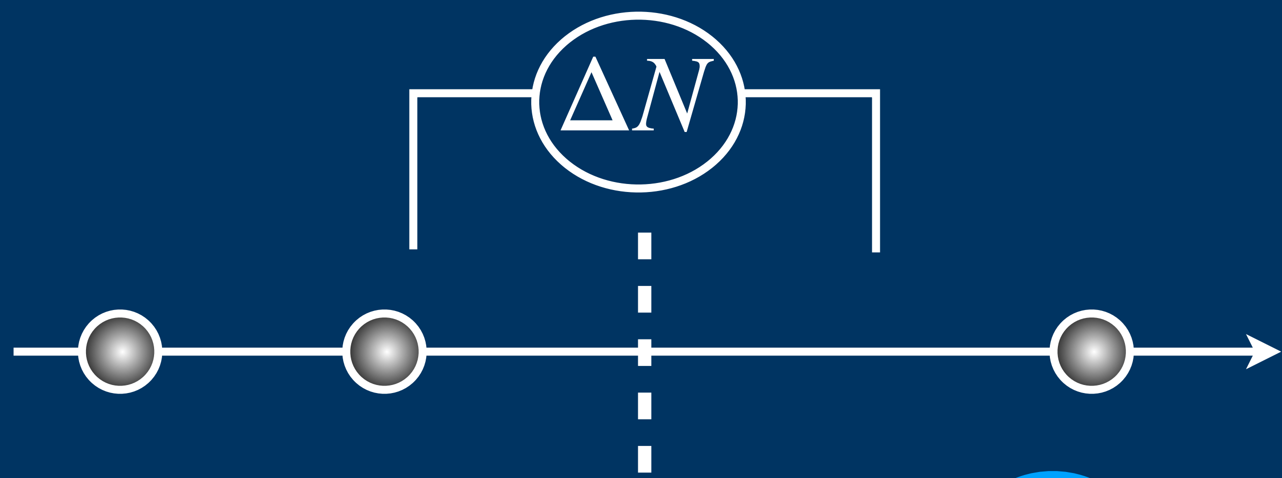
Crank. Mathematics of Diffusion



subdiffusive

$$< \Delta N^2 > = \frac{8\langle N \rangle}{\sqrt{\pi}} \; \frac{\sqrt{t}}{\sqrt{L^2/D}}$$

SM, *J. Chem. Phys.* 2021



$$< \Delta N^2 > = \frac{8\langle N \rangle}{\sqrt{\pi}} \frac{\sqrt{t}}{\sqrt{L^2/D}}$$

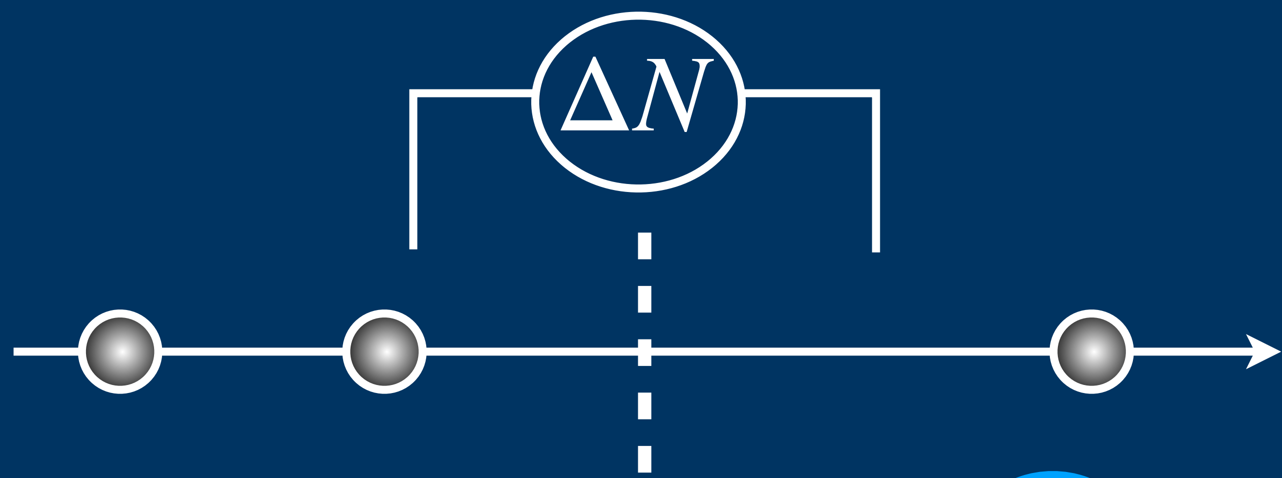
Subdiffusive noise
comes from
boundary crossings

$N(t)$ is a **fractional Brownian Motion** (?)
with Hurst index 1/4

SM, *J. Chem. Phys.* 2021

single file diffusion (1D diffusion with collisions)
is similar… but different (?)

Harris, *J. Appl. Probab.* 1965
Durr, Goldstein, Leibowitz, *Commun. Pure Appl. Math.* 1985
…



$$< \Delta N^2 > = \frac{8\langle N \rangle}{\sqrt{\pi}} \frac{\sqrt{t}}{\sqrt{L^2/D}}$$

Subdiffusive noise comes from **boundary crossings**

amplitude

$\boxed{\langle N \rangle}$

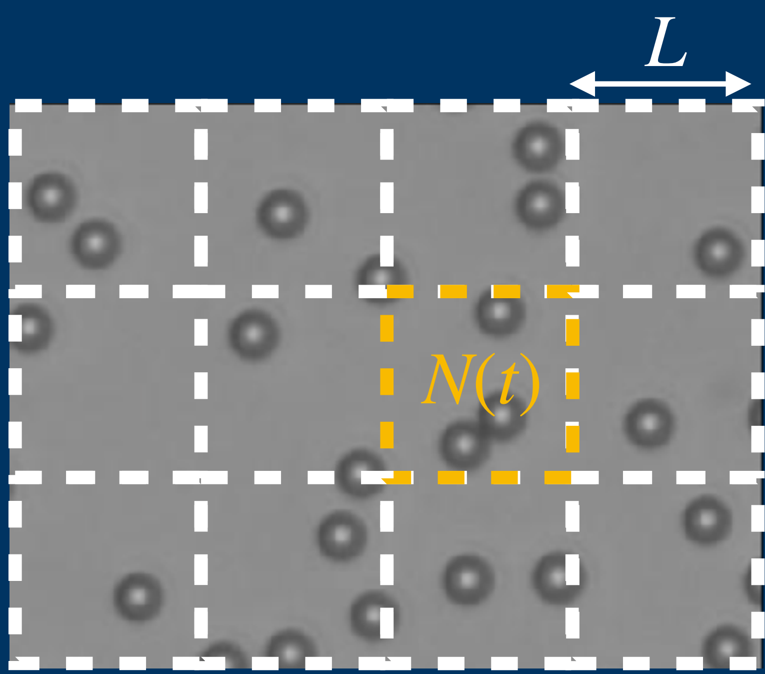
timescale

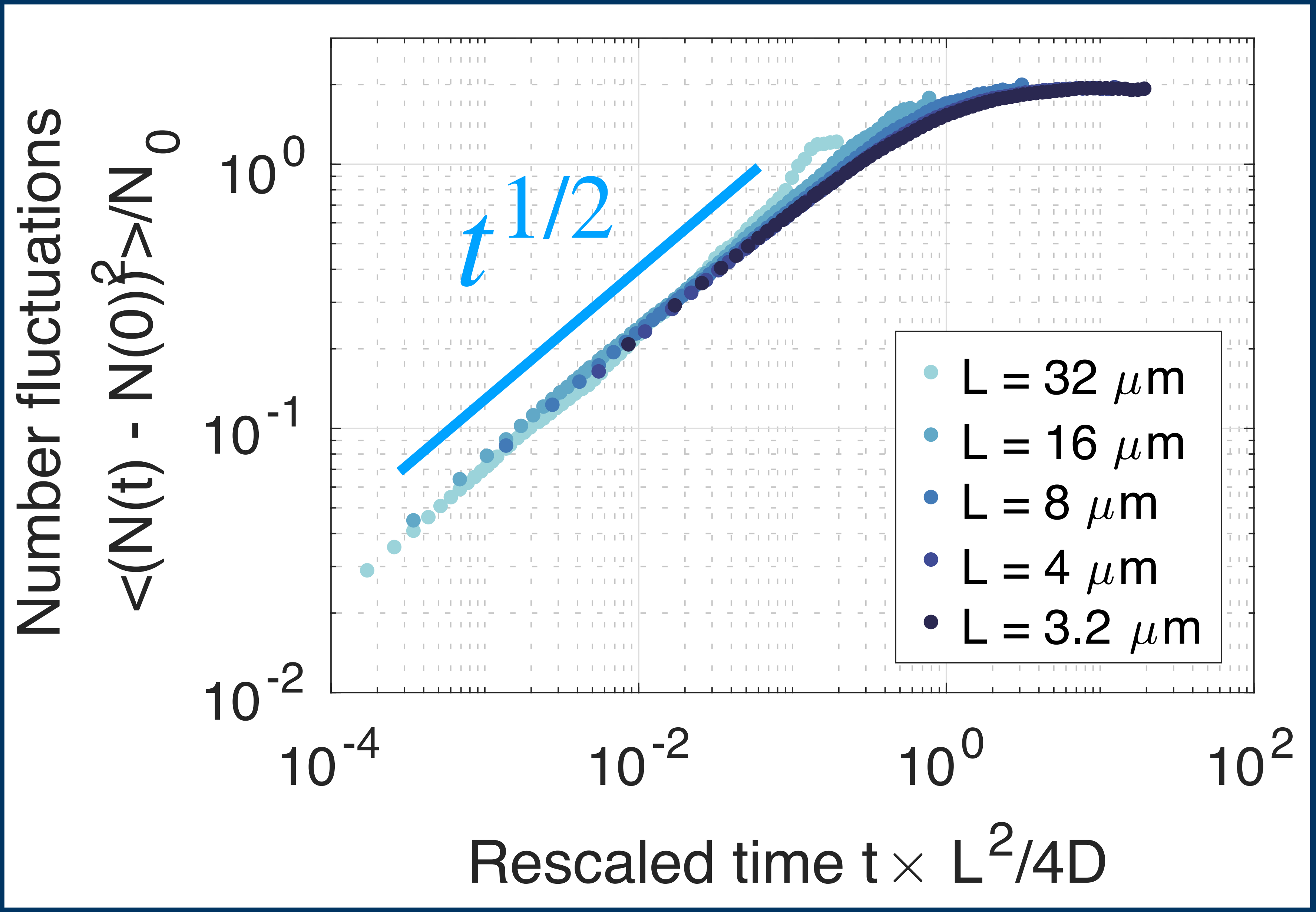
$\boxed{\tau_{\mathrm{Diff}} = L^2/D}$

… stat. phys.

SM, *J. Chem. Phys.* 2021

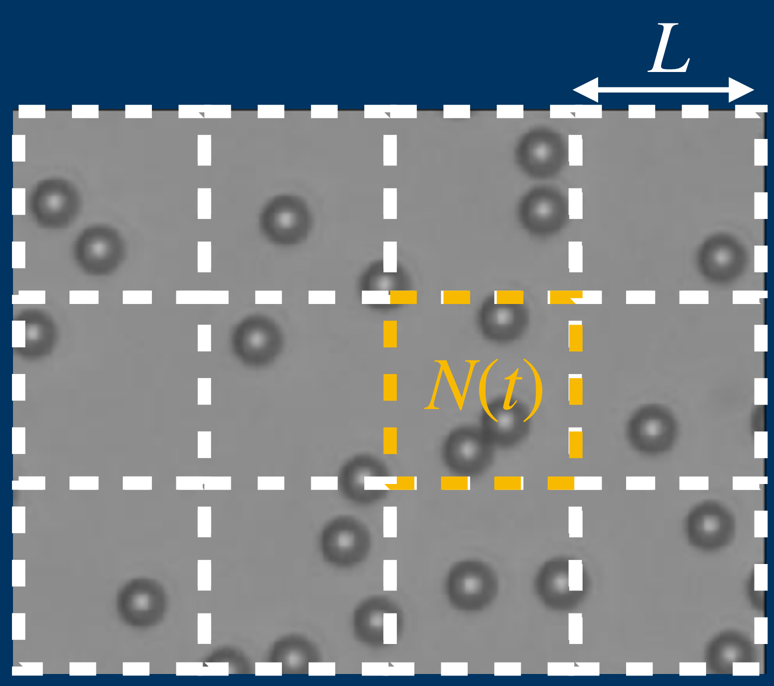
"Fancy Counting"

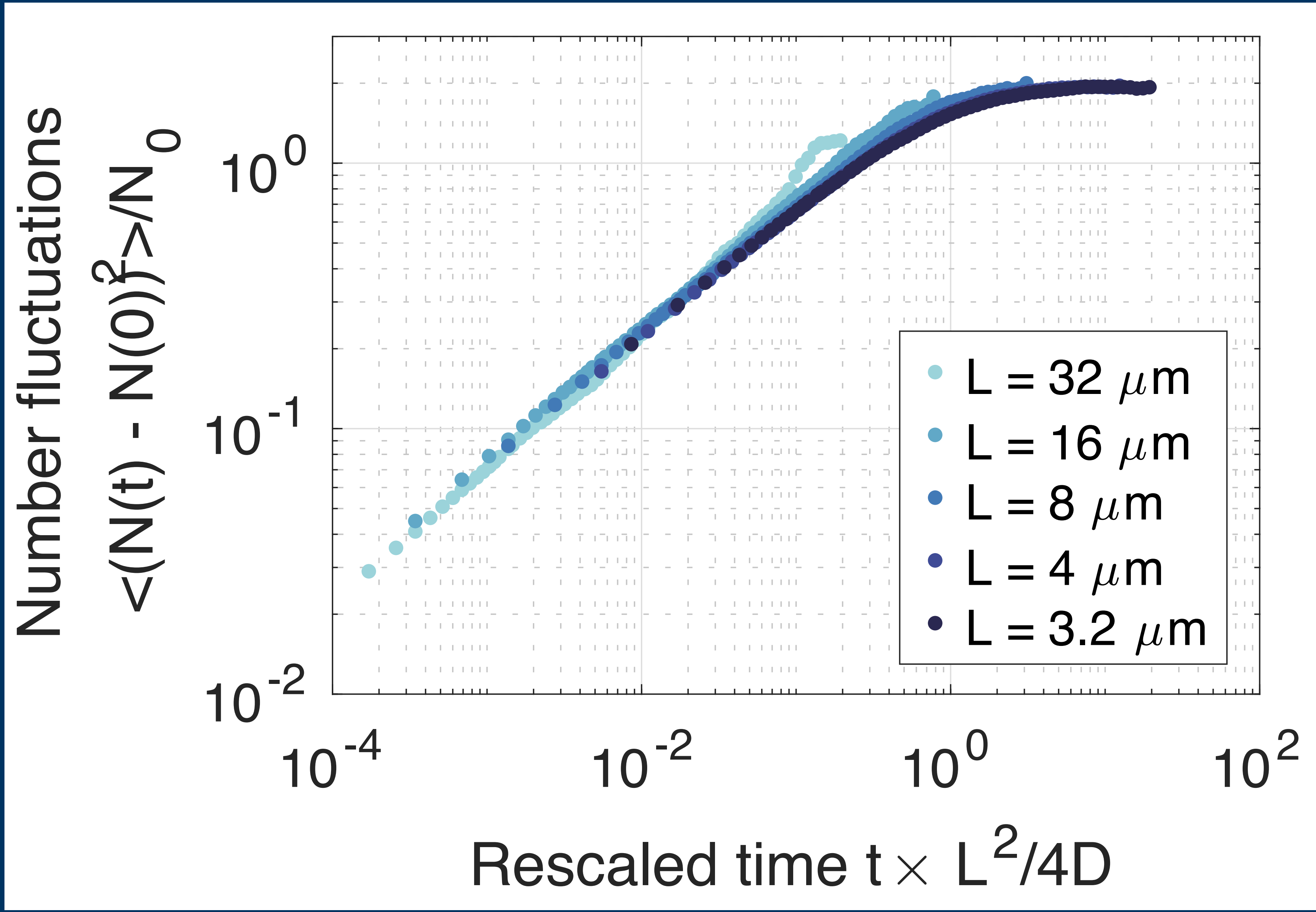




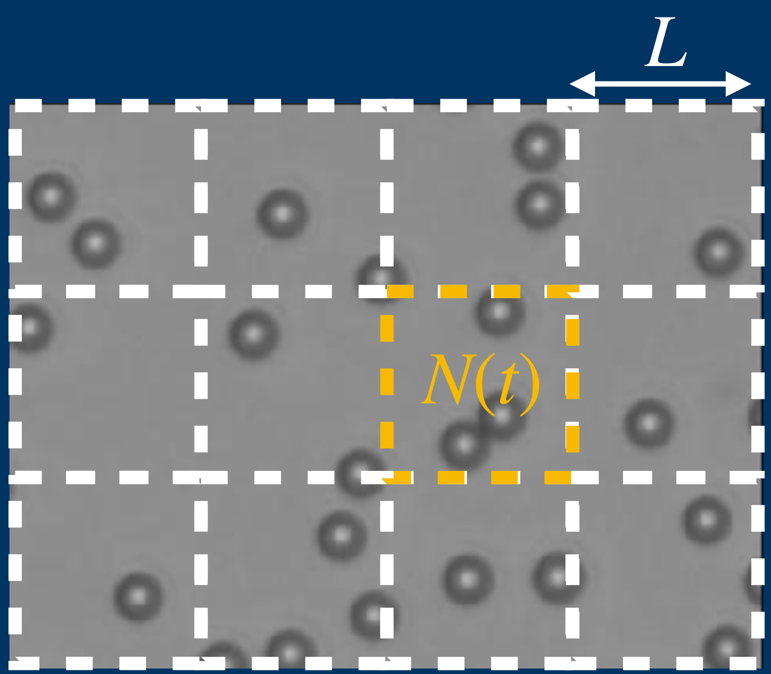
Subdiffusive behavior in a very simple system!

"Fancy Counting"





stochastic Density Functional Theory



particle trajectories | concentration field

$$X(t) \longleftrightarrow c(x,t)$$

$$\partial_t c = D\nabla^2 c + \sqrt{4Dc}\,\nabla\cdot\eta_c$$

$\eta_c(t) \in \mathcal{N}(0,1)$ **fluctuations**

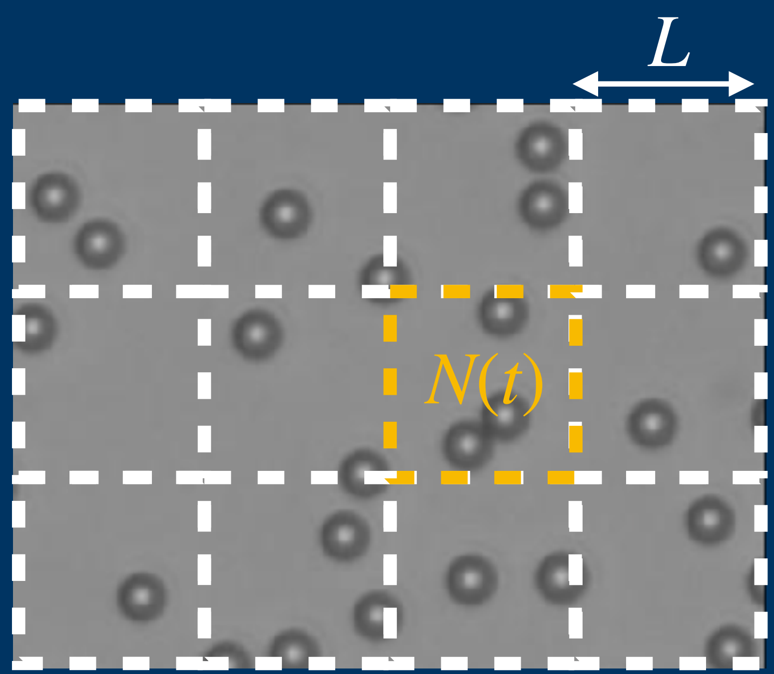
D.S. Dean, *J. Phys. A* 1996

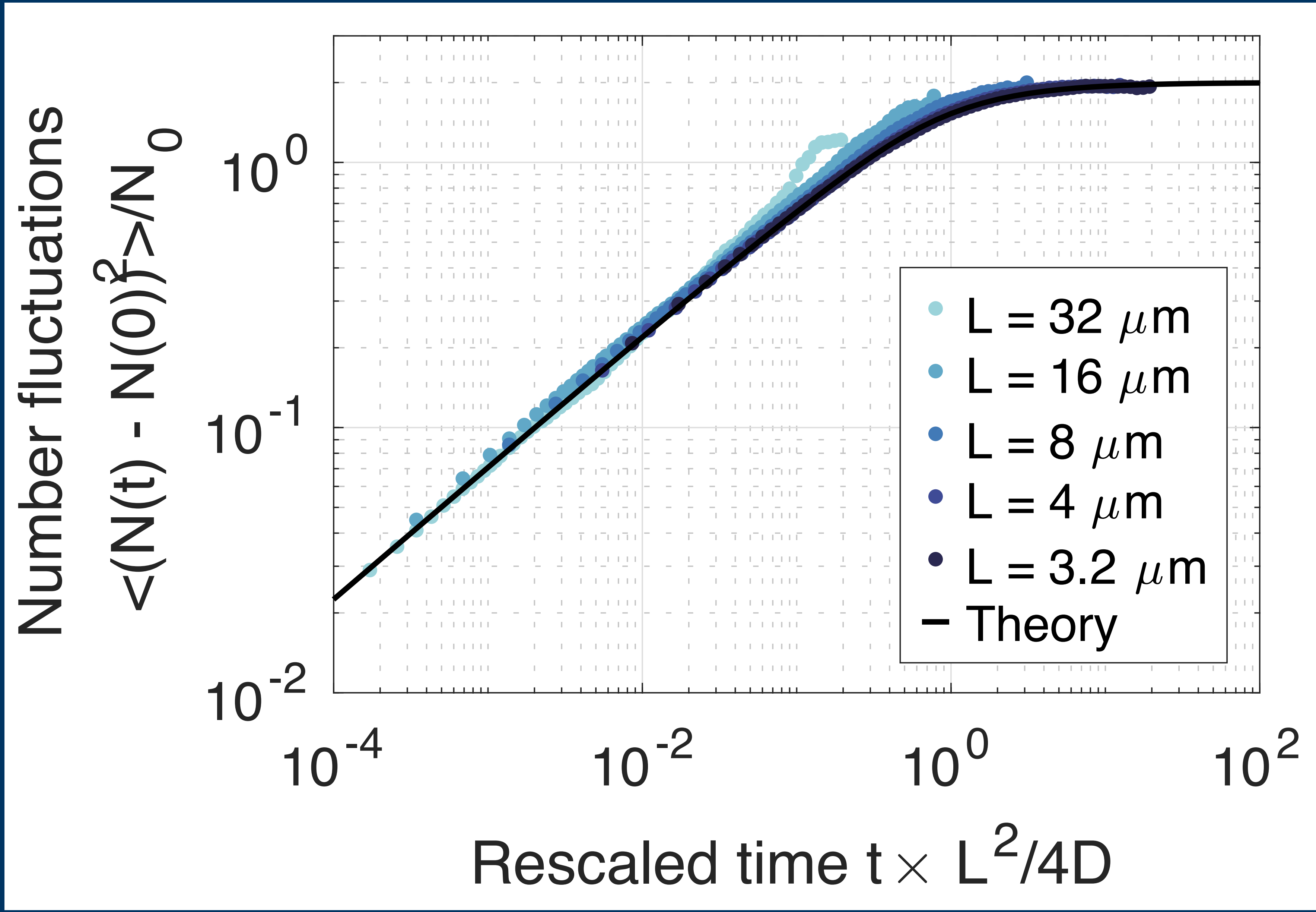
K. Kawasaki, *Physica A* 1994

$$C_N(t) = \iint_{V_{\text{box}}} \langle c(x,t)c(x',0)\rangle \,\mathrm{d}x\mathrm{d}x'$$

$$\boxed{C_N(t) = \left[f_0\left(\frac{Dt}{L^2}\right)\right]^2, \qquad f_0(\tau) = \left[\sqrt{\tau/\pi}\times\left(e^{-1/\tau}-1\right) + \mathrm{erf}(\sqrt{1/\tau})\right]^2}$$

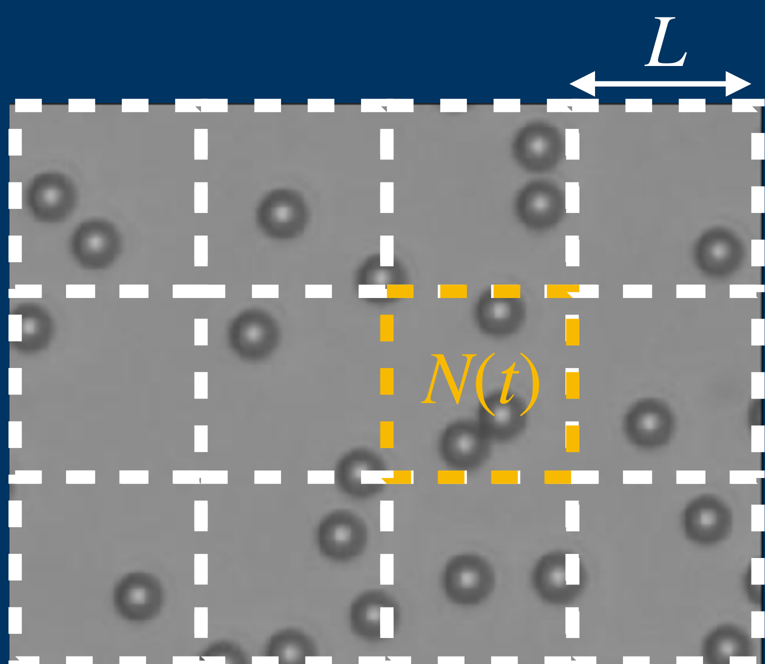
"Fancy Counting"

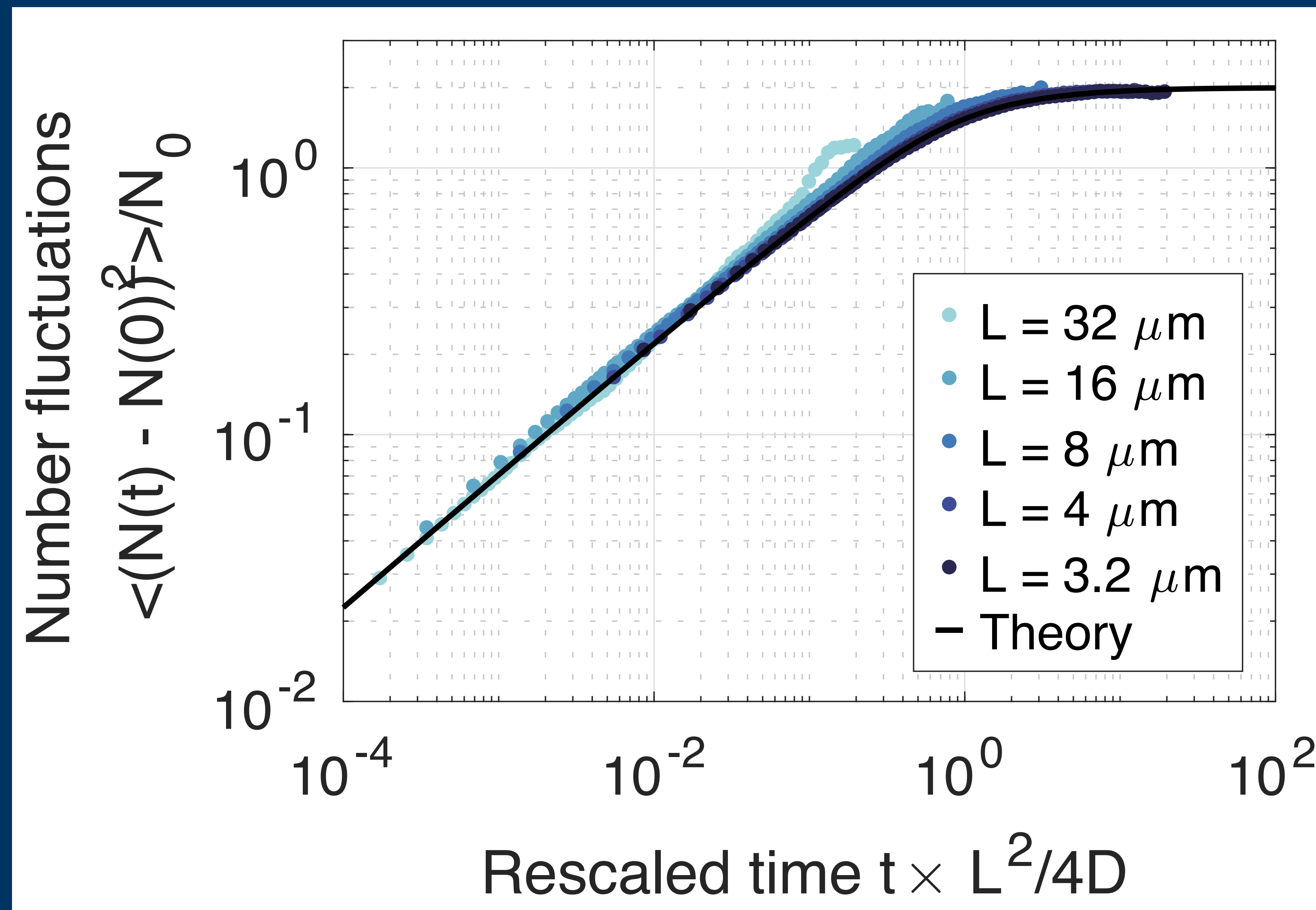




$$f(t) = 2 - 2\left[f_0\left(\frac{Dt}{L^2}\right)\right]^2, \quad f_0(\tau) = \left[\sqrt{\tau/\pi} \times \left(e^{-1/\tau} - 1\right) + \mathrm{erf}(\sqrt{1/\tau})\right]^2$$

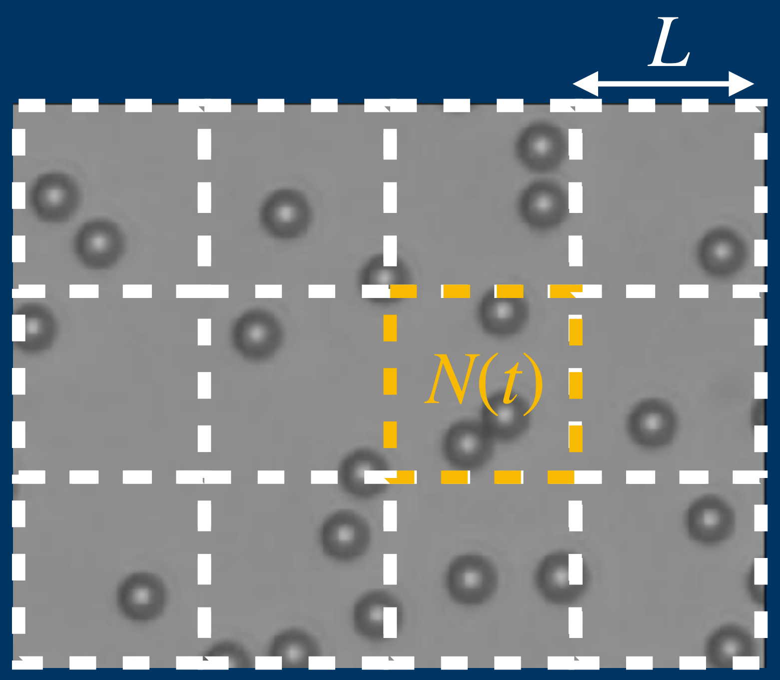
"Fancy Counting"



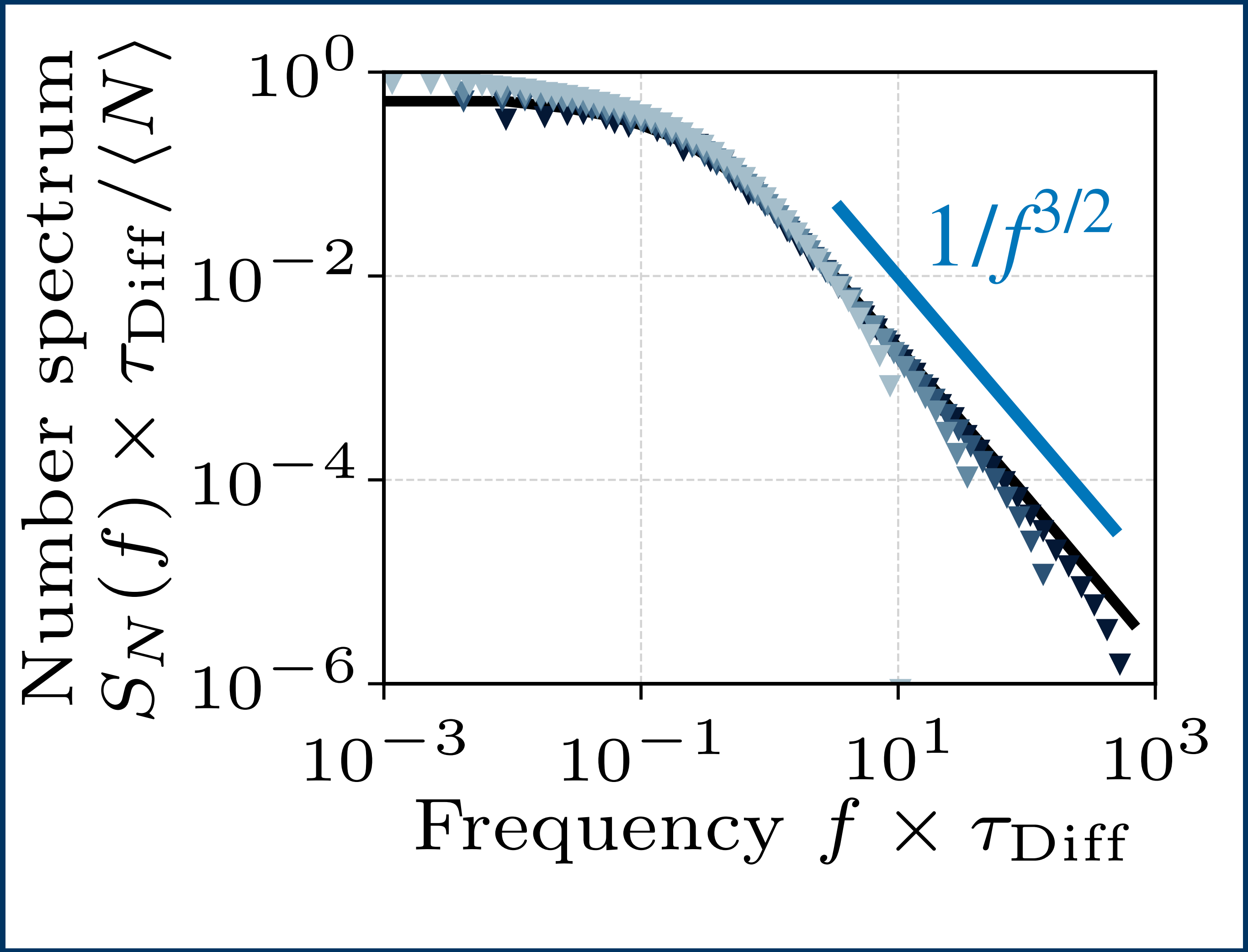


Method to measure the diffusion coefficient !

Power Spectra



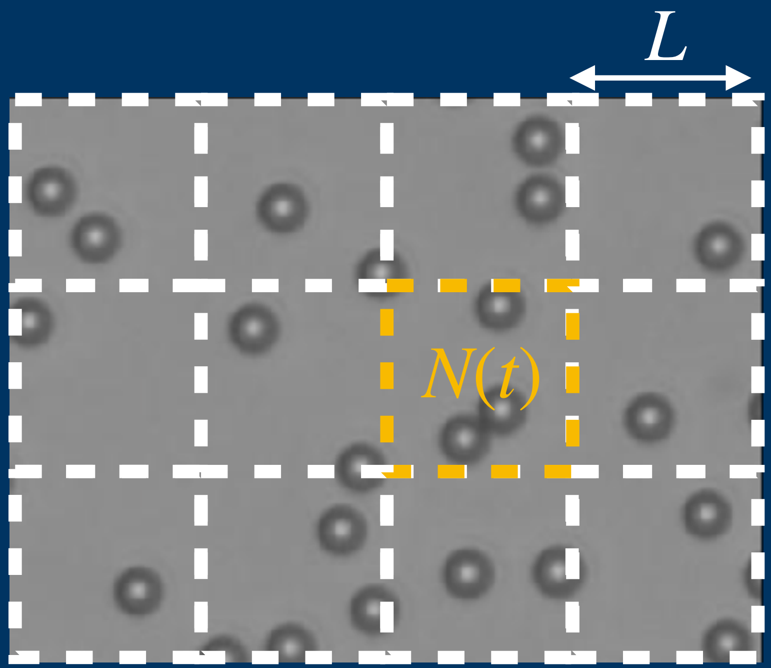
$$N(t) \longrightarrow S_N(f) = \frac{1}{T}\left|\int_0^T N(t)\, e^{-i2\pi ft}\, dt\right|^2$$

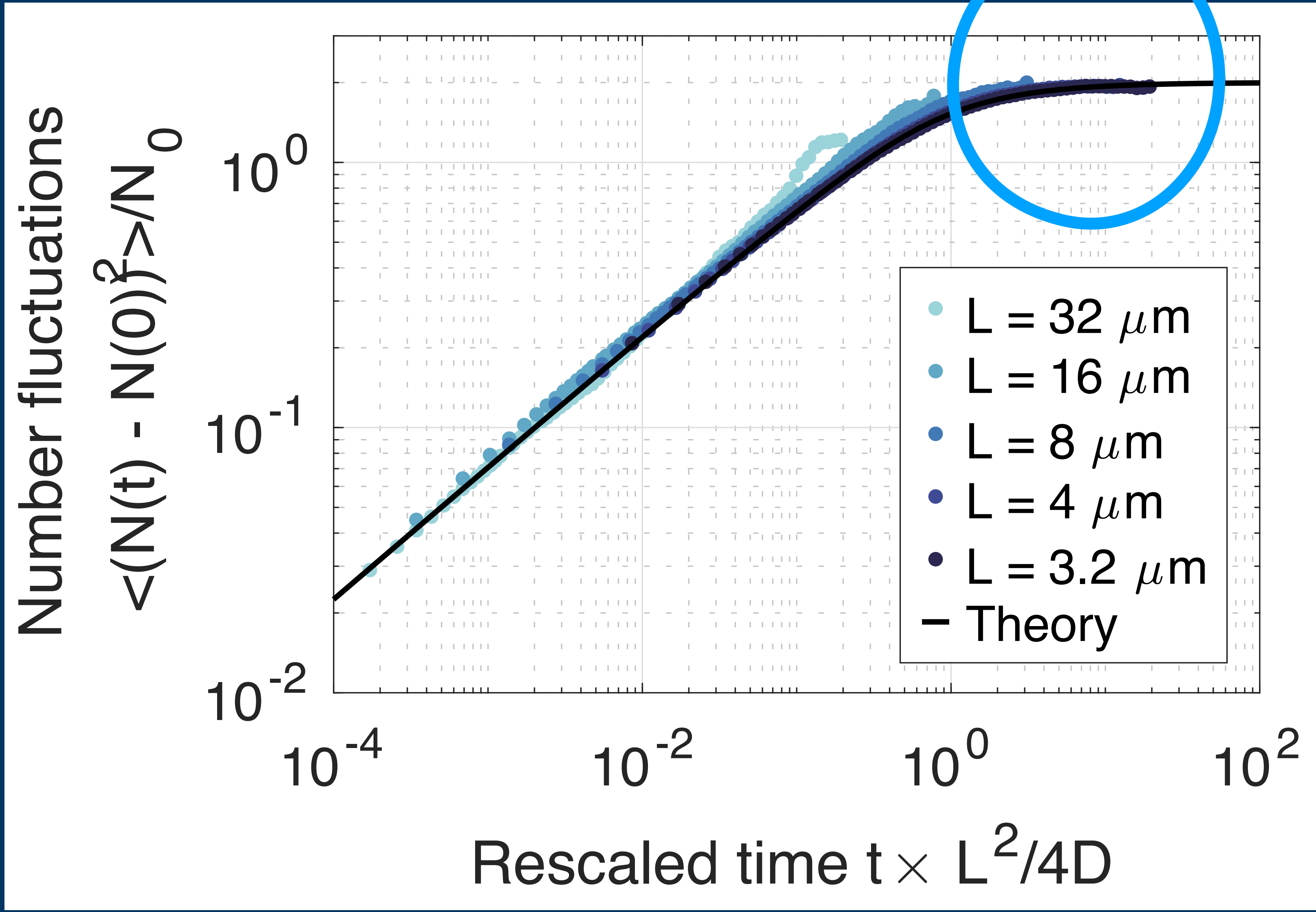


signature of fractional noise...

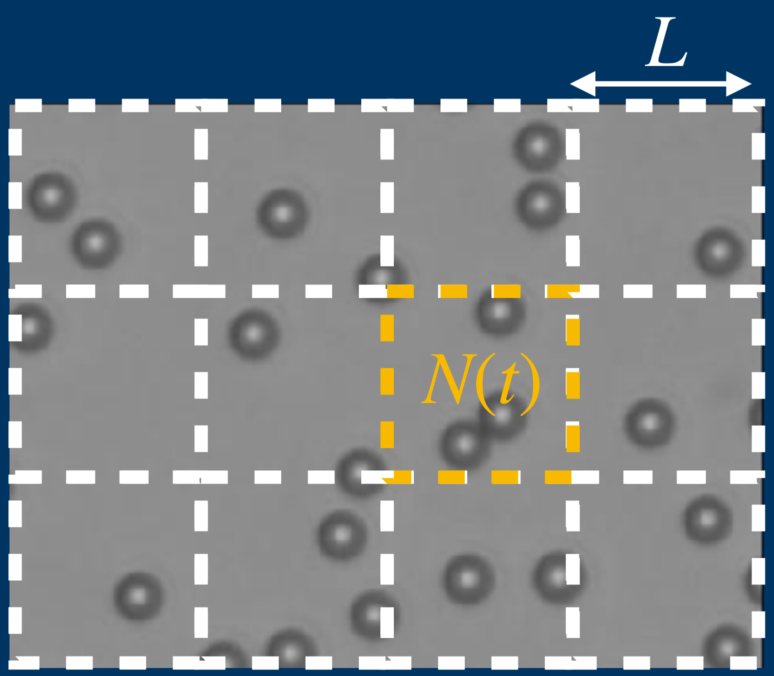
Plateau?

$$2\left(\langle N^2\rangle - \langle N\rangle^2\right)$$





stochastic Density Functional Theory



particle trajectories $\quad X(t) \longleftrightarrow c(x,t) \quad$ concentration field

$$\partial_t c = D\nabla^2 c + \sqrt{4Dc}\,\nabla\cdot\eta_c - \frac{D}{k_BT}\nabla\left[c\cdot\nabla\left(\mathscr{V}\star c\right)\right]$$

pair-wise interactions

[small fluctuations] $$S(k) \simeq \left(1 + \frac{C_0}{k_BT}\hat{\mathscr{V}}(k)\right)^{-1}$$

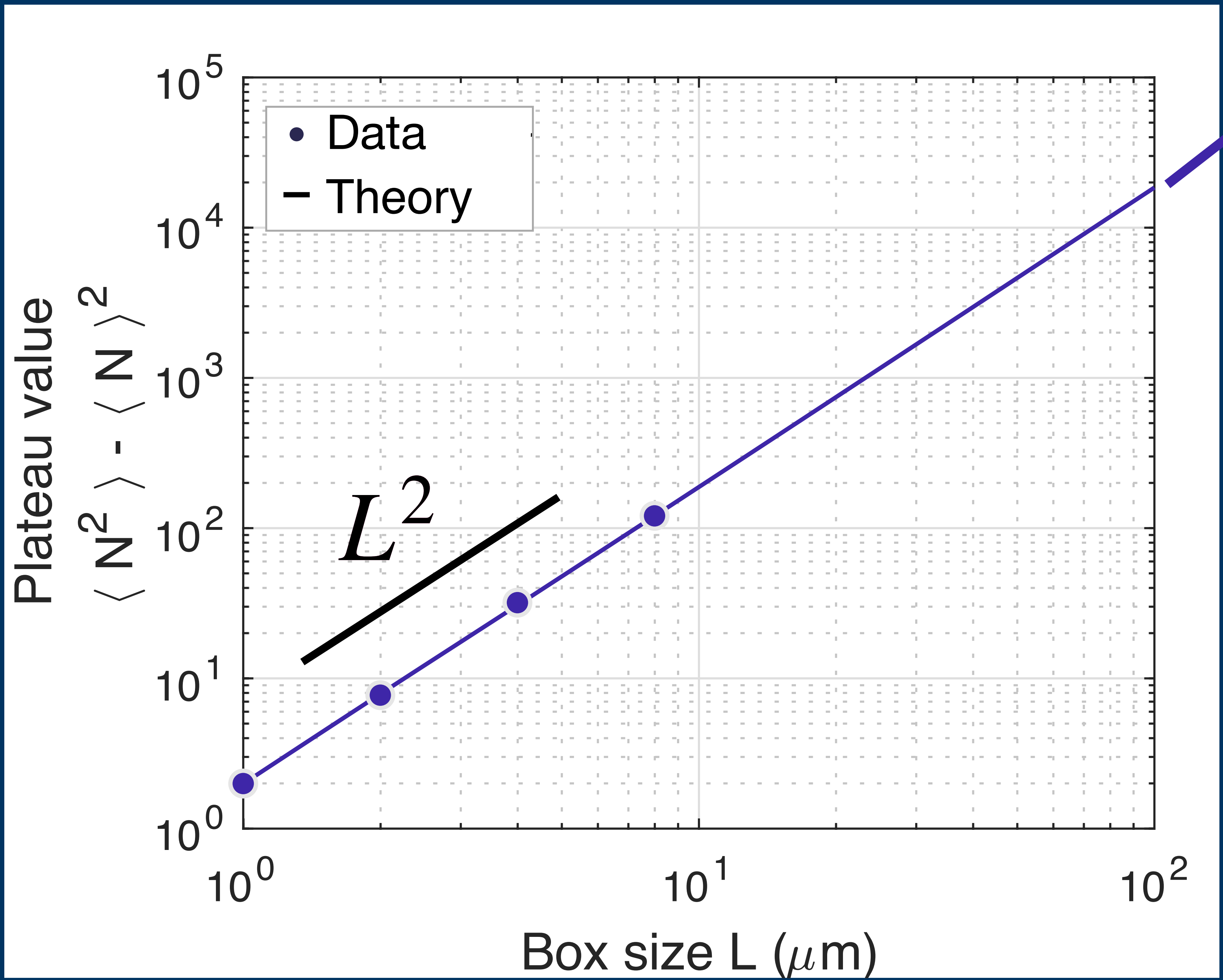
$$\boxed{C_N(t) = \langle N\rangle \int \frac{d^dk}{(2\pi)^d} S(k) e^{-\frac{Dk^2t}{S(k)}} f_V(k), \qquad f_V(k) = \frac{1}{L^d}\iint_{V_{\text{box}}} \mathrm{d}^d x \mathrm{d}^d x' e^{ik\cdot(x-x')}}$$

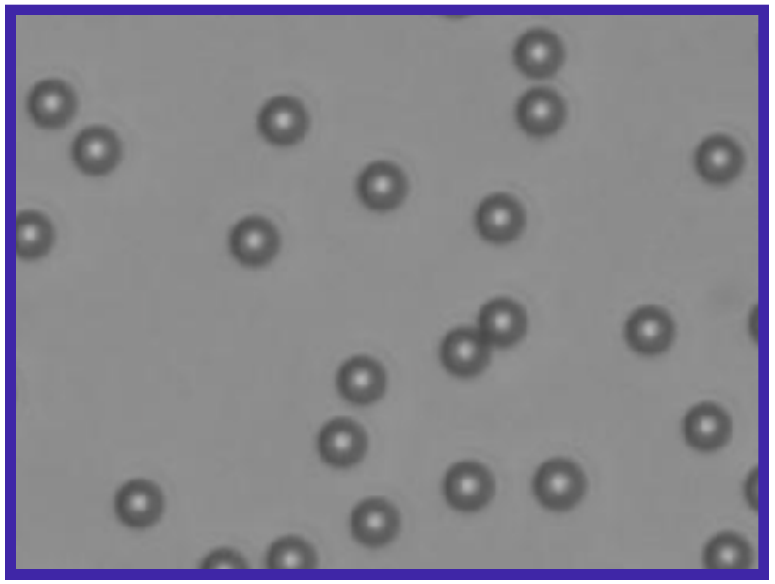
$$C_N(t) = \langle N \rangle \int \frac{d^d k}{(2\pi)^d} S(k) e^{-\frac{Dk^2 t}{S(k)}} f_V(k),$$

$$f_V(k) = \frac{1}{L^d} \iint_{V_{\text{box}}} \mathrm{d}^d x \mathrm{d}^d x' e^{ik\cdot(x-x')}$$

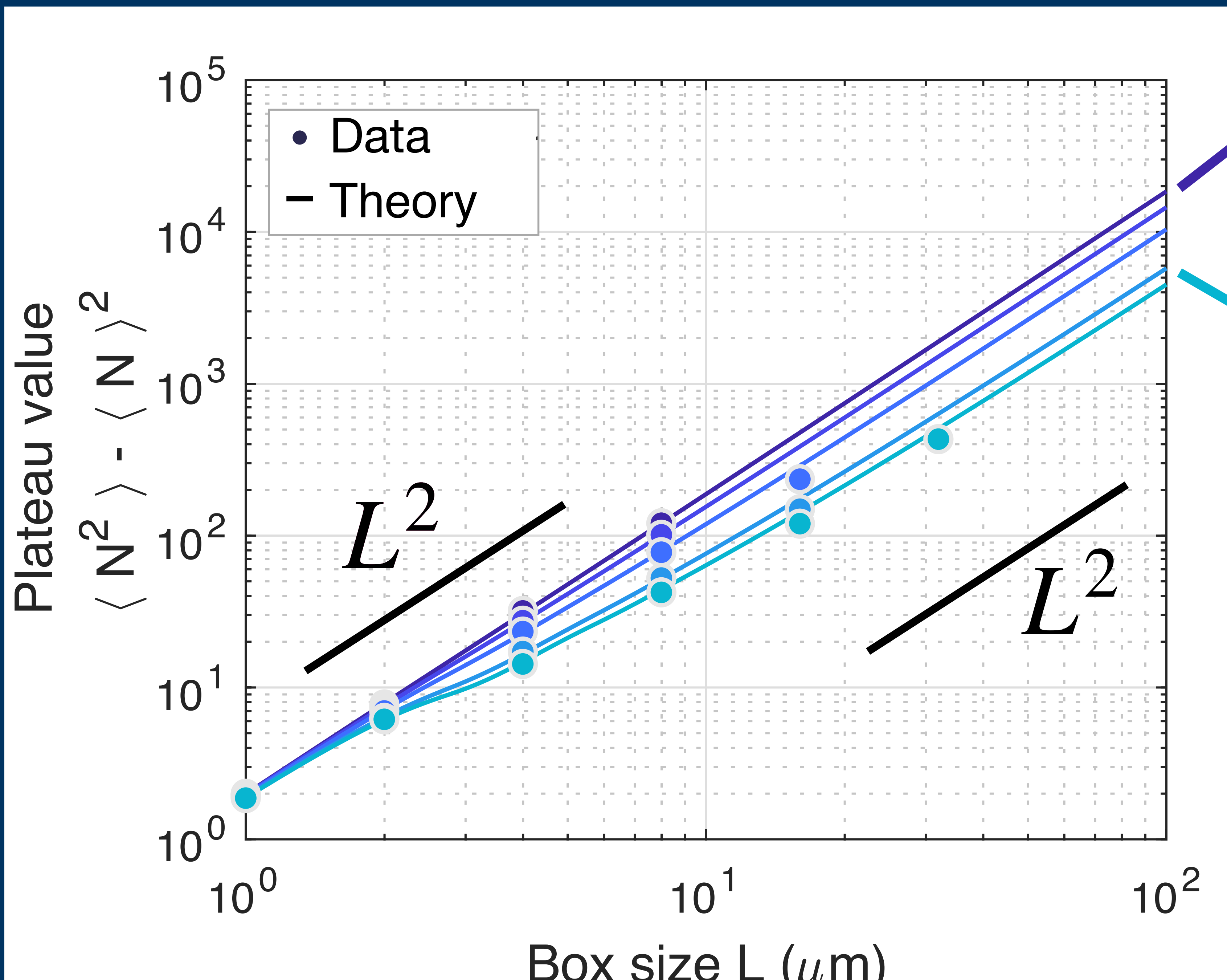
$$S(k) \simeq \left(1 + \frac{C_0}{k_B T} \hat{\mathscr{V}}(k) \right)^{-1}$$

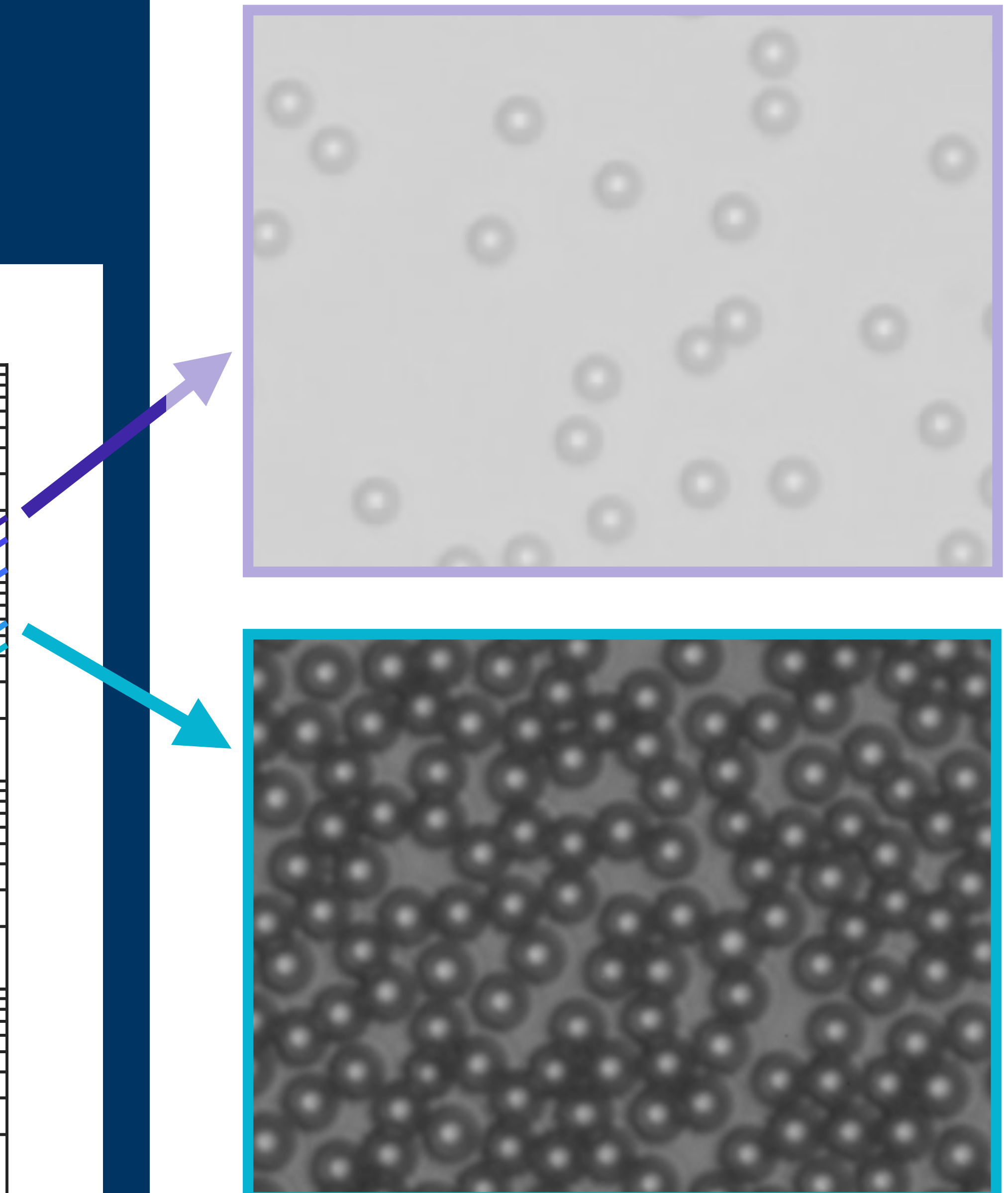
$$C_N(0) = \langle N \rangle \int \frac{d^d k}{(2\pi)^d} S(k) f_V(k)$$



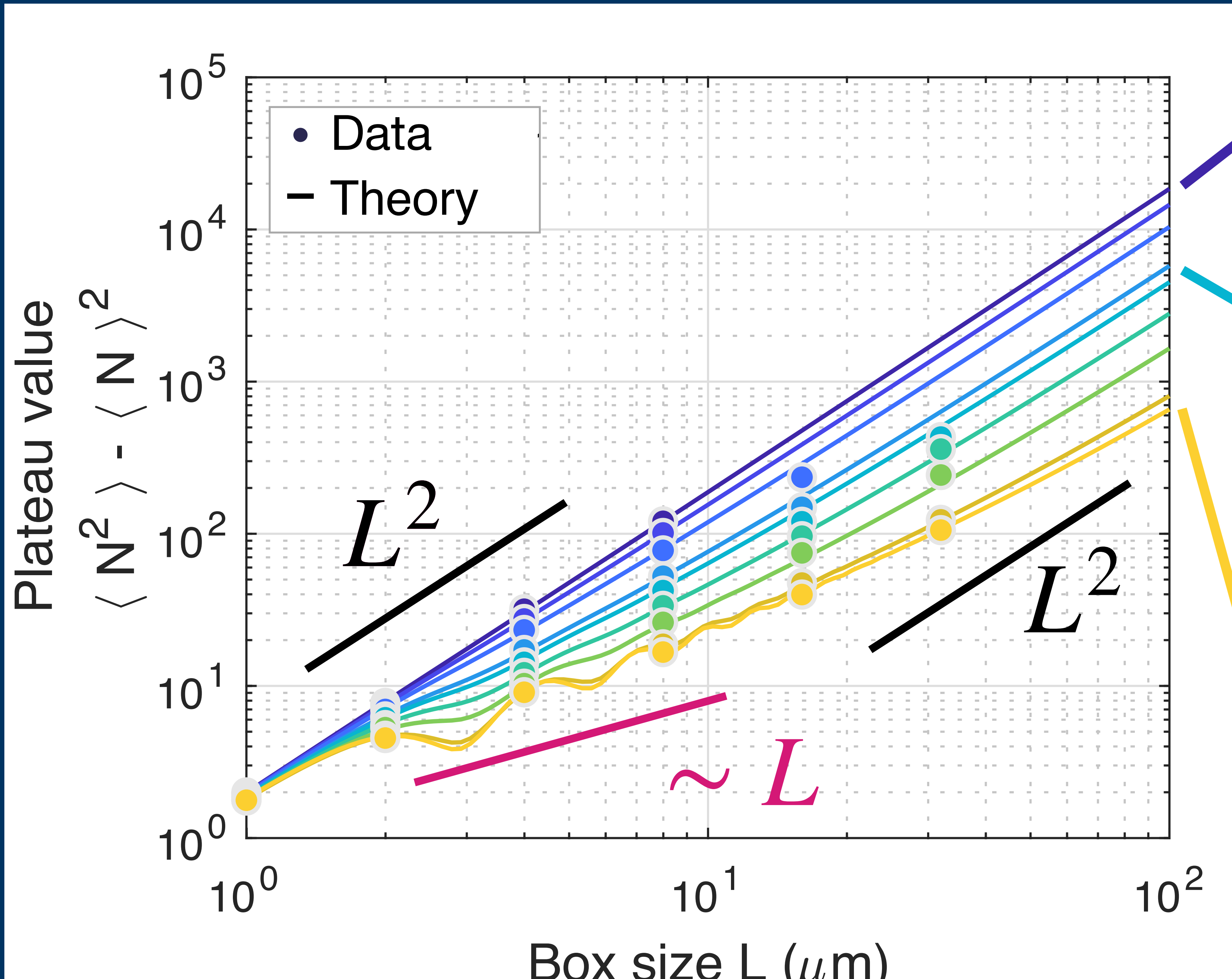


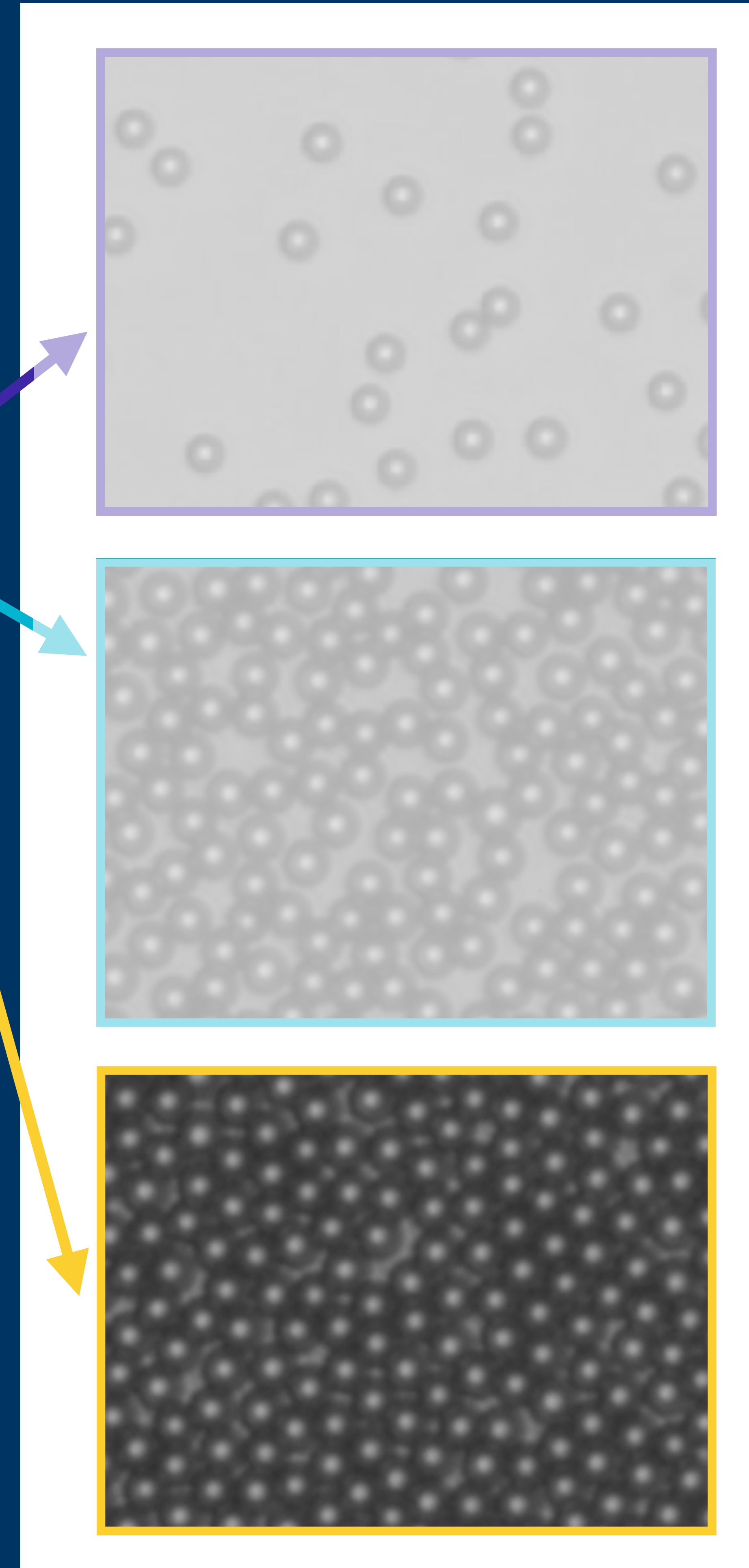
$$C_N(0) = \langle N \rangle \int \frac{d^d k}{(2\pi)^d} S(k) f_V(k)$$



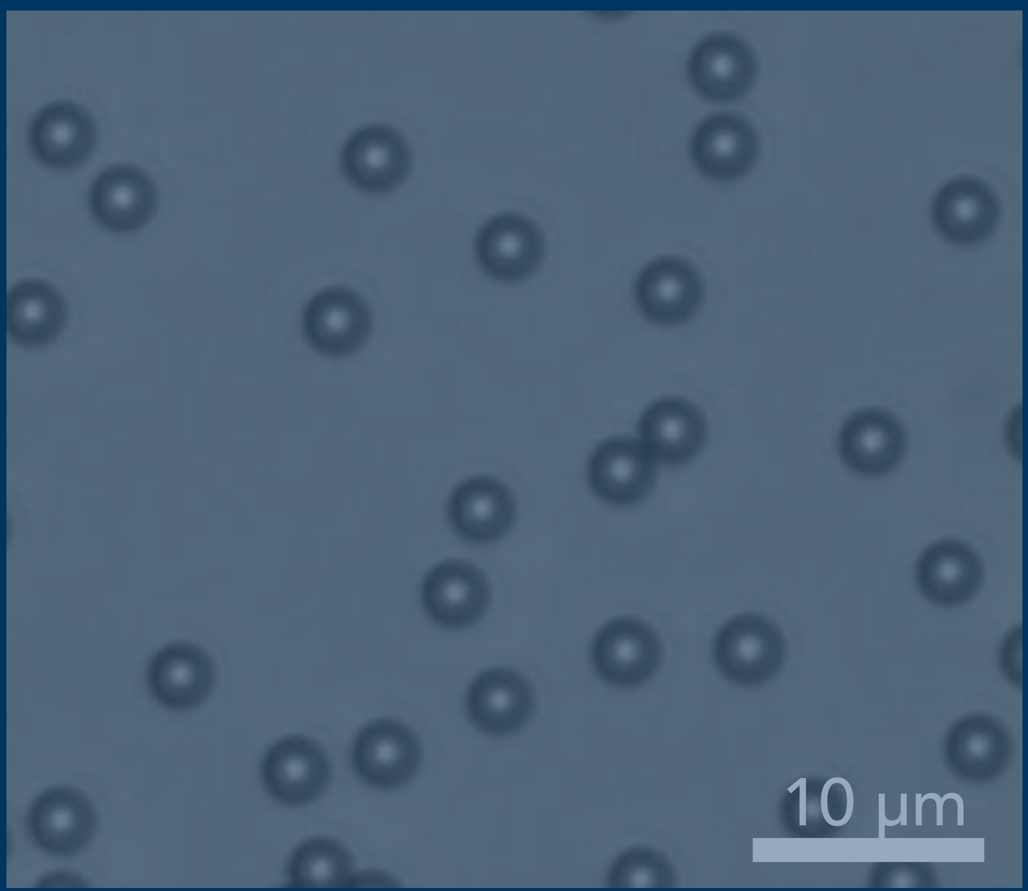


$$C_N(0) = \langle N \rangle \int \frac{d^d k}{(2\pi)^d} S(k) f_V(k)$$

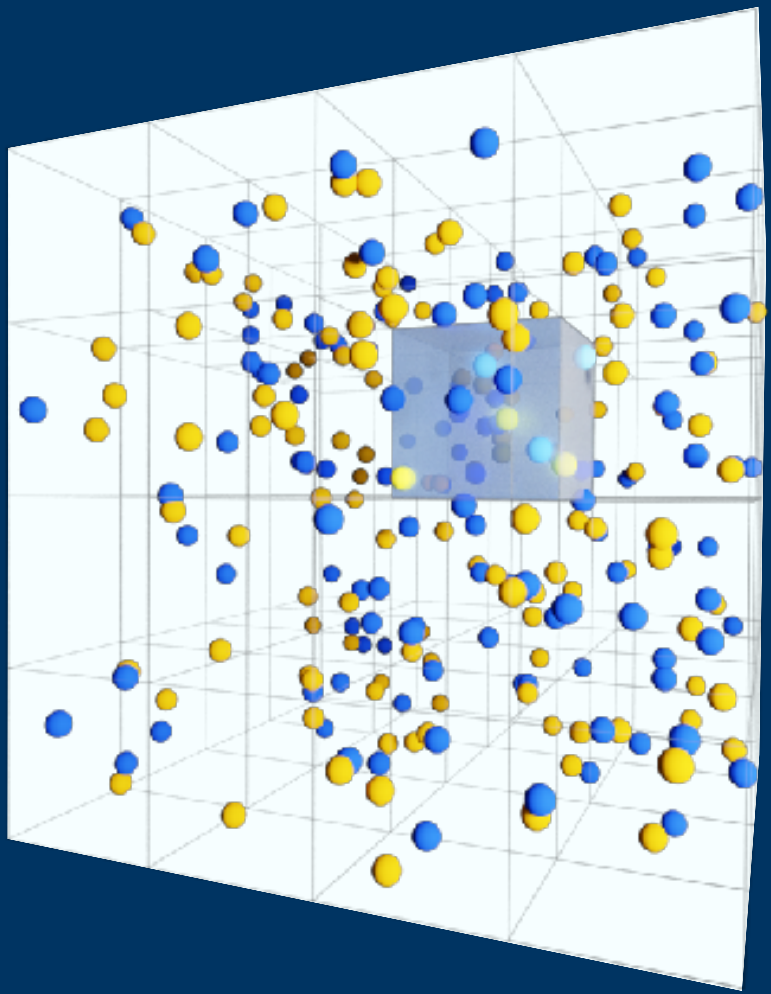




Hyperuniformity in small boxes?

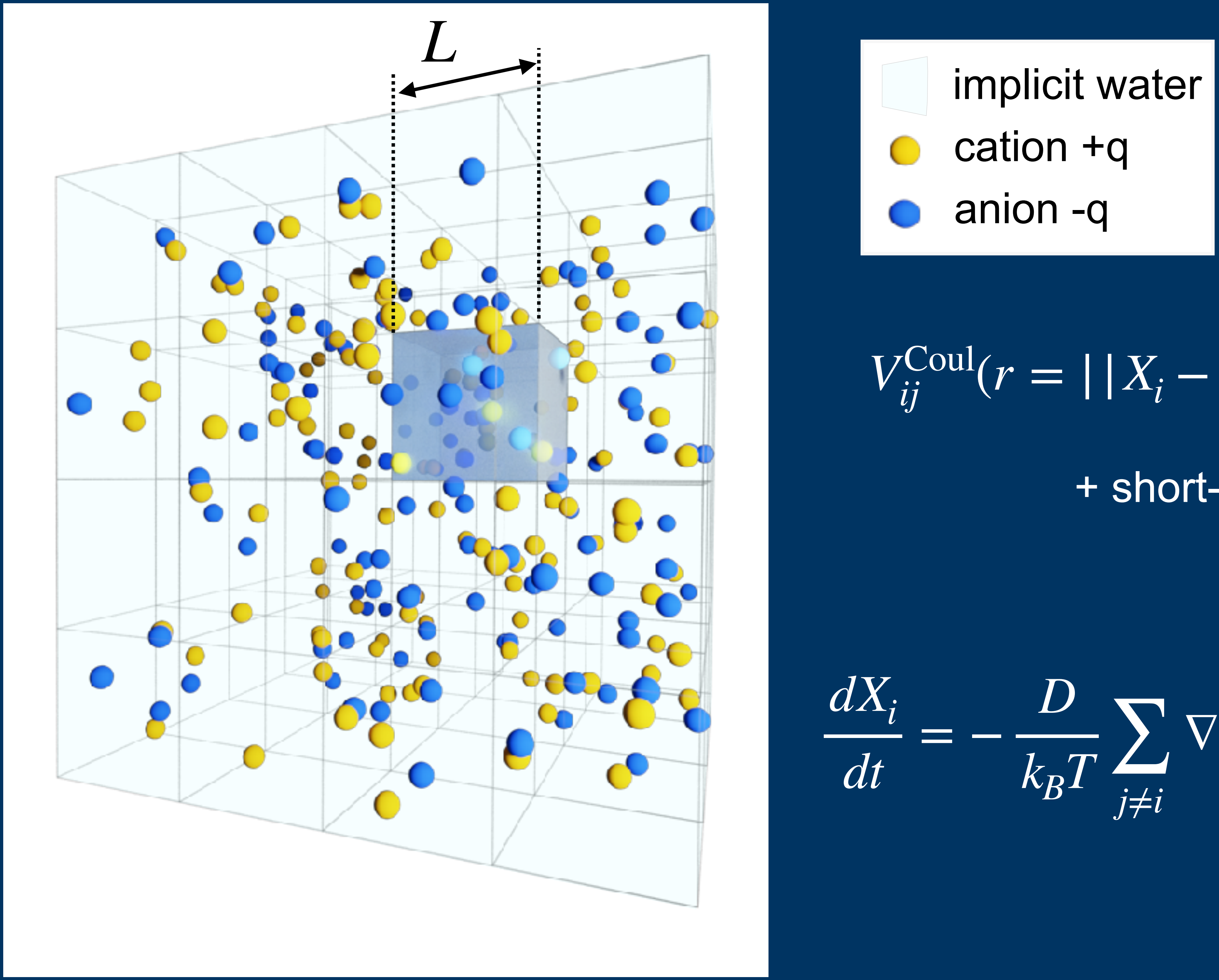


2D - short range interactions



3D - long range interactions

Model system: Ionic Solutions

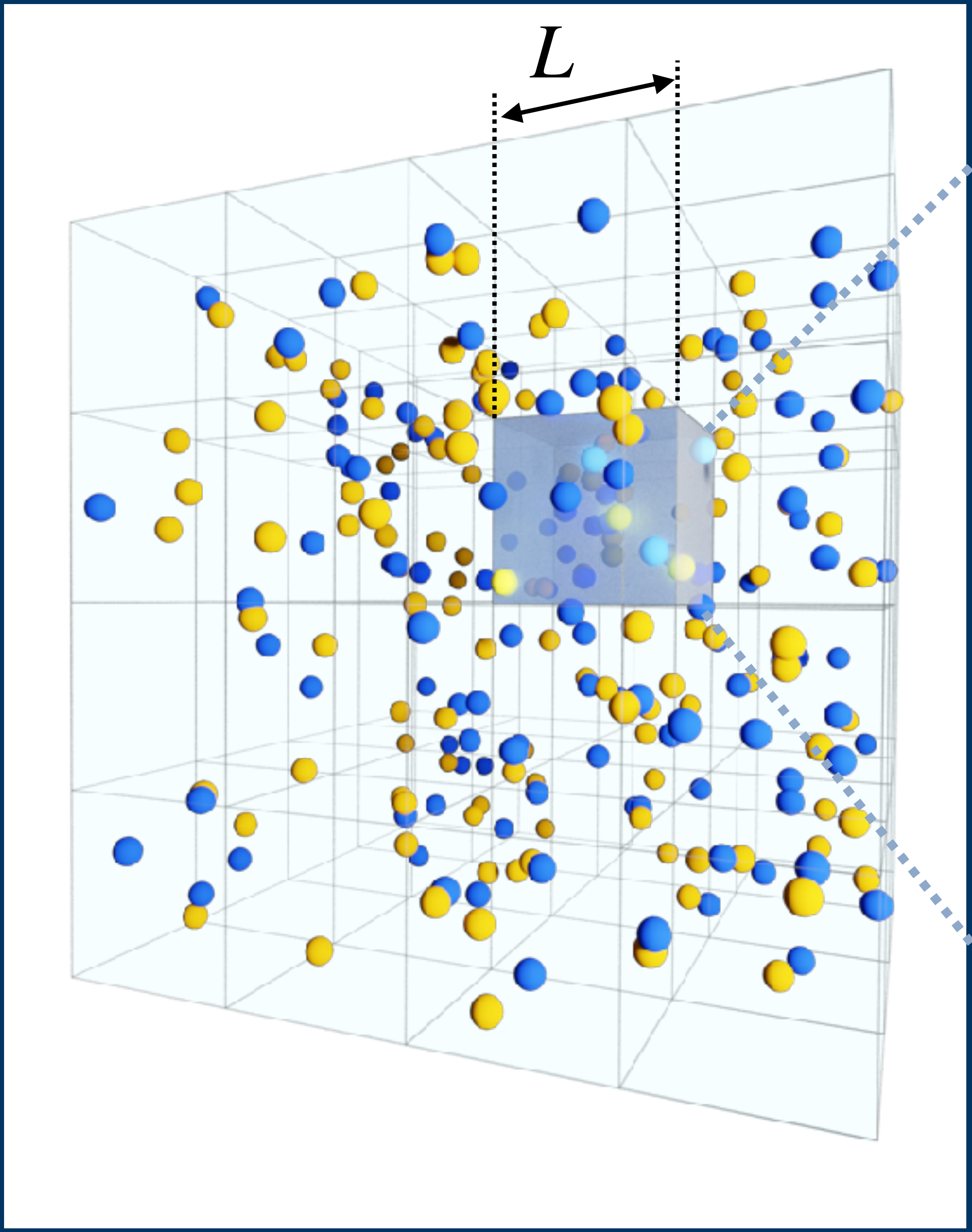


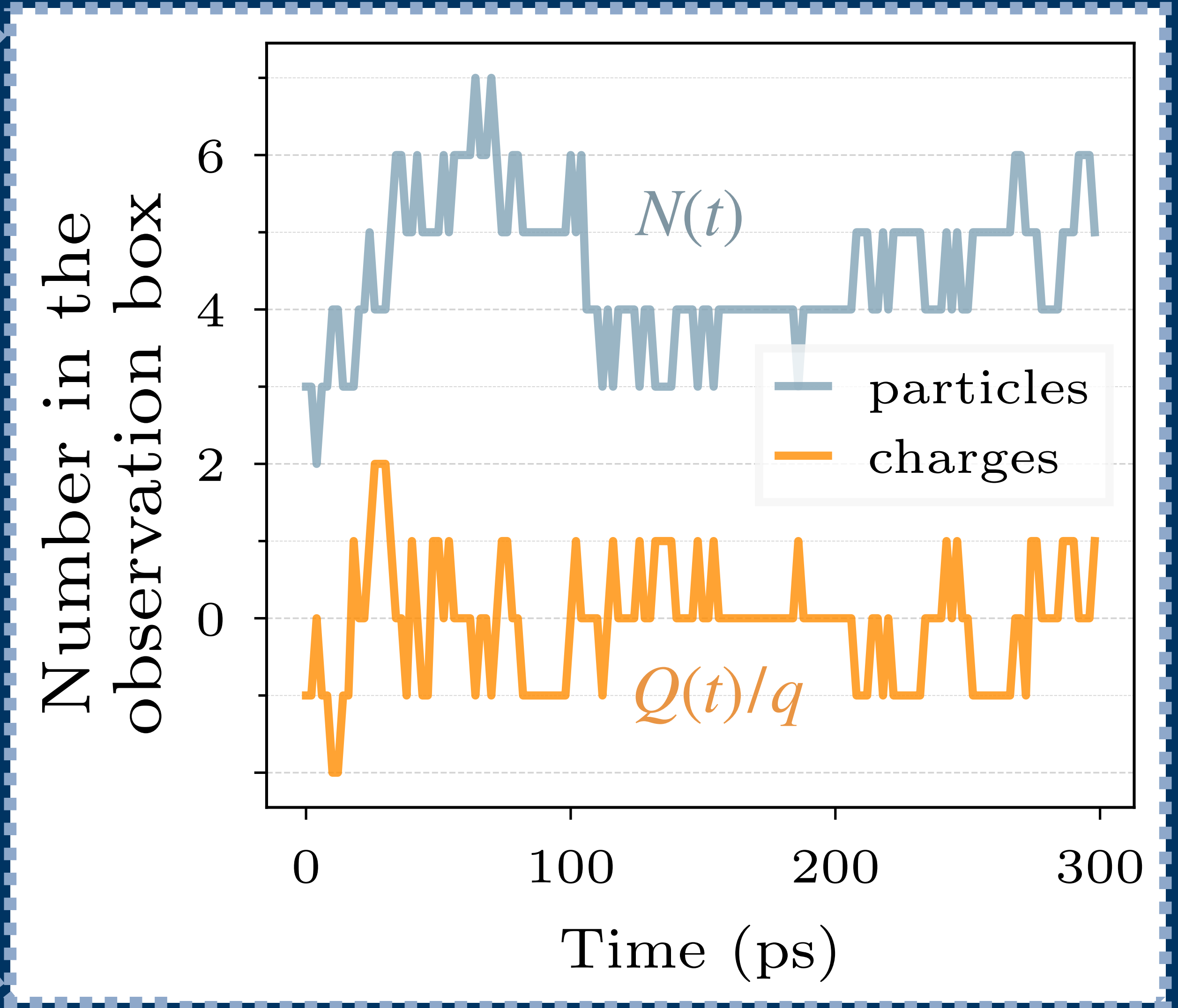
$$V_{ij}^{\mathrm{Coul}}(r = ||X_i - X_j||) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r}$$

+ short-range repulsion

$$\frac{dX_i}{dt} = -\frac{D}{k_B T}\sum_{j\neq i} \nabla V_{ij}^{\mathrm{Coul}}(||X_i - X_j||) + \sqrt{2D}\eta_i(t)$$

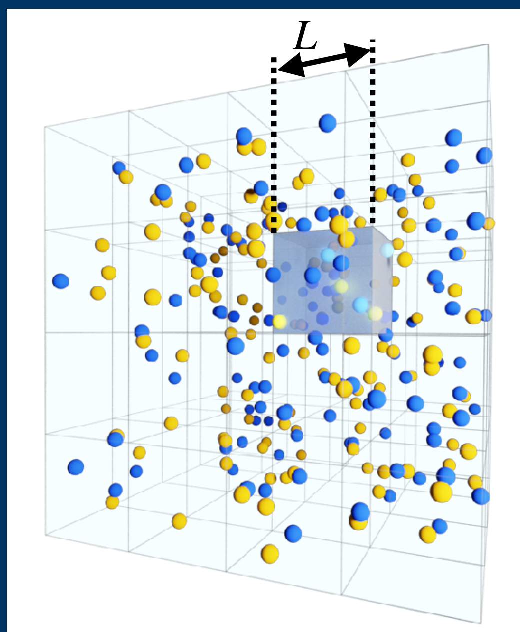
Model system: Ionic Solutions

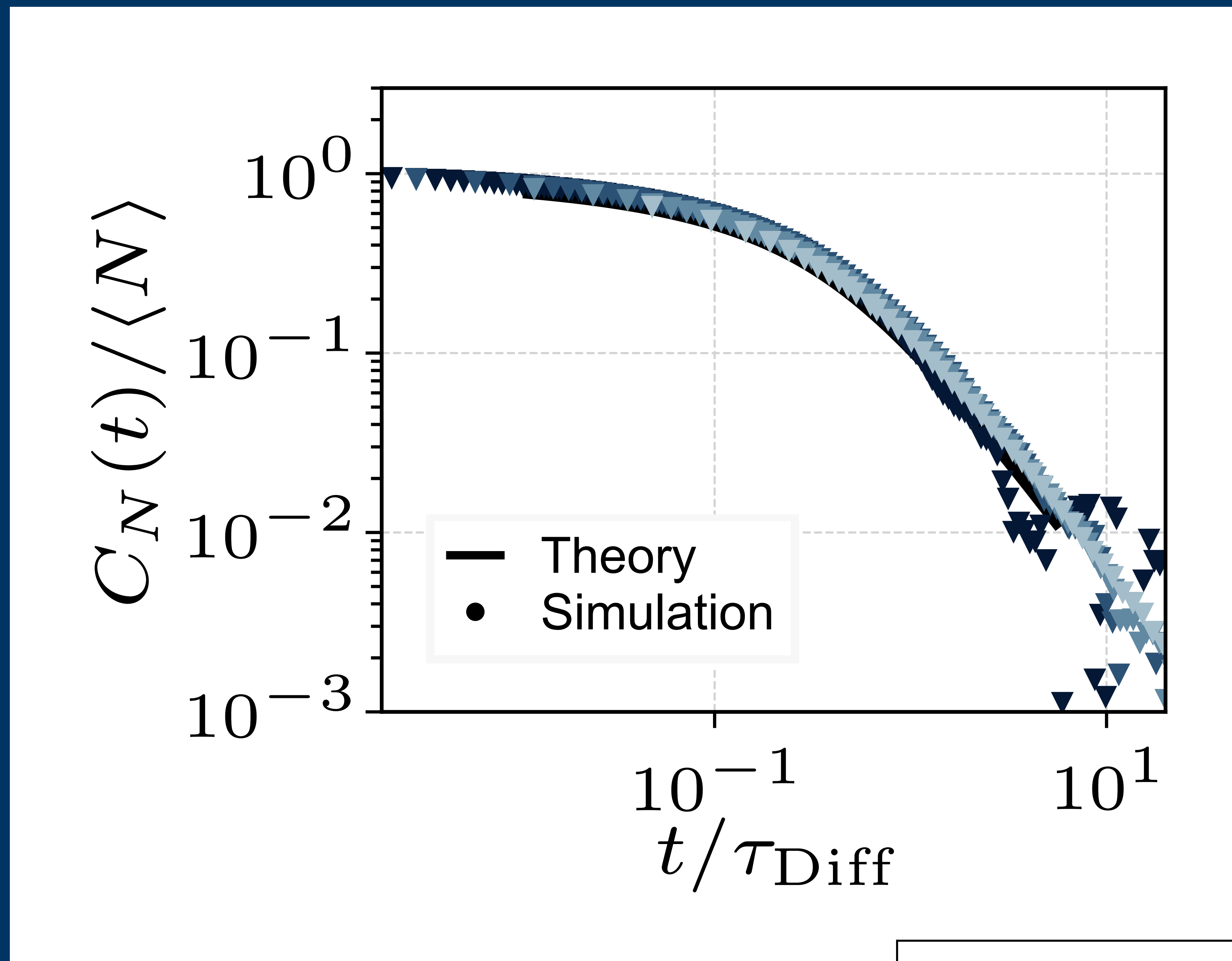




Particle Number

$$C_N(t) = \langle N(t)N(0)\rangle - \langle N\rangle^2$$



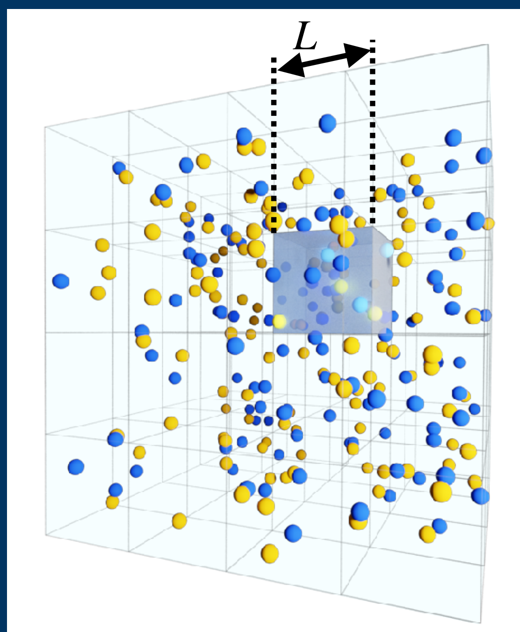


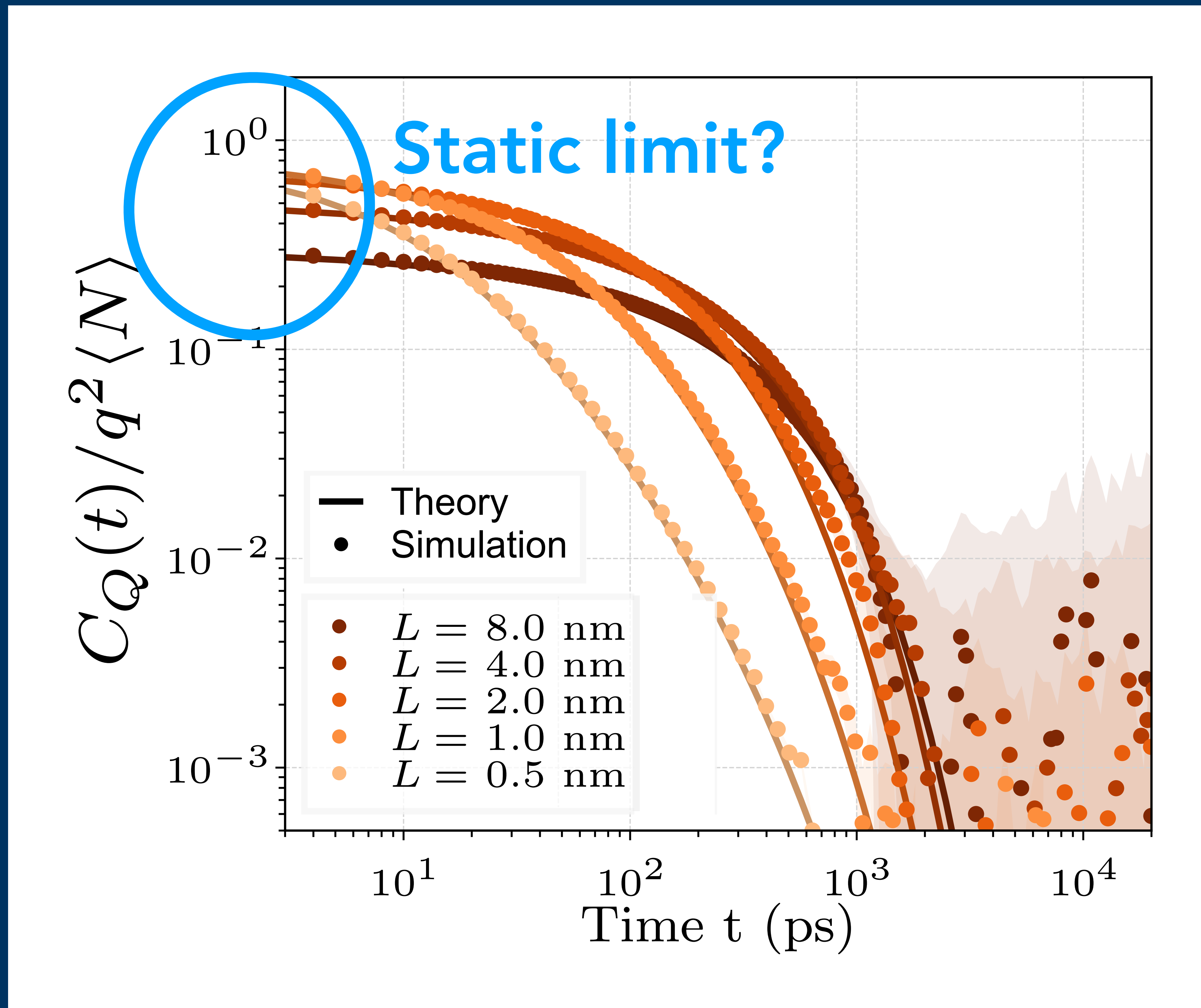
same dynamics as for colloids

$$\tau_{\mathrm{Diff}} = L^2/D$$

Charges

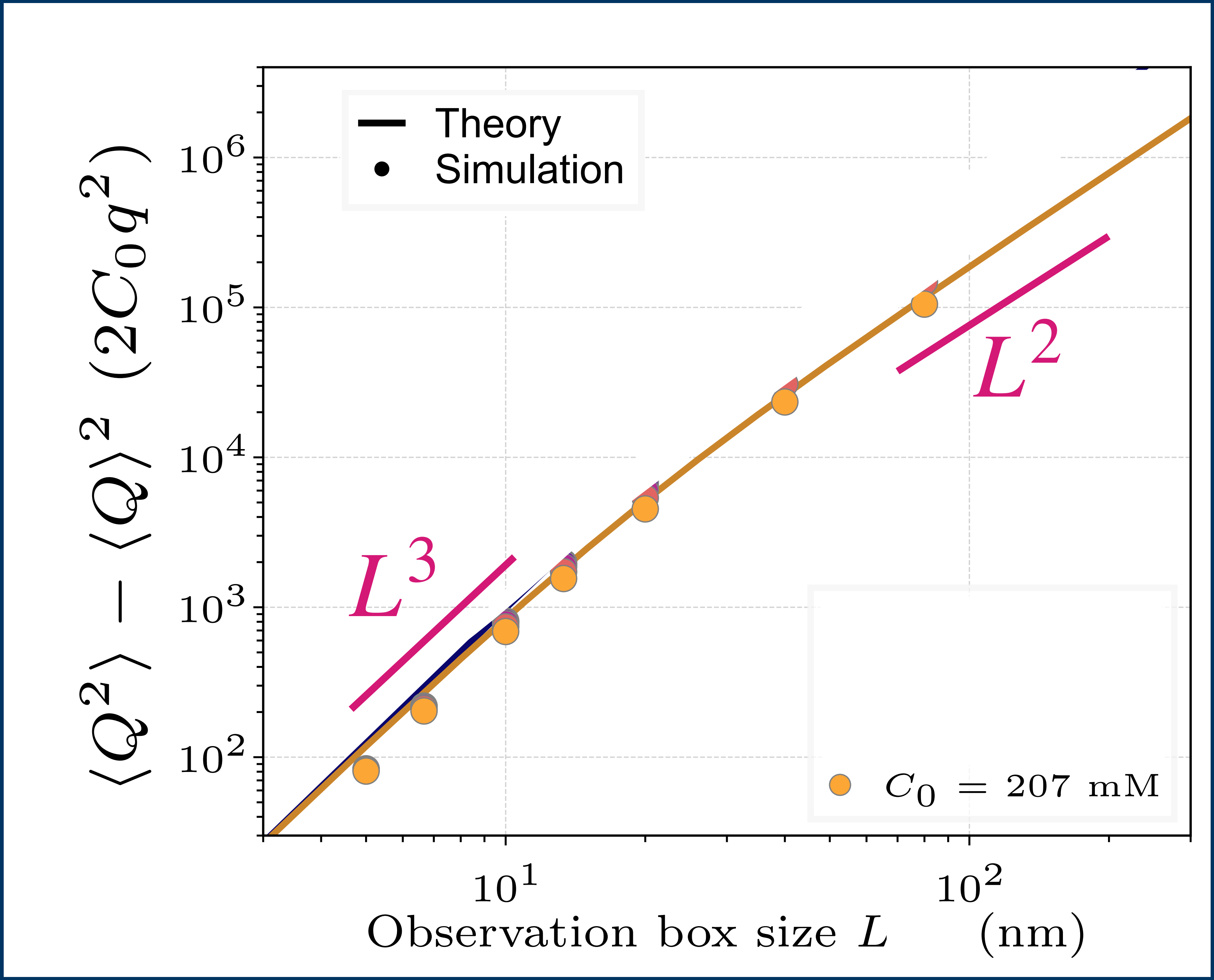
$$C_Q(t) = \langle Q(t)Q(0)\rangle - \langle Q\rangle^2$$



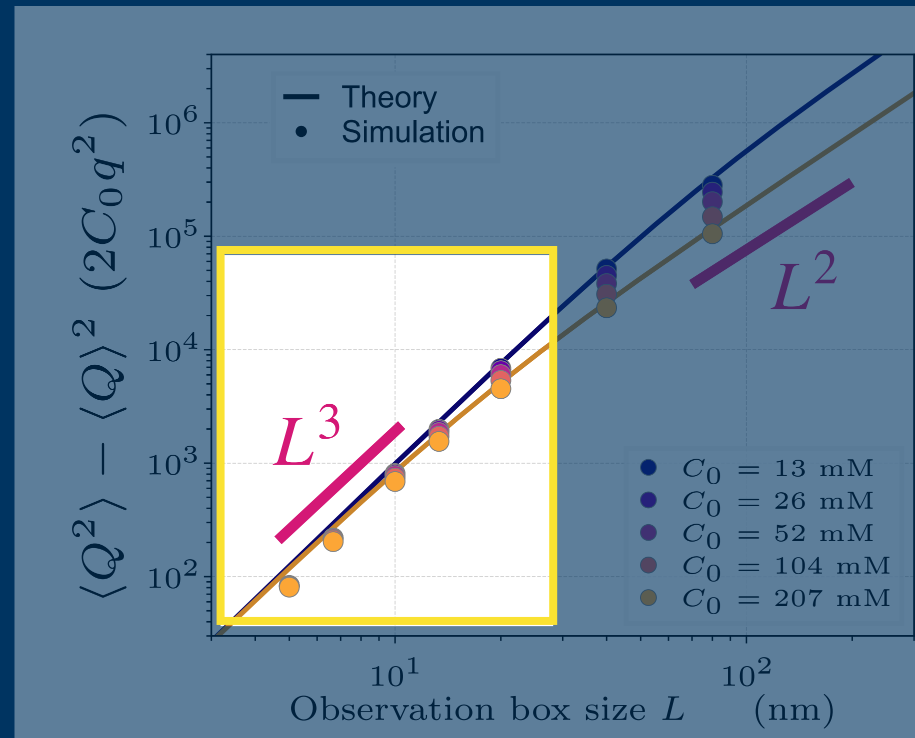


no simple rescaling for charges...

Static charge fluctuations



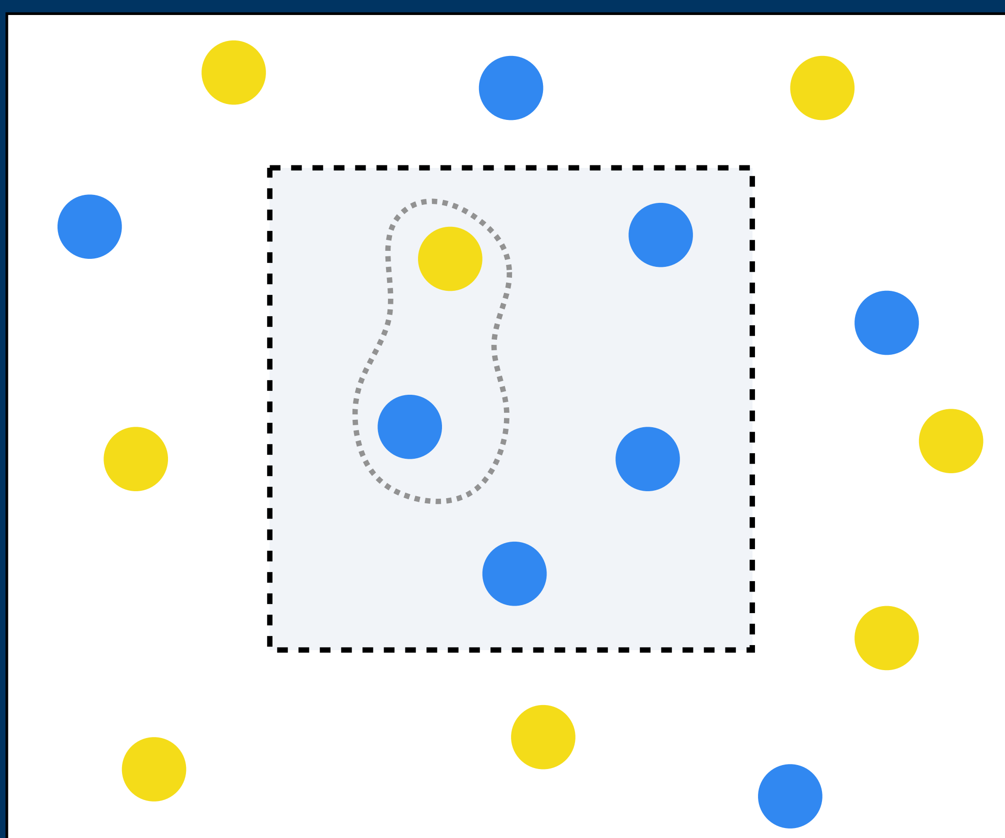
Martin & Yalcin, Beijeren & Felderhof, Lebowitz, Luijten, Fisher, …

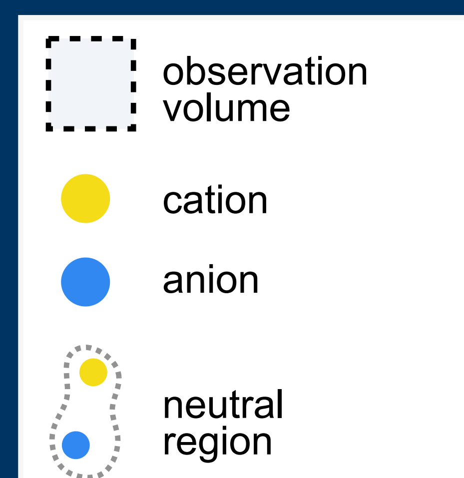


Debye Screening length

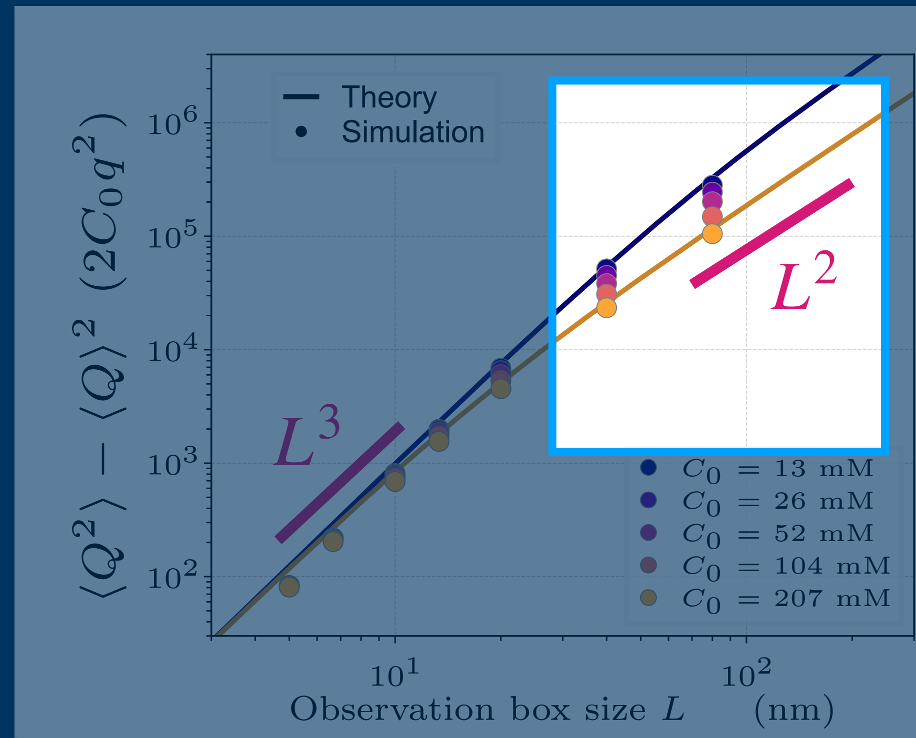
$$\lambda_D = \sqrt{\frac{k_B T \epsilon_0 \epsilon_r}{2q^2 C_0}}$$

$$L \ll \lambda_D$$





$$\langle Q^2 \rangle \sim \langle N \rangle \sim L^3$$

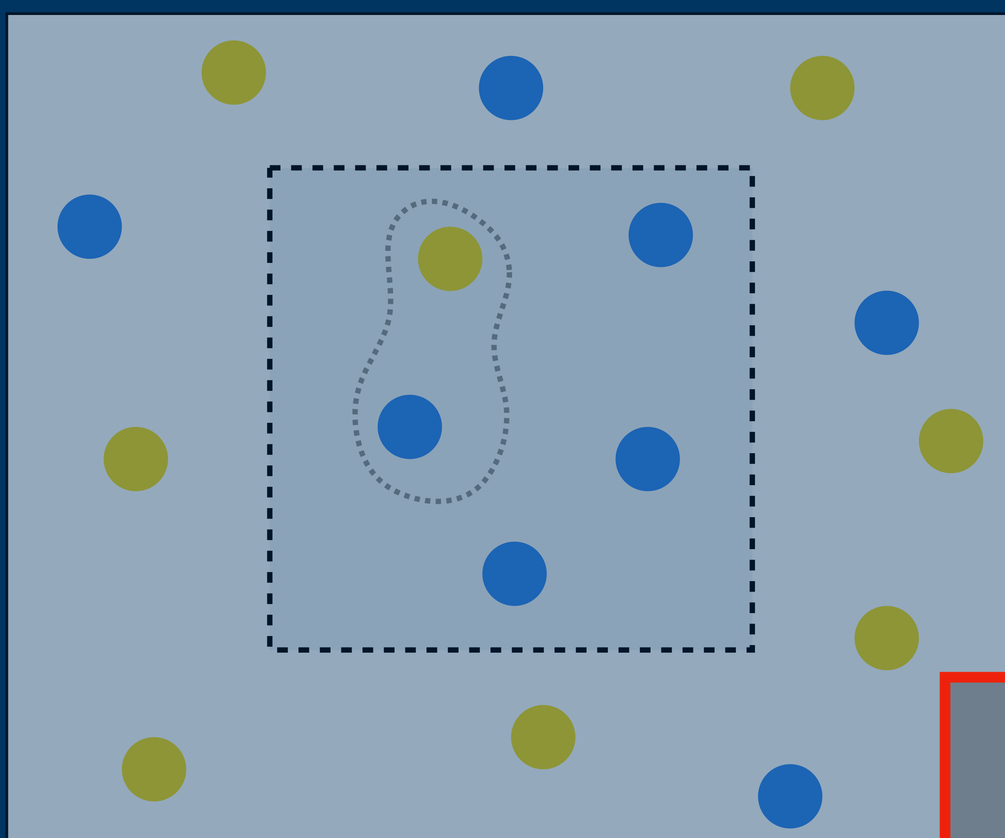


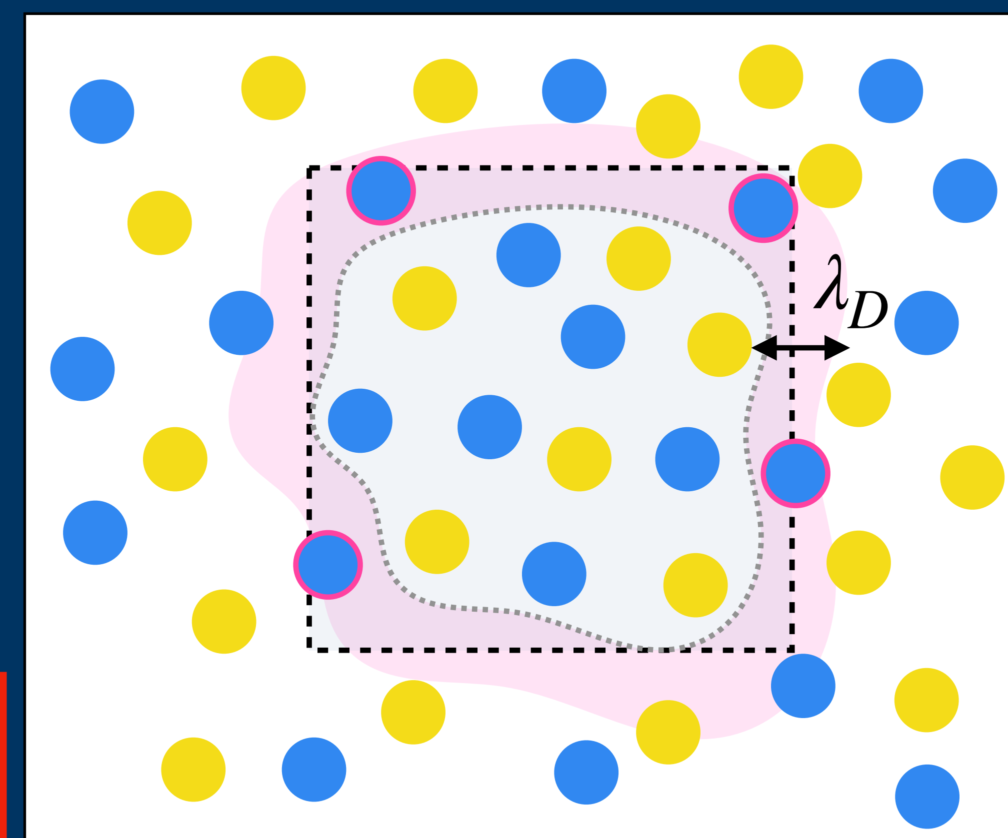
Debye Screening length

$$\lambda_D = \sqrt{\frac{k_B T \epsilon_0 \epsilon_r}{2 q^2 C_0}}$$

$L \ll \lambda_D$

$L \gg \lambda_D$



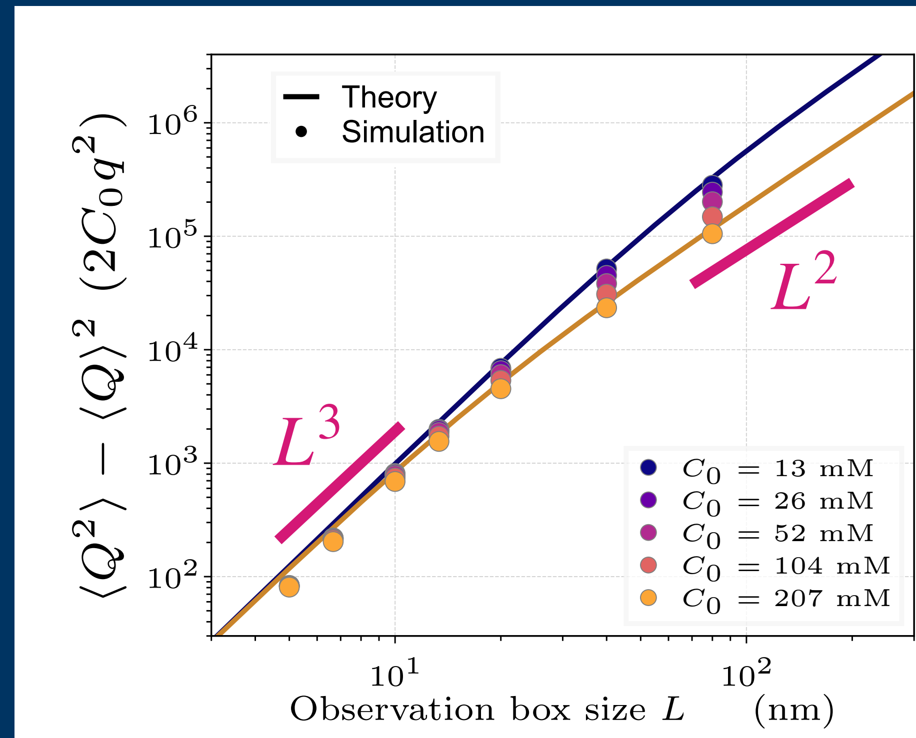


$\langle Q^2 \rangle \sim \langle N \rangle \sim L^3$

hyper-uniformity

Lebowitz/Torquato

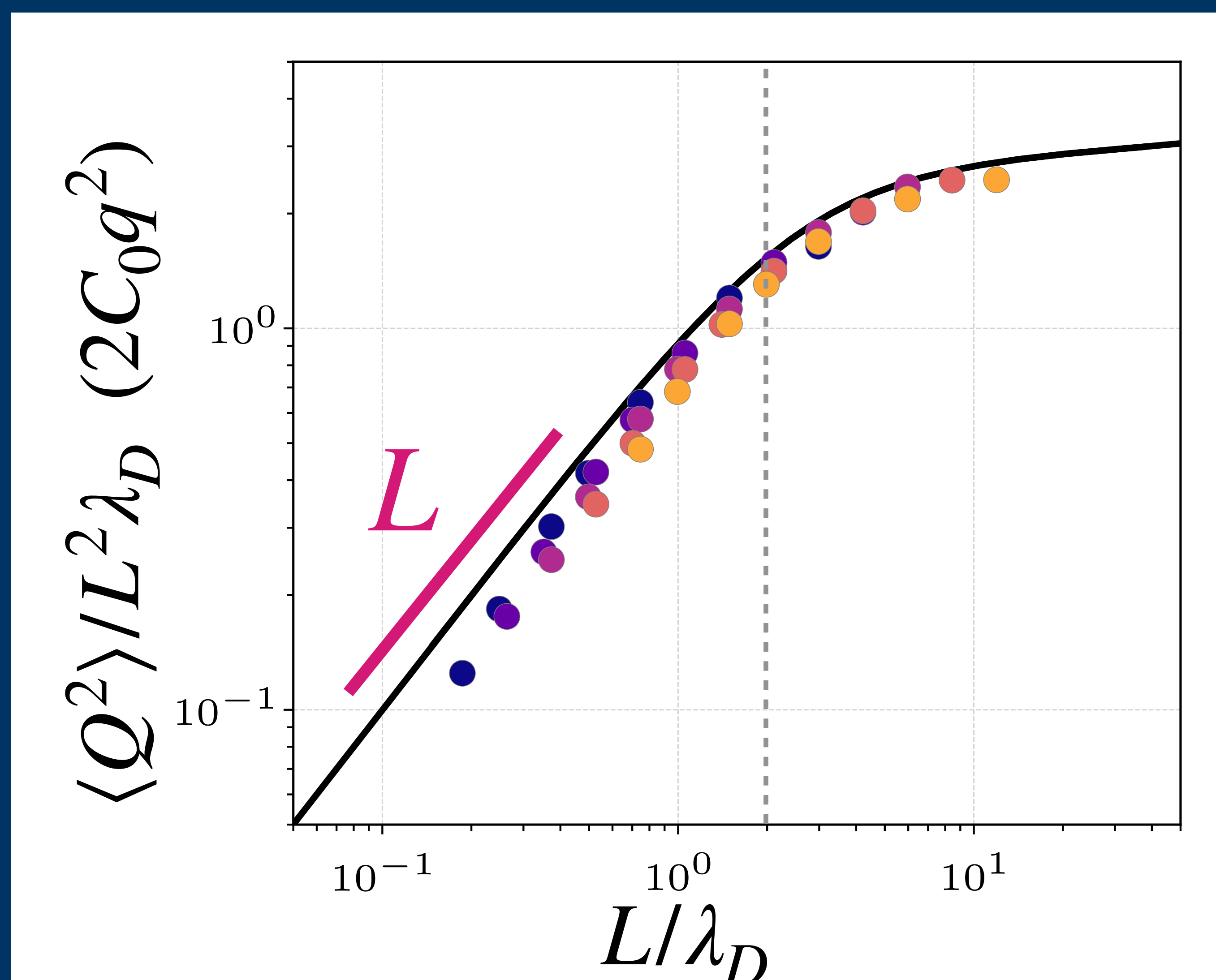
$\langle Q^2 \rangle \sim L^2 \lambda_D$



Debye Screening length

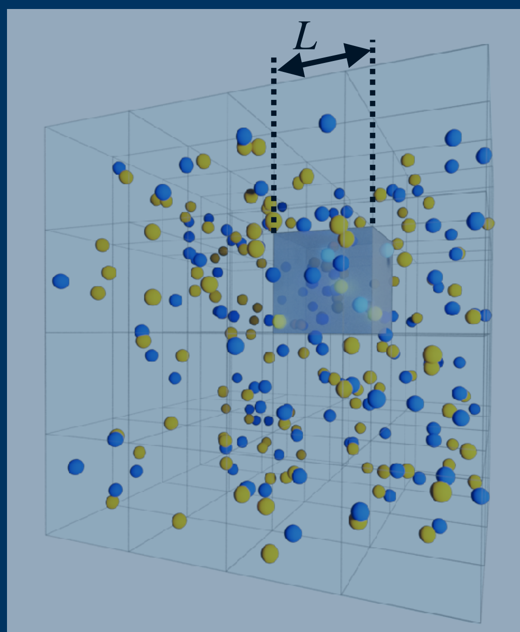
$$\lambda_D = \sqrt{\frac{k_B T \epsilon_0 \epsilon_r}{2q^2 C_0}}$$

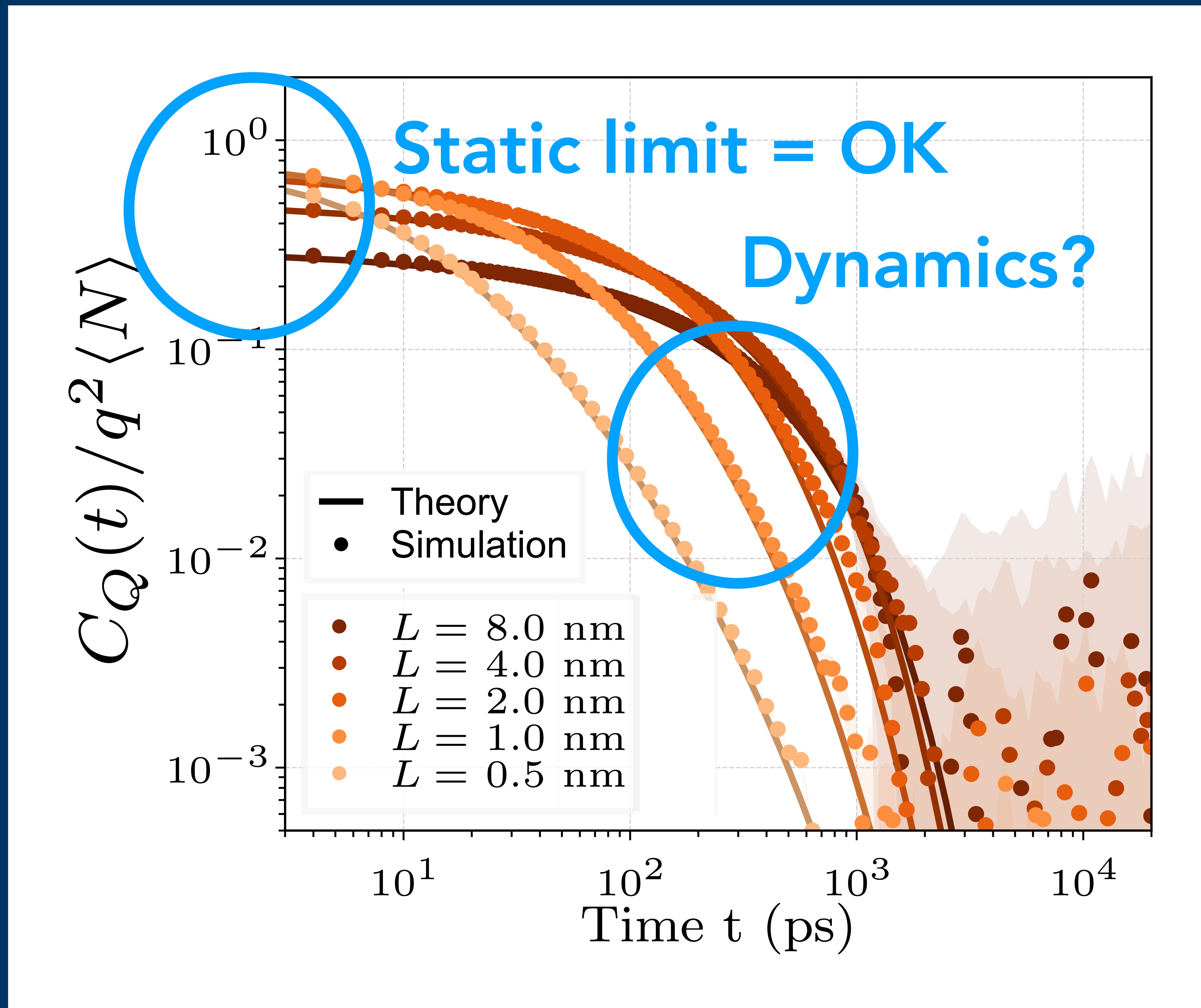
rescaling



Charges

$$C_Q(t) = \langle Q(t)Q(0)\rangle - \langle Q\rangle^2$$

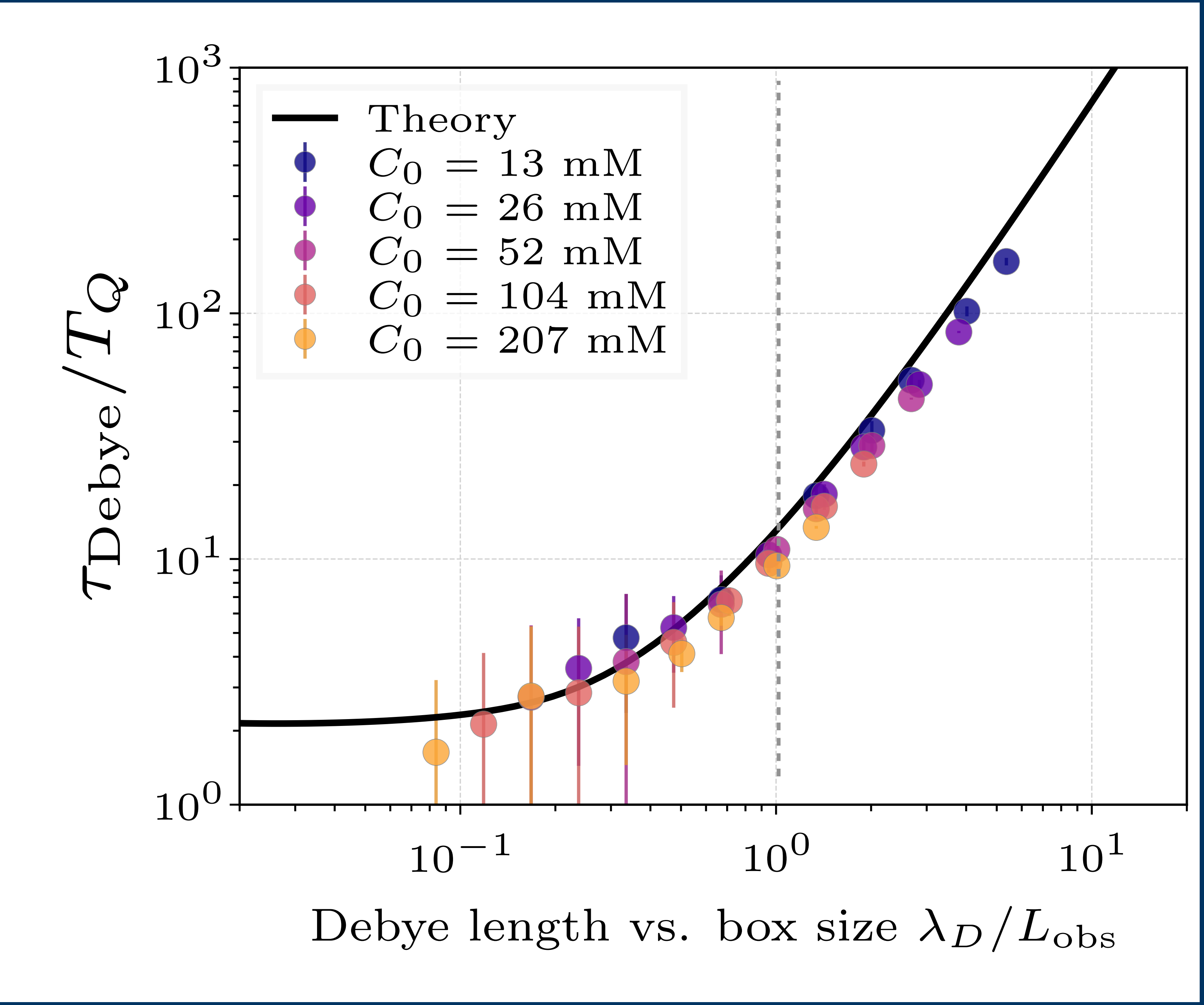


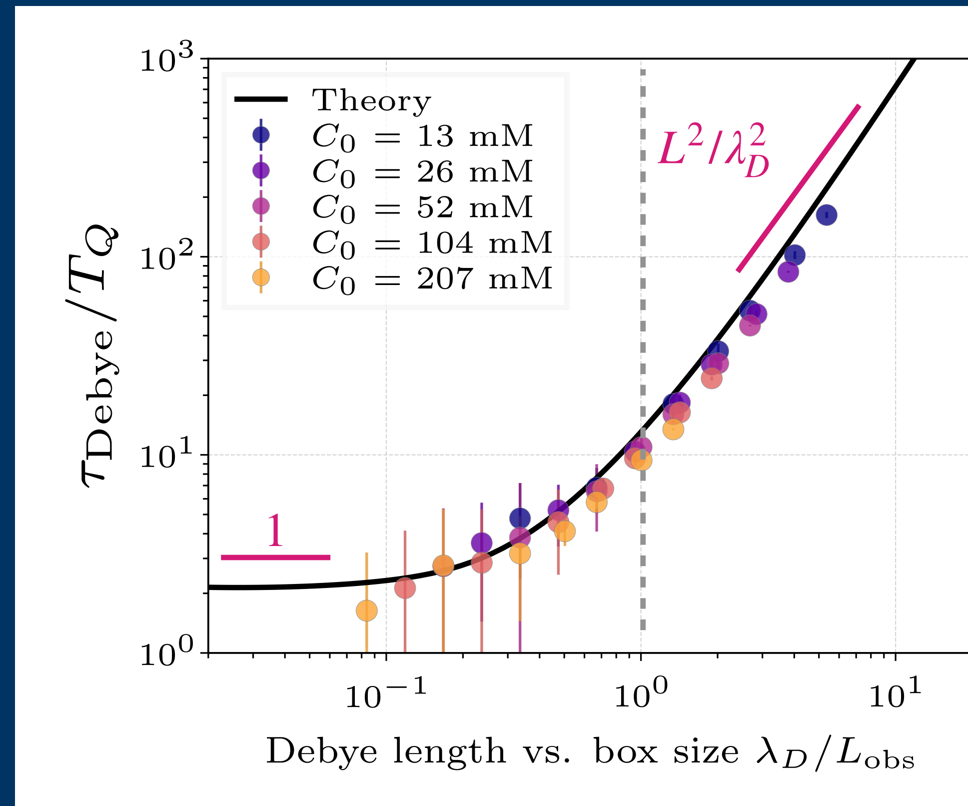


no simple rescaling for ions…

Relaxation dynamics?

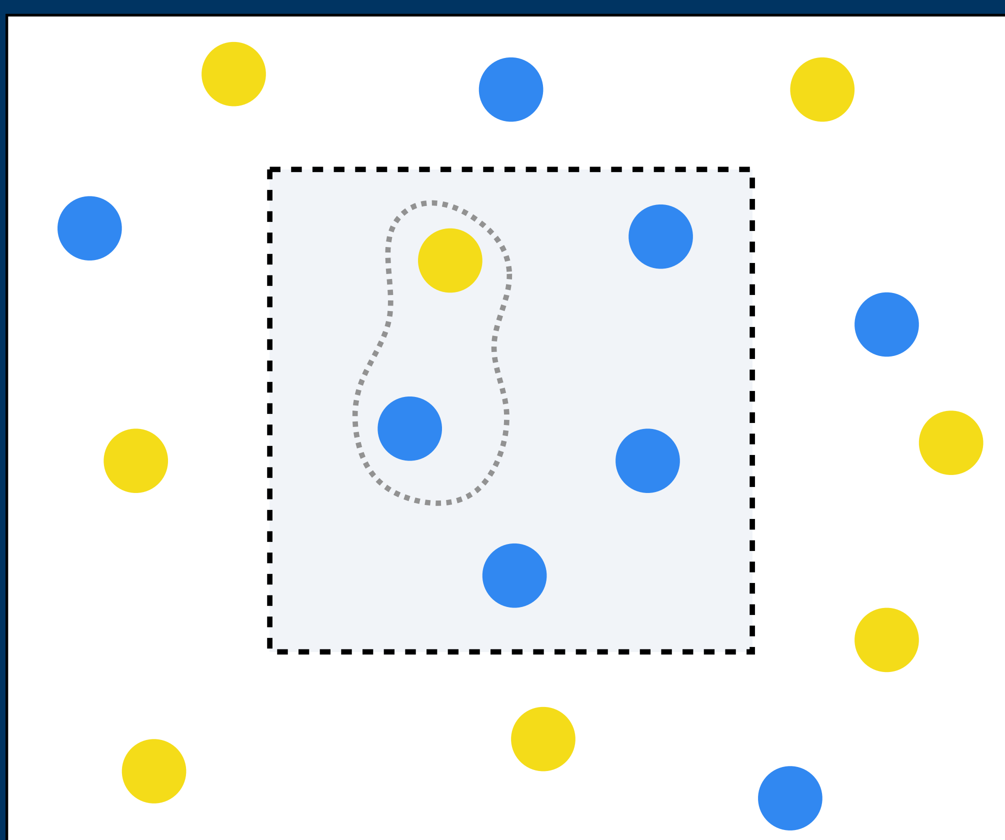
$$T_Q = \int_0^\infty \left(C_Q(t)/C_Q(0) \right) \,\mathrm{d}t$$

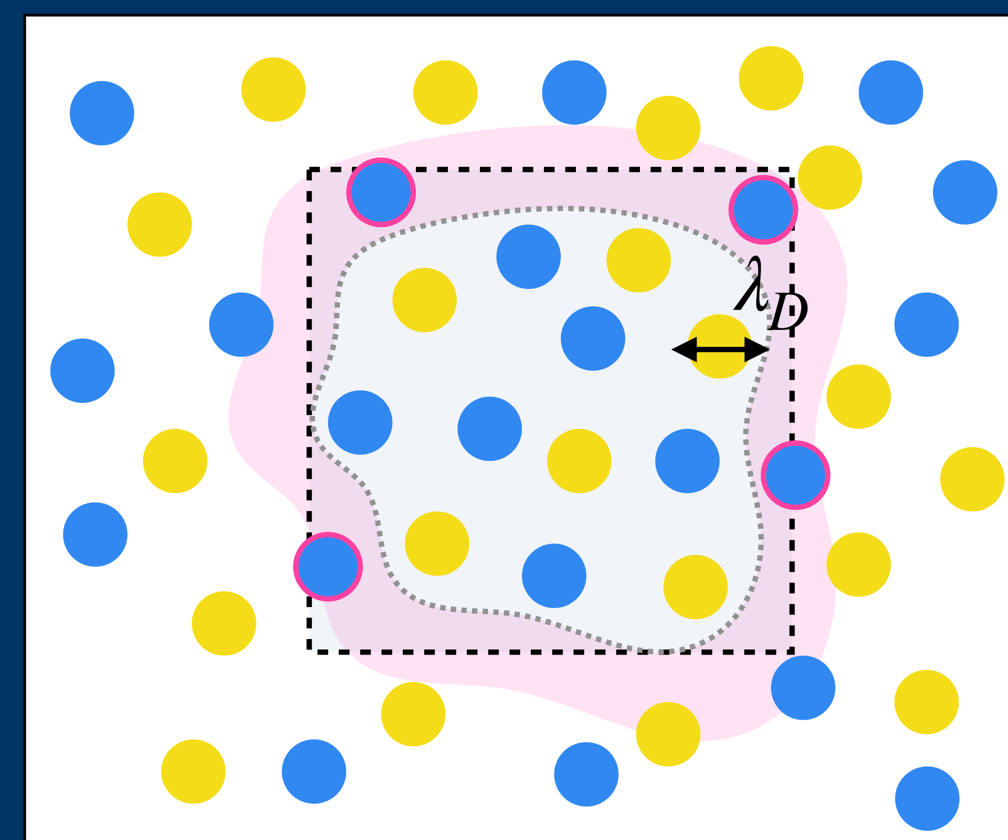




$L \ll \lambda_D$

$L \gg \lambda_D$



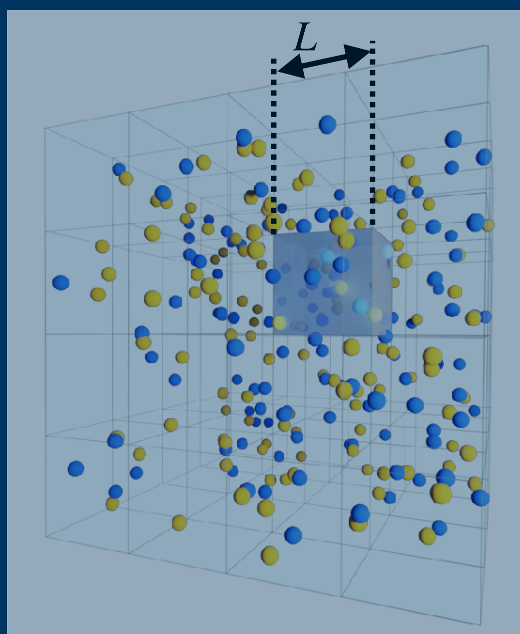


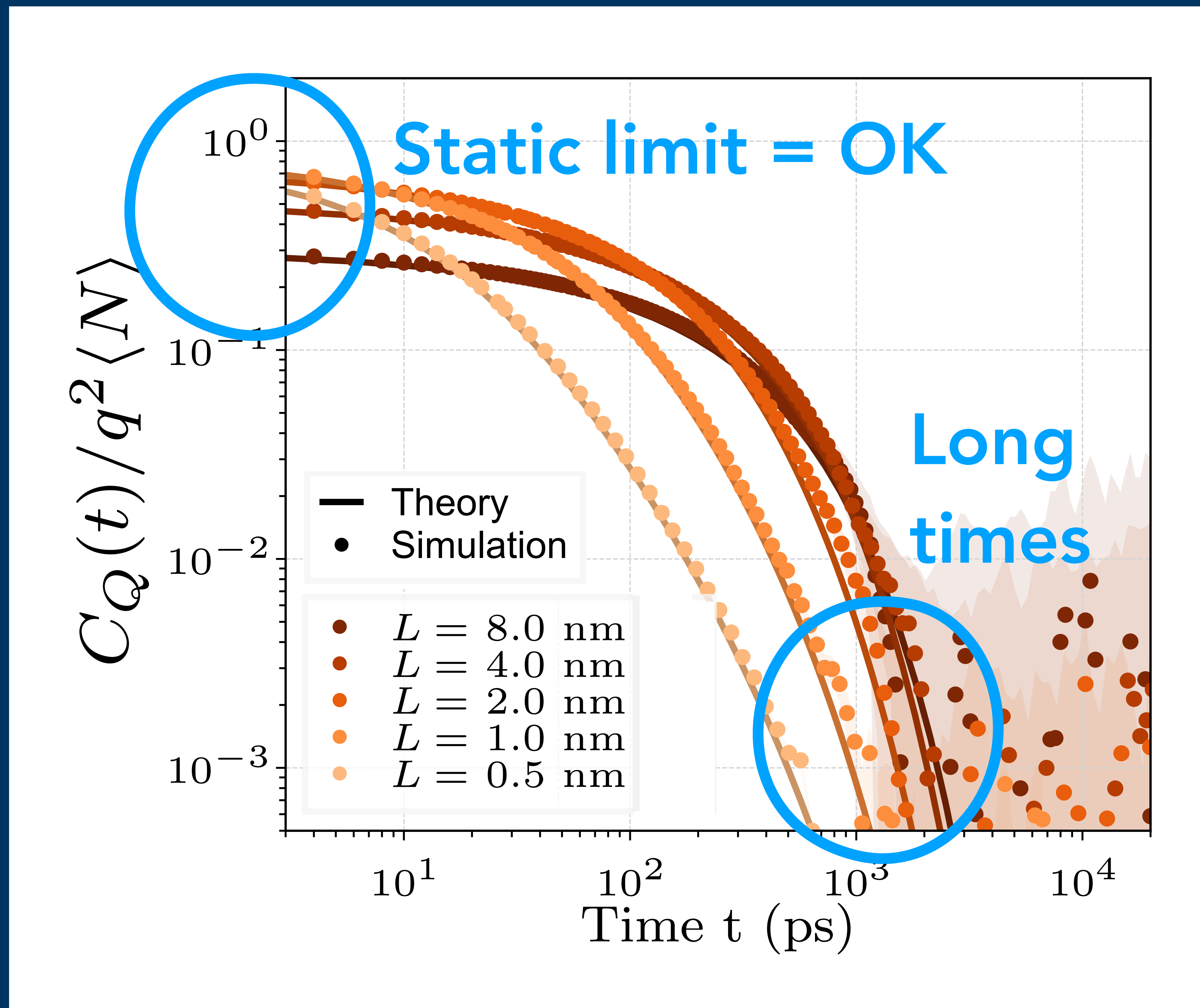
$$T_Q = \tau_{\mathrm{Diff}} = L^2/D$$

$$T_Q = \tau_{\mathrm{Debye}} = \lambda_D^2/D$$

Charges

$$C_Q(t) = \langle Q(t)Q(0)\rangle - \langle Q\rangle^2$$





no simple rescaling for ions...

Long times

$$C_Q(t) = \langle Q(t)Q(0)\rangle - \langle Q\rangle^2$$

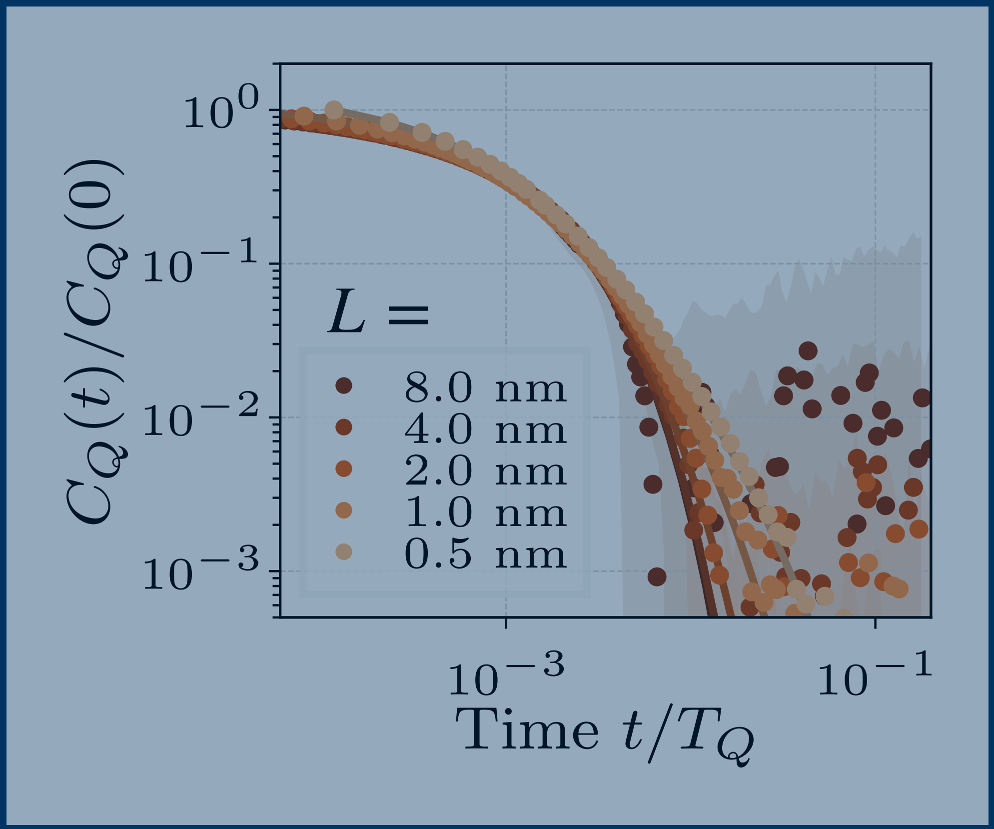
$$t \gg \tau_{\text{Diff}}, \tau_{\text{Debye}}$$

$$\tau_{\text{Diff}} = L^2/D$$
$$\tau_{\text{Debye}} = \lambda_D^2/D$$

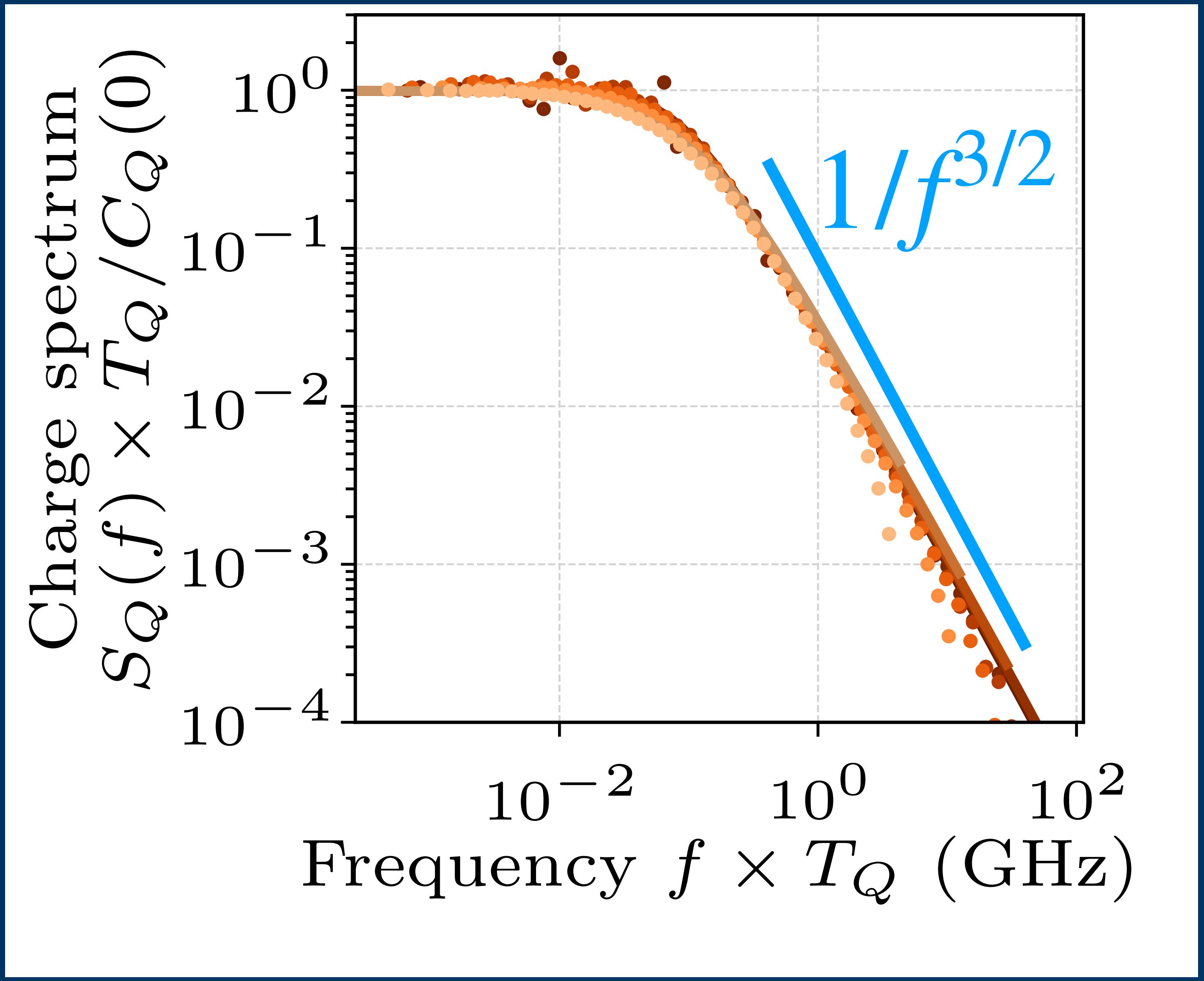
$$C_Q(t) \simeq L\lambda_D^2 \left(\frac{\tau_{\text{Diff}}}{t}\right)^{5/2} e^{-\frac{t}{\tau_{\text{Debye}}}}$$

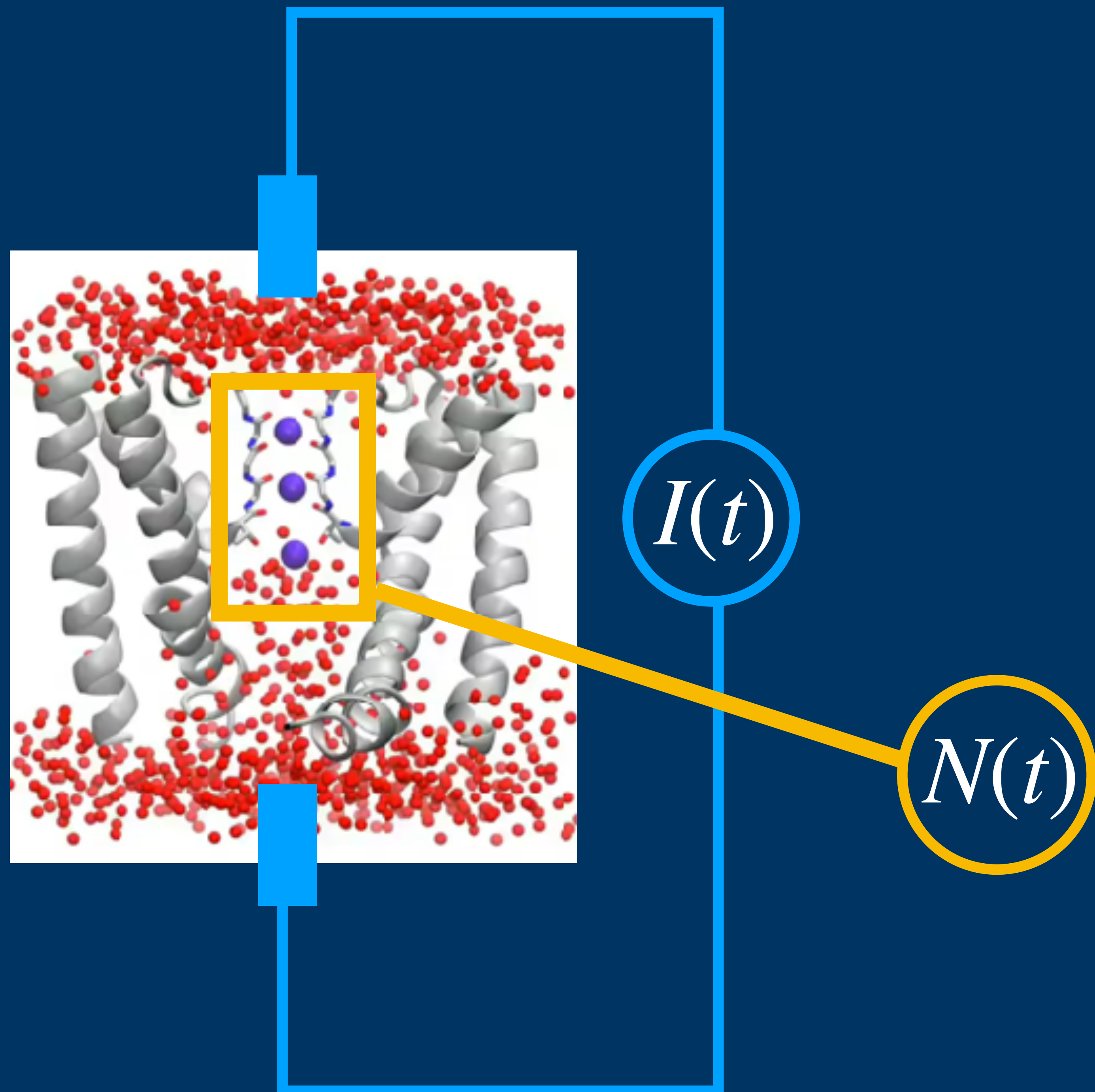
hyperuniformity “increases”

Fractional noise…



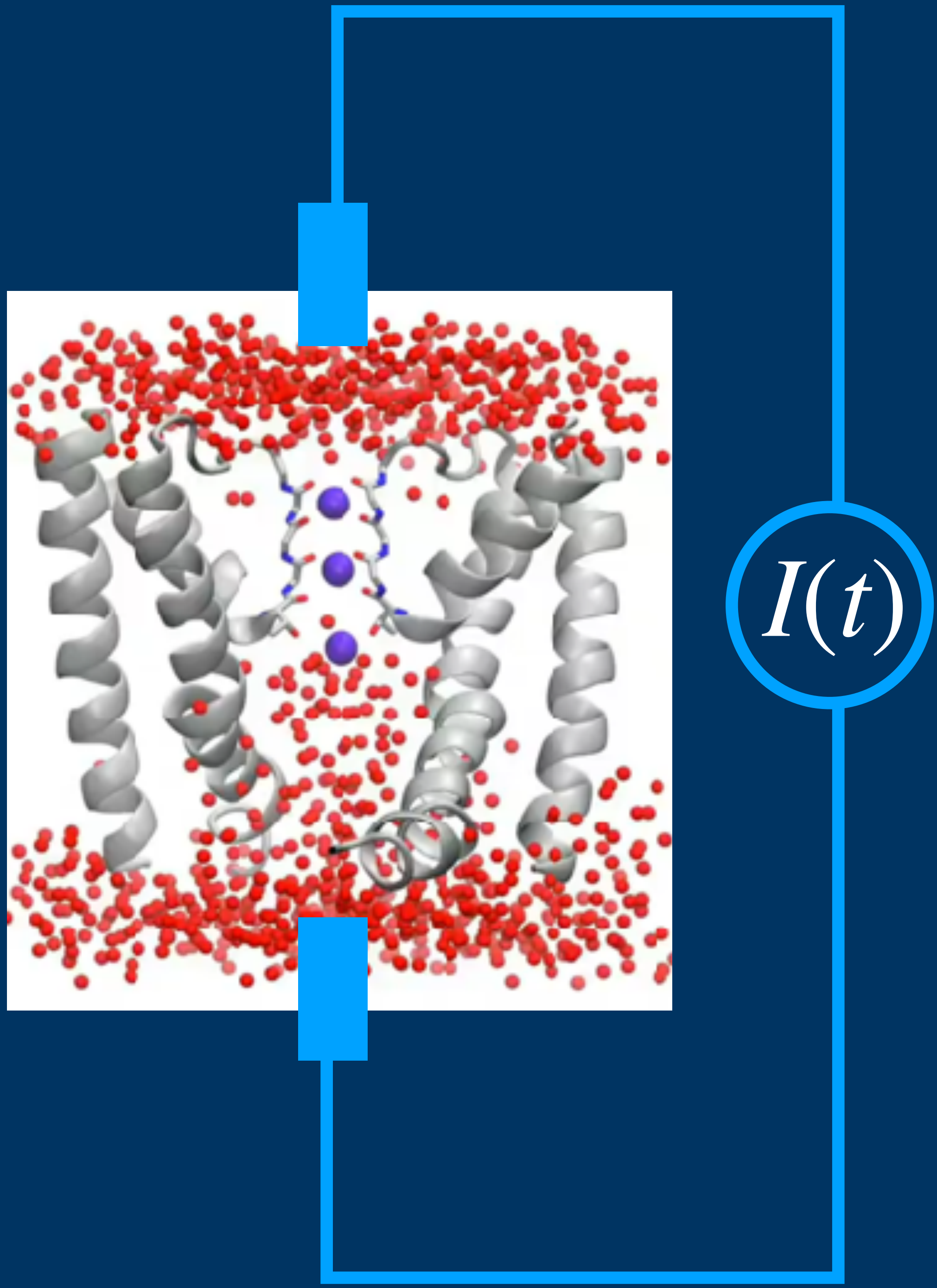
$$Q(t) \rightarrow \quad S_Q(f) = \frac{1}{T} \left| \int_0^T Q(t)\, e^{-i2\pi f t}\, dt \right|^2$$



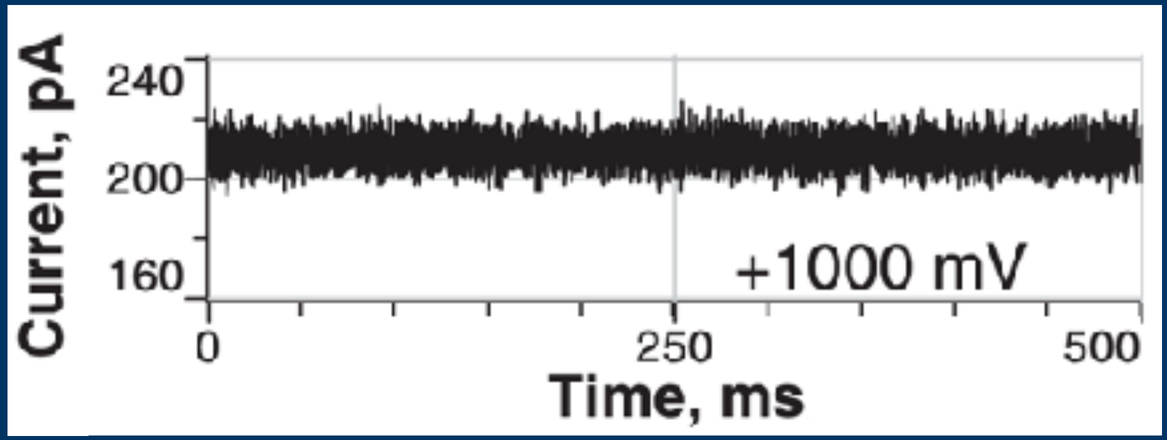


$$I(t) \propto \frac{\mathrm{d}N(t)}{\mathrm{d}t}$$

counting particles
can inform us on function!



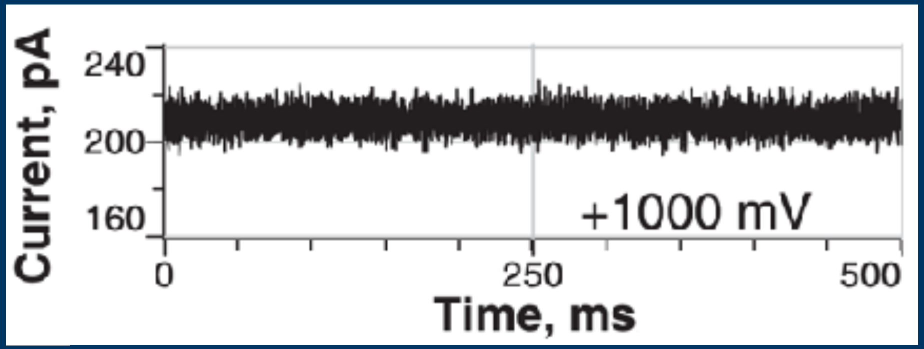
I(t)

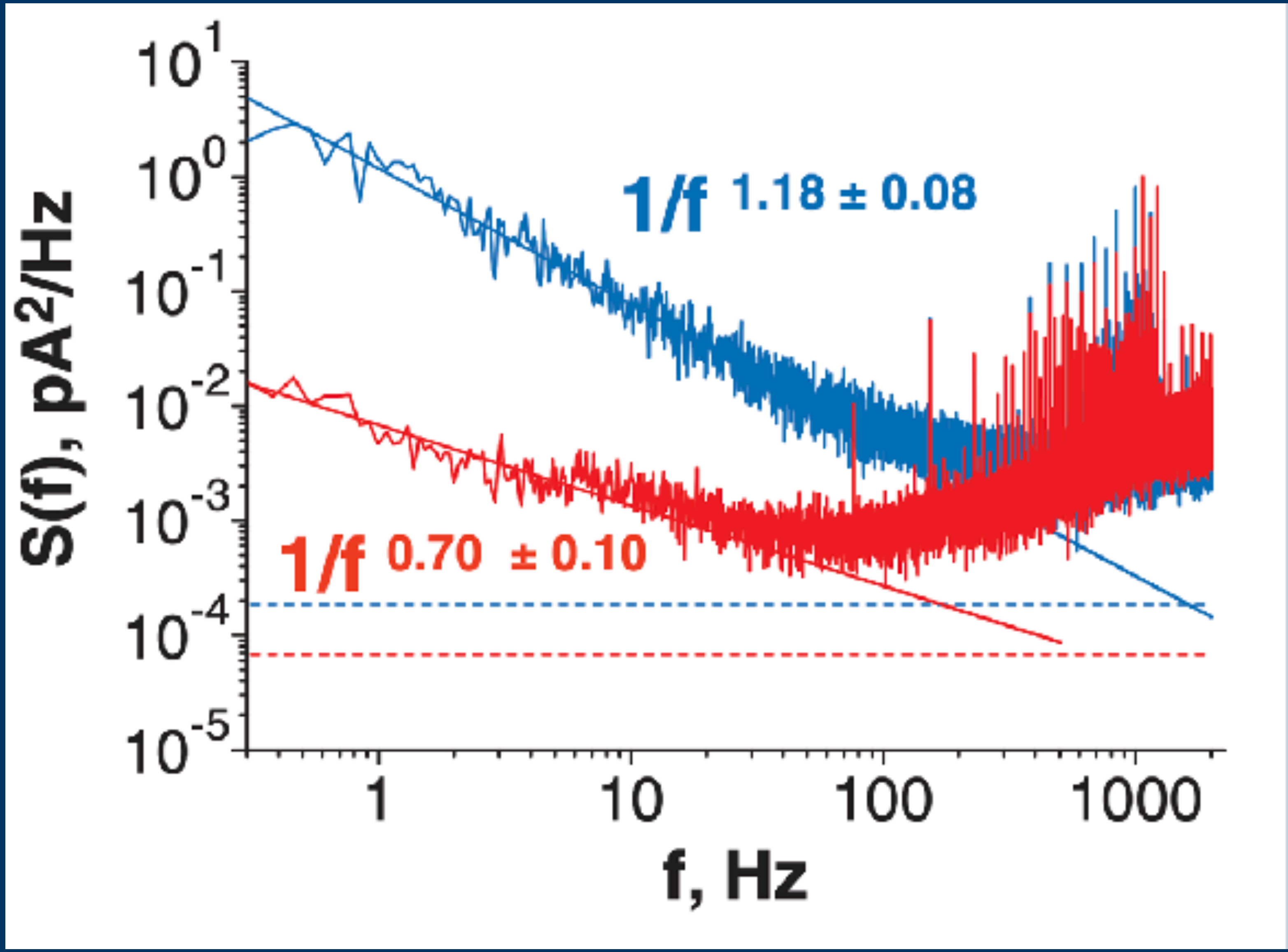


Current, pA
240
200
160
+1000 mV
0
250
500
Time, ms

Noise signatures

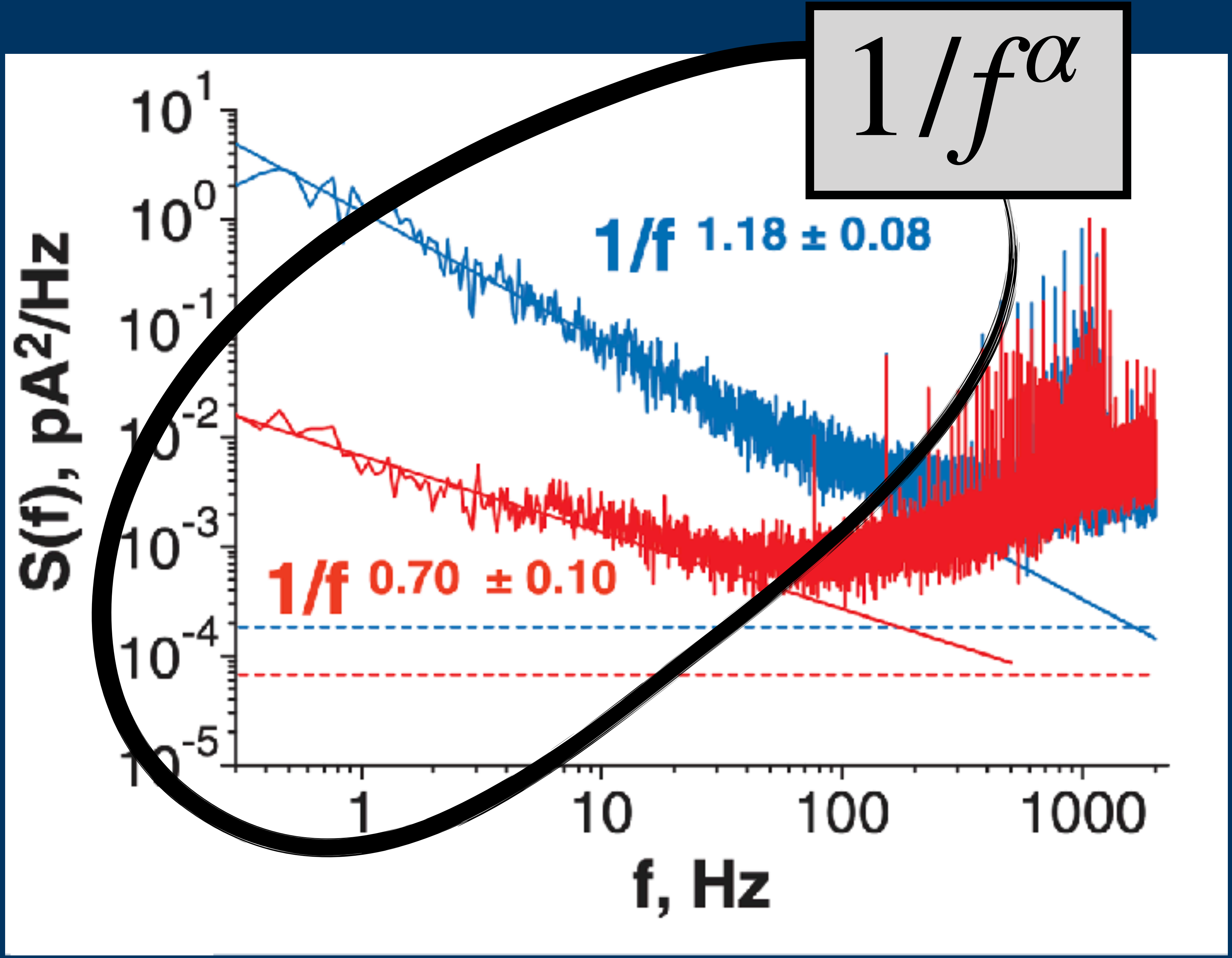
$$I(t) \longrightarrow S(f) = \frac{1}{T}\left| \int_0^T I(t)\, e^{-i2\pi f t}\, dt \right|^2$$





Powell et al. PRL (2009)

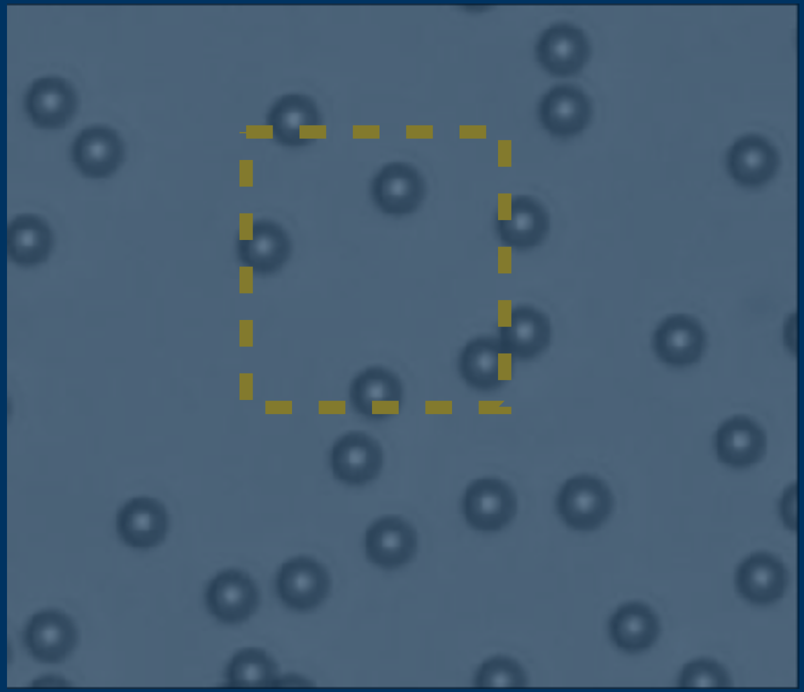
Low frequency noise

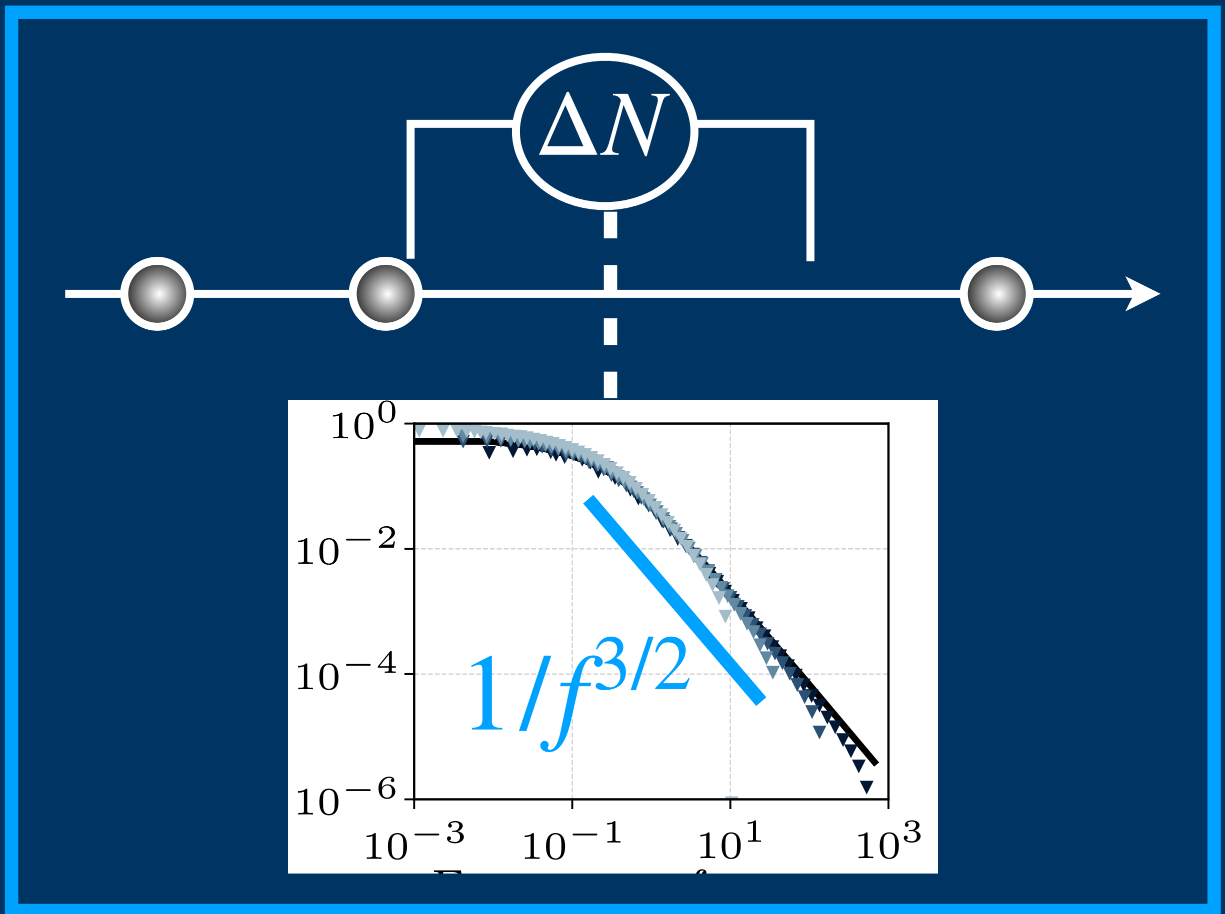


Powell et al.
PRL (2009)

There are **dynamic clues** in finite volumes!

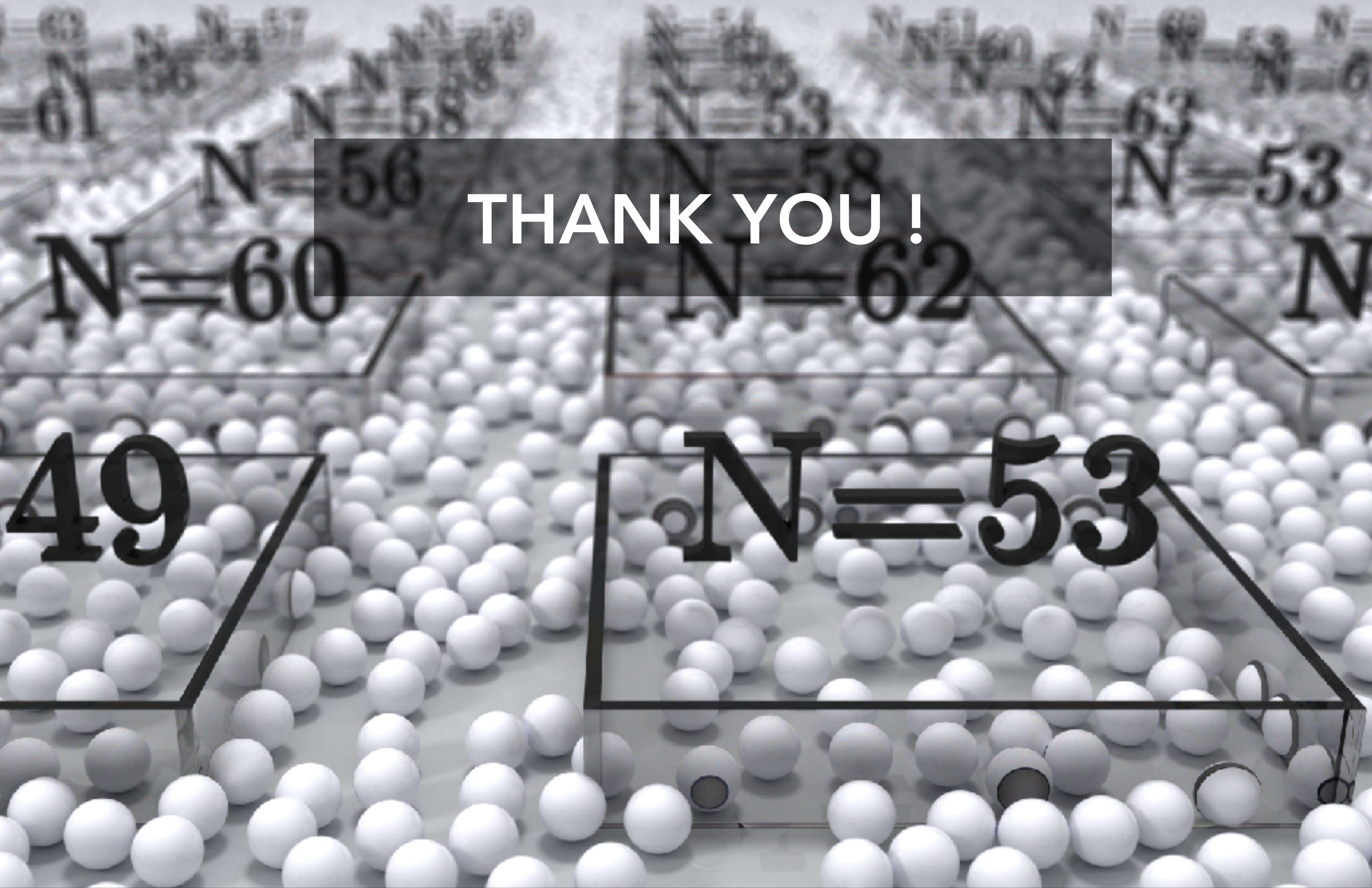
diffusion coefficient,
relaxation timescale,
interactions….





Fractional noise is intrinsic in Brownian motion

- *boundary crossings*
- *traces in the noise spectrum*



THANK YOU !

@MarbachSophie

http://sophie.marbach.fr

SM, *J. Chem. Phys.* 2021
Thorneywork, Sprinkle, SM, *in progress…*
MT Hoang Ngoc, Rotenberg, SM, *ArXiv* 2023