Solute Dispersion in Porous Media

Beyond Percolation Scaling

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What is dispersion?

- Migration apart of particles under influence of fluid flow and molecular diffusion

Where is it relevant?

“underpins processes as diverse as cellular mitosis, blood perfusion in the brain, chromatography, filtration, secondary oil recovery, ground water remediation, catalysis, and the behavior of packed bed reactors.” degradation of building materials tissue physiology, migration and epidemiology.

Most common approach

- The advection-dispersion equation (ADE)
- It models solute transport on a continuum as due to diffusion like processes (D_h) and being carried along by the flow (advection) *v*.

$$\frac{\partial C}{\partial t} = D_h \nabla^2 C - \mathrm{v} \cdot \nabla C$$

Are there problems with the ADE?

- $D_h >> D_m$ has nothing to do with molecular diffusion, D_m.
- D_h depends in a non-trivial way on velocity.
- D_h increases with time (or transport distance) in a way that cannot be predicted from the ADE.
- The distribution tails are seldom, if ever, Gaussian, which underestimates solute arrivals at both short and long times.
- All these features drop out of a proper accounting for effects of heterogeneity and connectivity on solute paths through the medium; first term is extraneous.
- The chief lacks of the ADE are admitted to be its treatment of heterogeneity and connectivity.

Anything good about ADE?

- Works at scale of single pore, where it is used to evaluate relative effects of diffusion and advection (Peclet number).

Why percolation theory?

- **Previous approaches (e.g., the ADE) have failed to predict the observed behavior**
- **Percolation theory (PT) is a mathematics of pathways and connections in disordered materials**
- **Can treat heterogeneity with a wide range of flow resistance (critical path analysis, CPA), even far from percolation threshold**
- **It accounts for tortuosity of flow paths**
- **It can incorporate geological correlations**

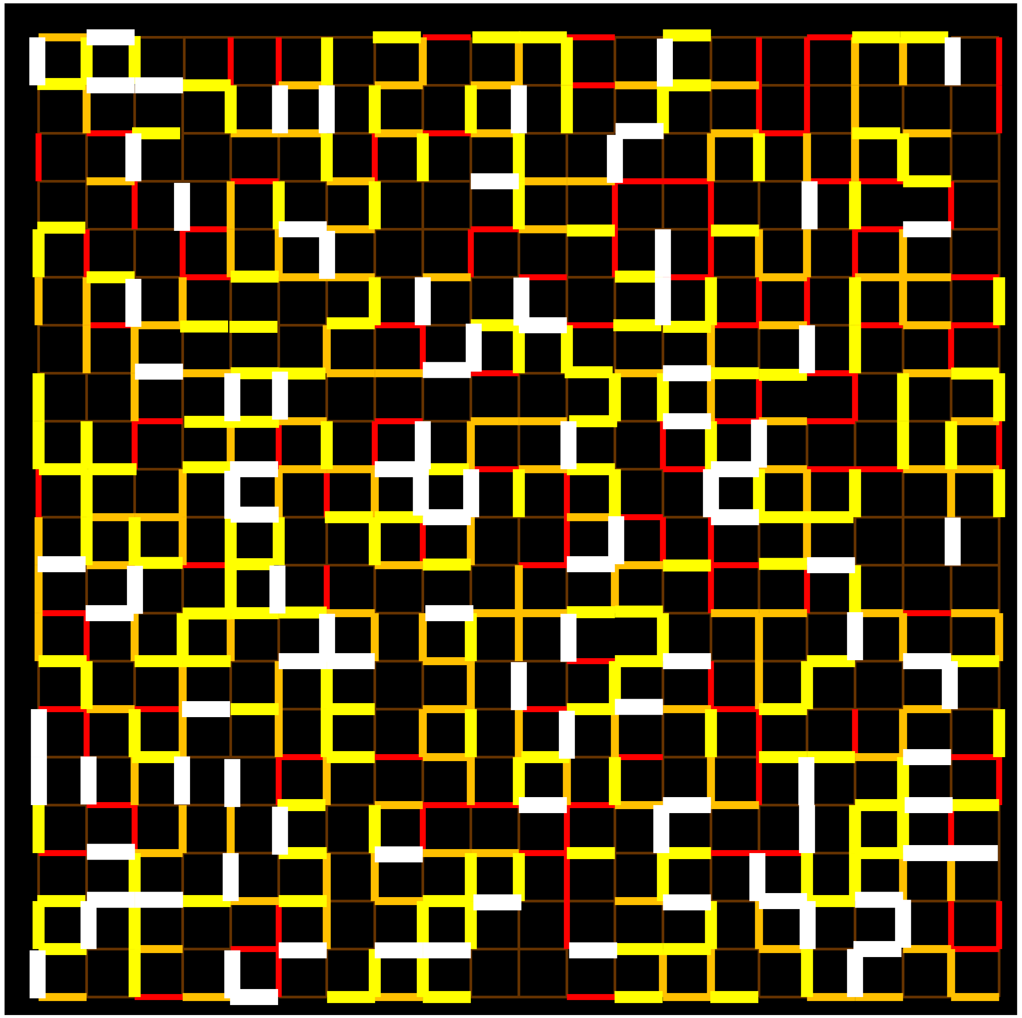
Organization

- Introduce concept of critical path analysis (CPA) to find the critical conductance $\boldsymbol{g_c}$ of a system.

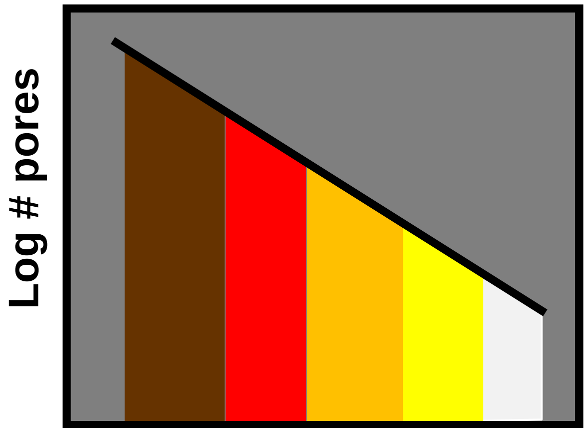
1. Apply CPA framework to cluster statistics of percolation theory to find spanning probability, $W(g\,;x)$ that system of length x can be spanned by interconnected cluster of conductances of arbitrary smallest value, g.
2. Apply critical scaling of percolation theory to find how the solute transit time, t, depends on the length of the system and the governing value, g.
3. Arrival time distribution $W(t;x) = g\,W(g\,;x) \,/\, (\,dt(g)/dg\,)$

- Analogous procedure gives spatial distribution.
- Calculate moments by standard procedures.

First, some percolation theory concepts



On left a model porous medium.



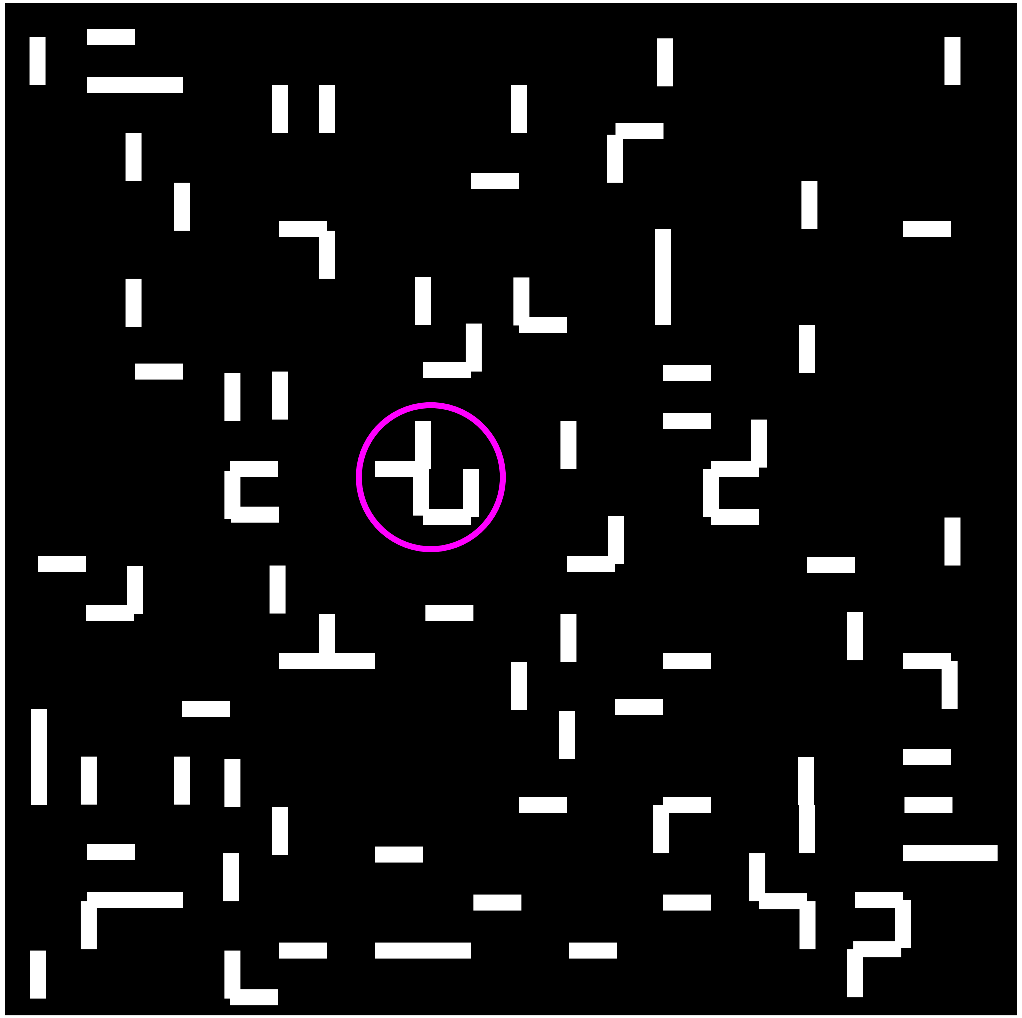
In fractal medium we have “pore size distribution”

$$W(r) = \frac{3-D}{r_m^{3-D}} r^{2-D}$$

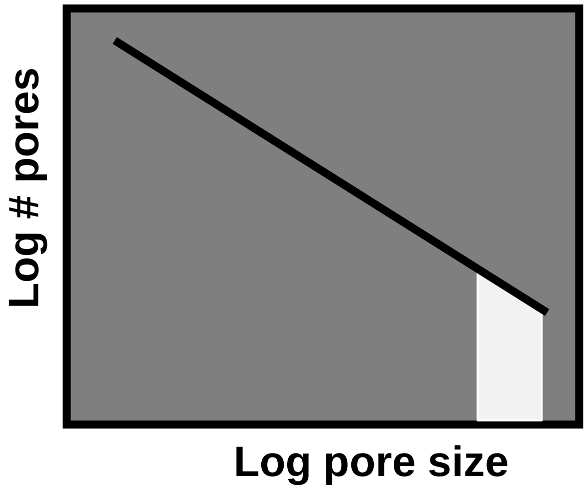
r_m: largest pore radius

D: fractal dimension

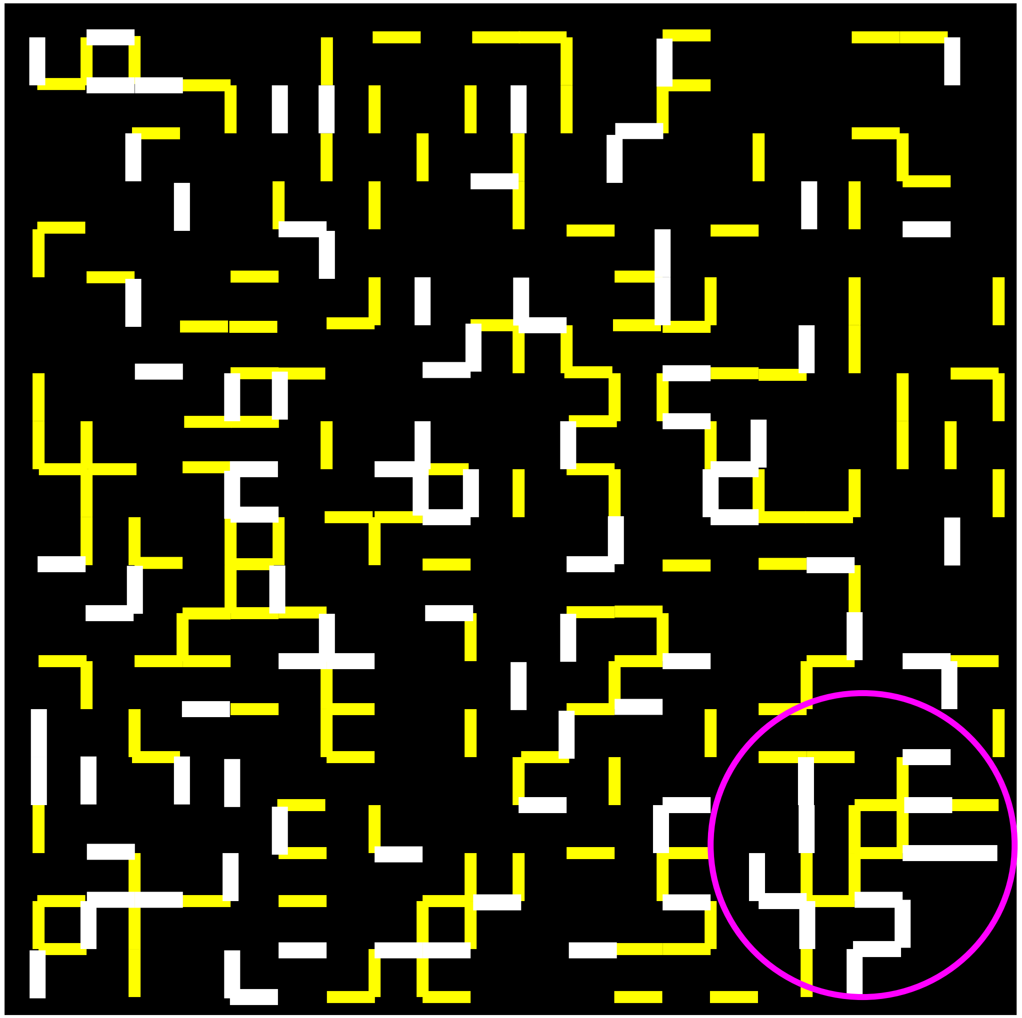
The biggest pores don’t connect



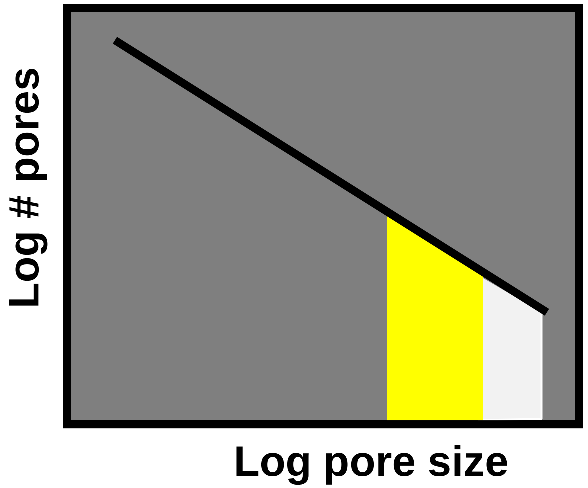
Cluster with largest “volume”



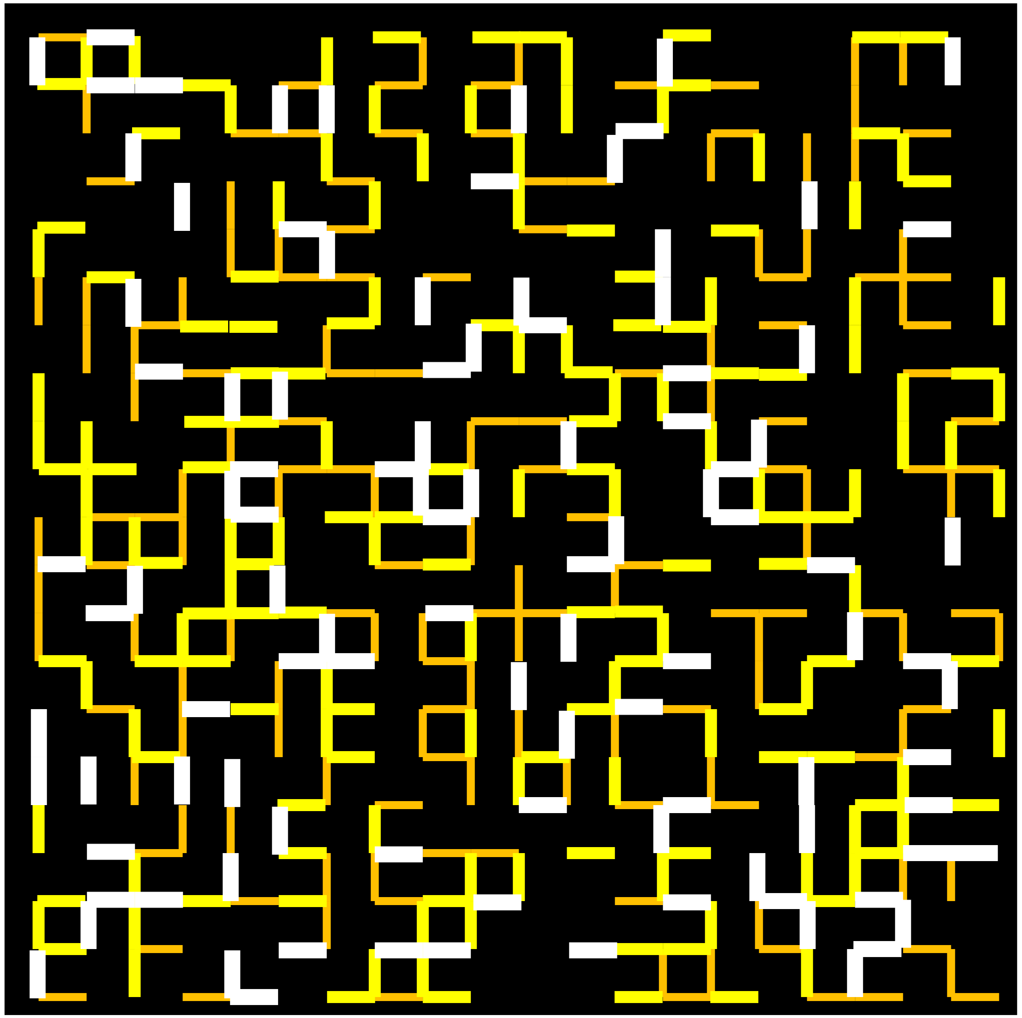
The next-biggest still don't connect



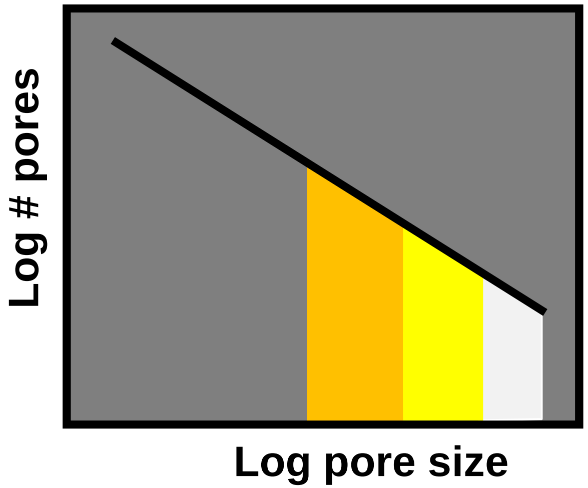
Cluster with largest "volume"



Something important happened

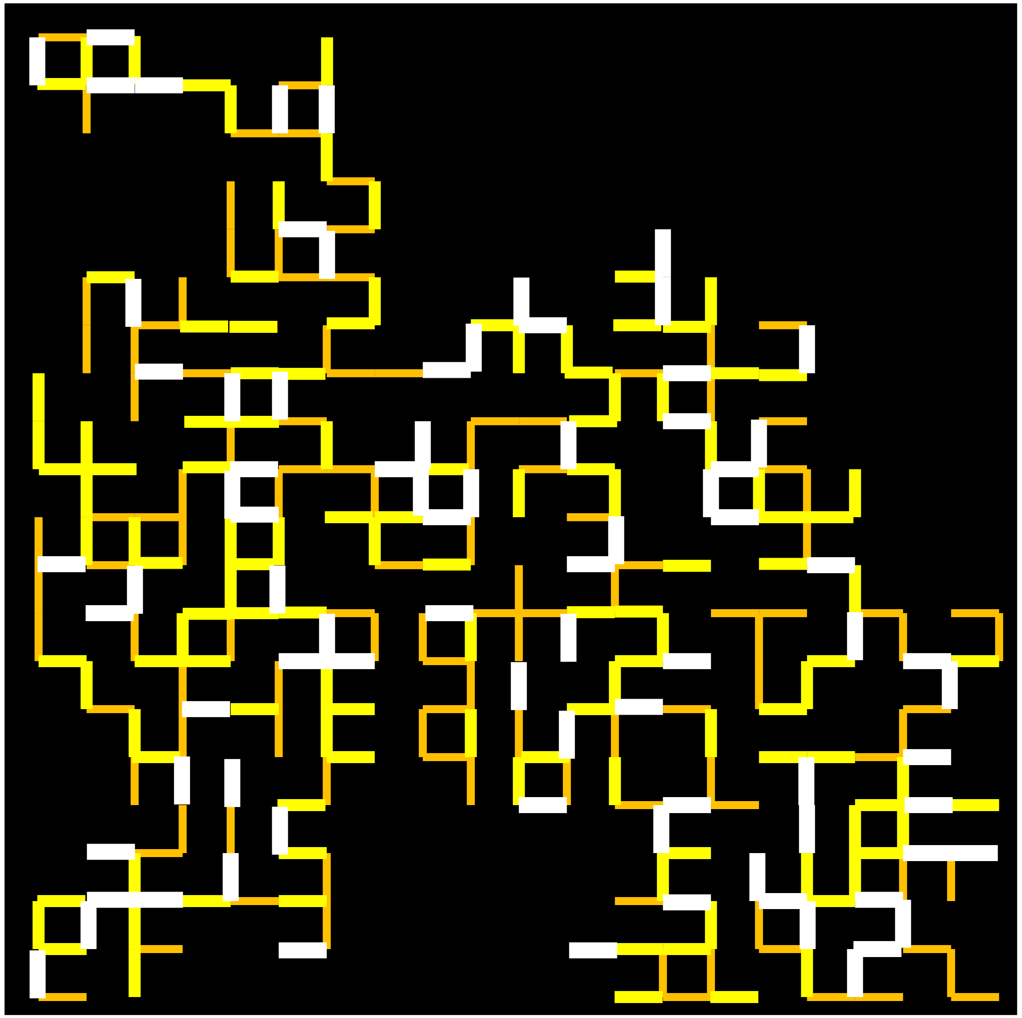


Now the system percolates



In other words: Largest cluster reaches infinite size

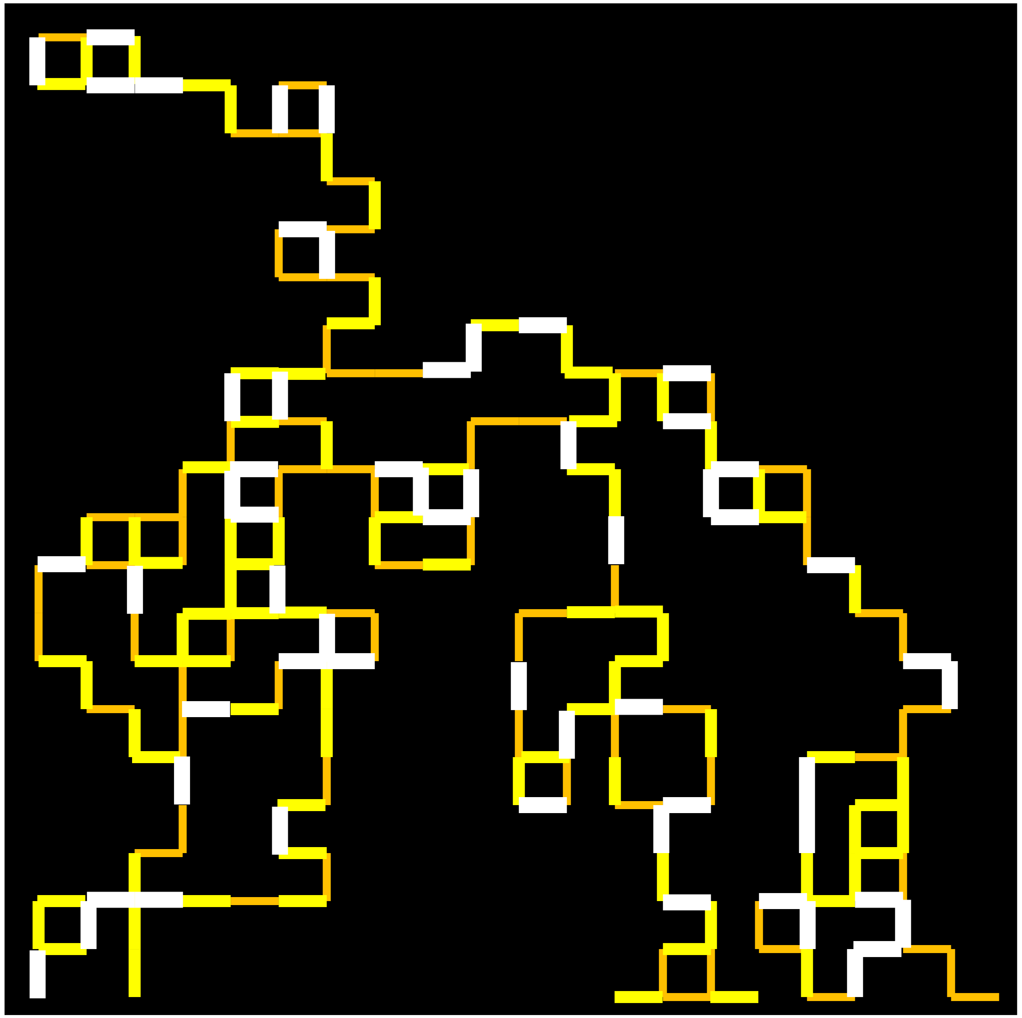
How big is the bottleneck pore?



Infinite cluster
(finite clusters have been deleted)

Bottleneck pore size
Critical radius r_c

Bottleneck pore has conductivity g_c

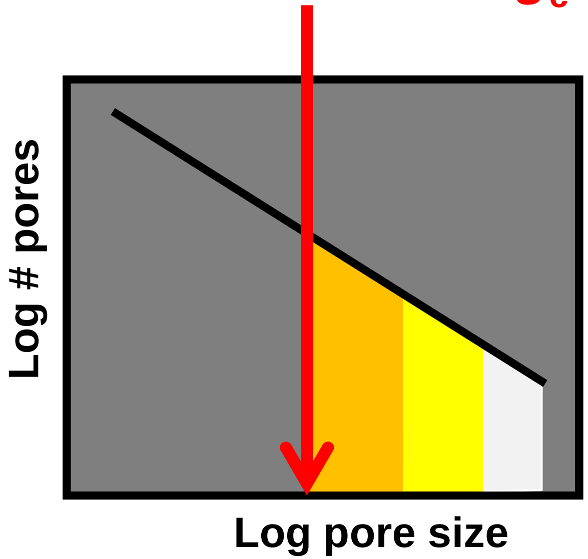


Backbone

- Bonds that actually conduct
- Dangling ends have been deleted

Bottleneck pore size

Critical conductance g_c



$$W(r) = \frac{3-D}{r_m^{3-D}} r^{2-D}$$ IMPLIES $$W(g) \propto g^{\frac{-D}{3}}$$

$$\int_{g_c}^{g_m} W(g)dg = p_c$$

Analogously (for future information)

$$\int_{g}^{g_m} W(g)dg = p$$

We just got

- critical conductance, g_c

Percolation theory gives us

- cluster size statistics
- cluster topology

How can we work in PT using g and g_c?

In percolation theory, quantities of interest are expressed in terms of p and p_c. Results of previous slides transform p and p_c to g and g_c. This transformation of variables allows representation of correlation length, cluster statistics, tortuosity, etc. in terms of a conductance value.

Cluster statistics

$$n_s \approx s^{-\tau} \exp\left\{-\left[(p-p_c)s^{\sigma}\right]^2\right\}$$

Use transformation and Let N $^{1/\sigma\nu}$ = s. Use $\frac{\tau-1}{\sigma\nu} = d$

$$n_N = \frac{1}{N^{d+1}} \exp\left\{-\left[\left(\frac{Nl}{L}\right)^{\frac{1}{\nu}} \left|1-\left(\frac{g}{g_c}\right)^{\frac{3-D}{3}}\right|\right]^2\right\}$$

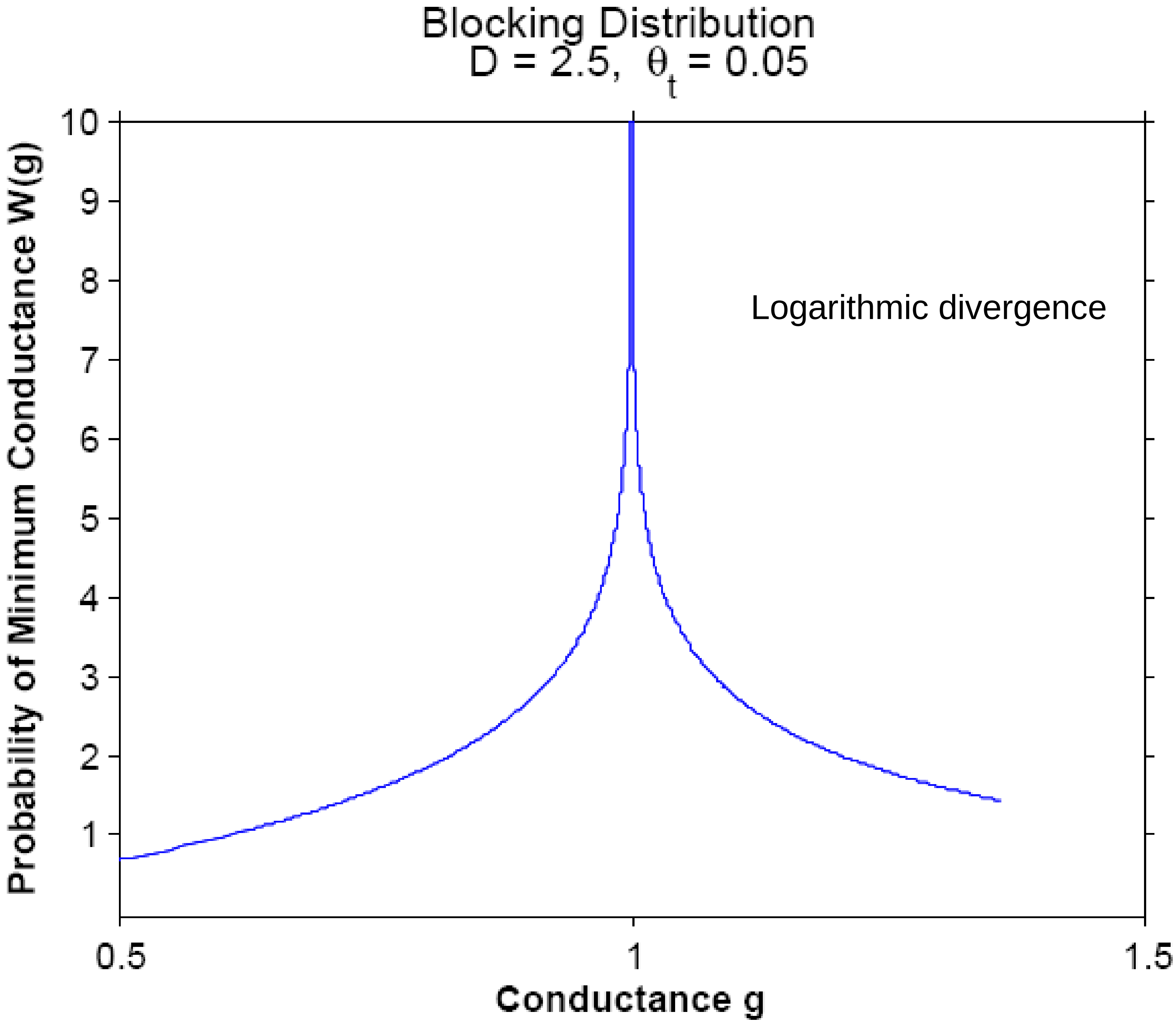
Result (after integrating over all clusters larger than system):

$$W(g;x) \propto \frac{1}{\beta} Ei\left[\alpha \left(\frac{x}{L} \right)^{\beta} \right]$$

$$Ei[z] = \int_z^{\infty} \frac{\exp[-y]}{y} dy$$

$$\alpha = \left| 1 - \left(\frac{g}{g_c} \right)^{\frac{3-D}{3}} \right|^2 \qquad \text{and} \qquad \beta = \frac{2}{\nu}$$

Result is not a power-law, exponential integral has logarithmic divergence at $g = g_c$

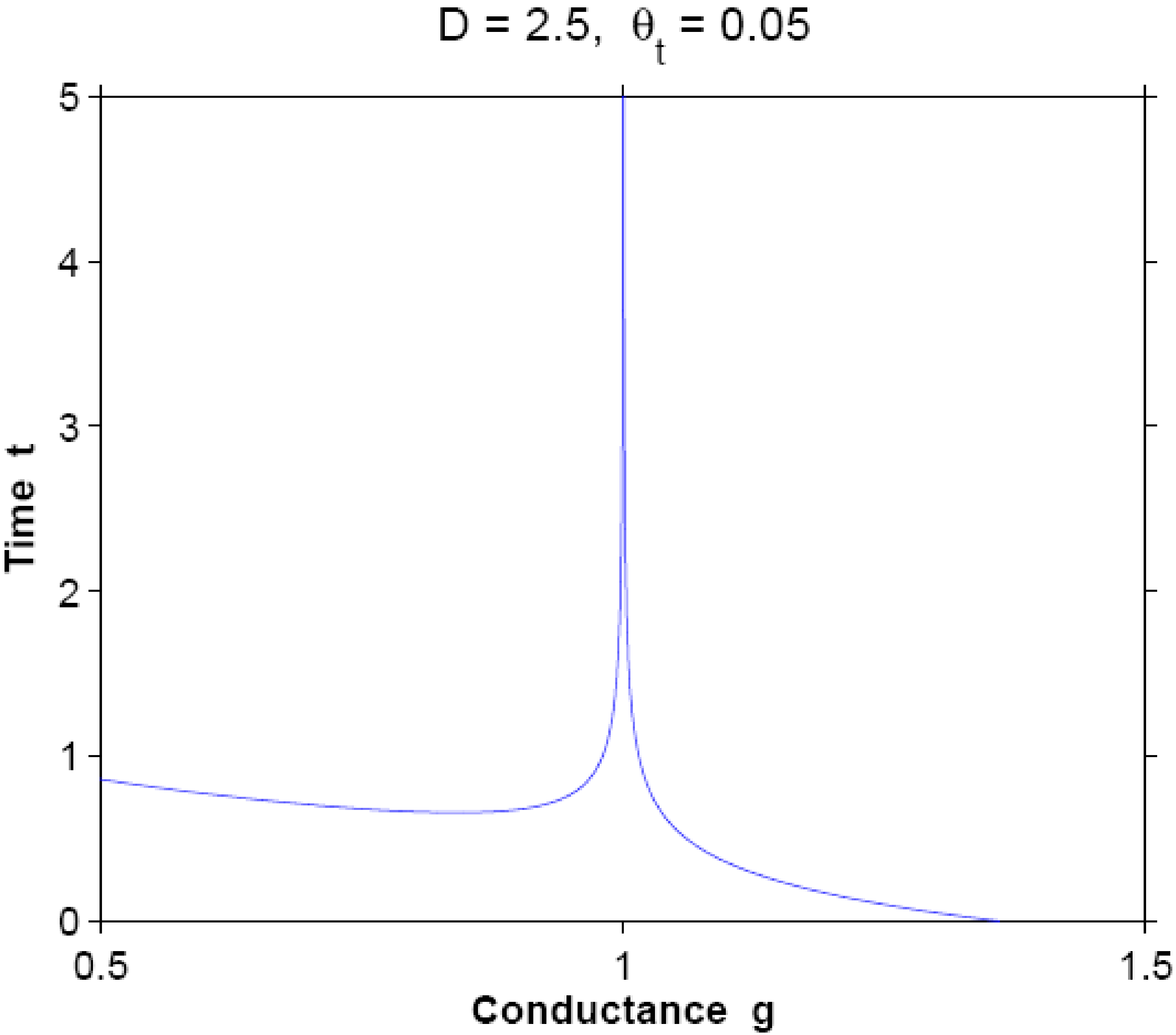

Blocking Distribution
D = 2.5, θt = 0.05
Logarithmic divergence
Probability of Minimum Conductance W(g)
Conductance g
10
9
8
7
6
5
4
3
2
1
0.5
1
1.5

Calculate $t(g)$, the time particles take to traverse a cluster characterized by g.

There are two contributions: one from the conductance distribution ***W(g)***, and one from topology via percolation theory.

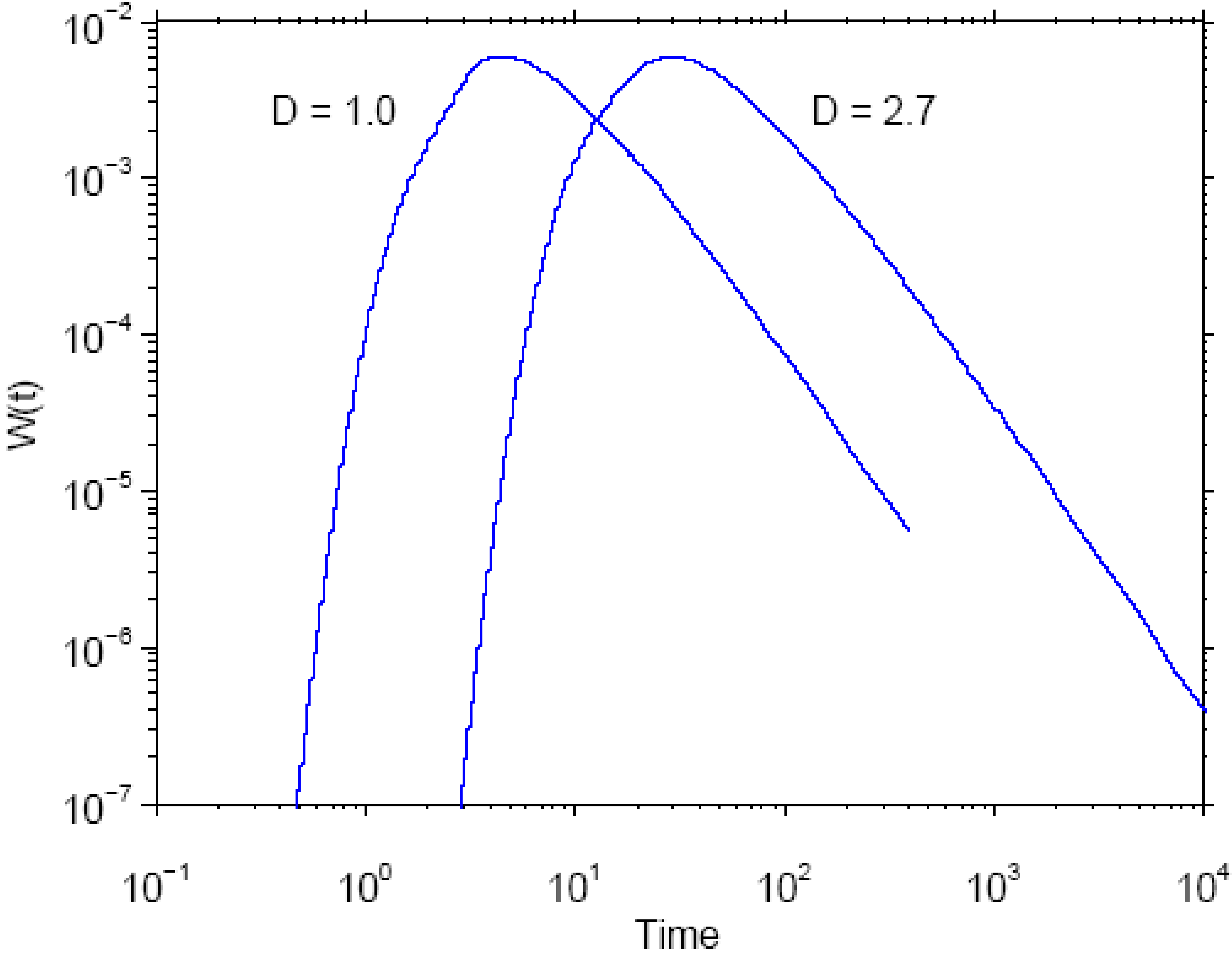
$$t = \left(\frac{x}{L}\right)^{D_b} \frac{t_0}{3-D} \frac{1}{(1-V_c)^{\Lambda-\nu}} \left[\left(1+\frac{V_c}{1-V_c}\right)\left(\frac{g_c}{g}\right)^{1-D/3} - 1\right] \left[\frac{1}{\left|\left(\frac{g}{g_c}\right)^{1-D/3} - 1\right|}\right]^{(D_b-1)\nu}$$

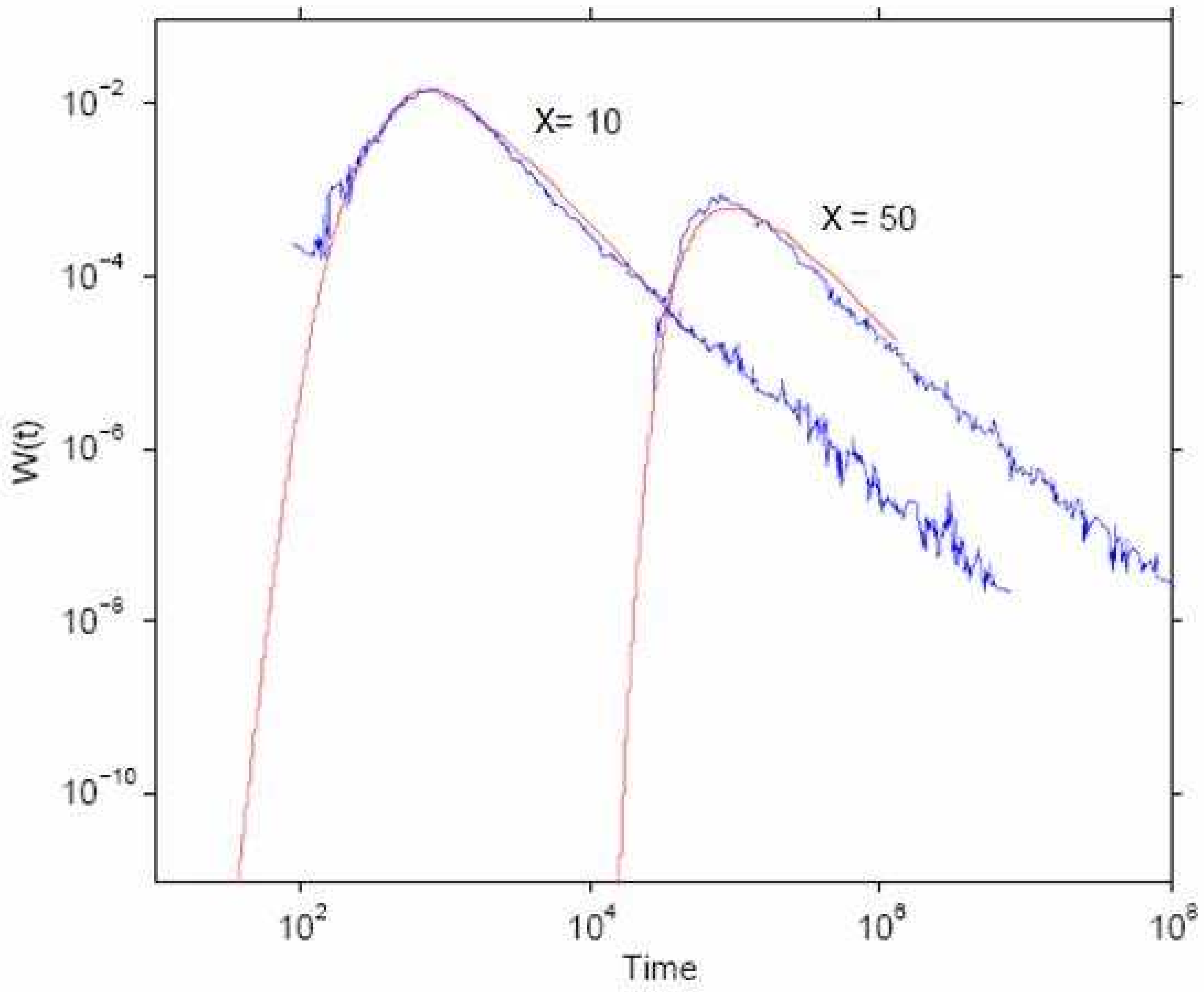
$$\equiv \left(\frac{x}{L}\right)^{D_b} t_g$$



Power-law
divergence

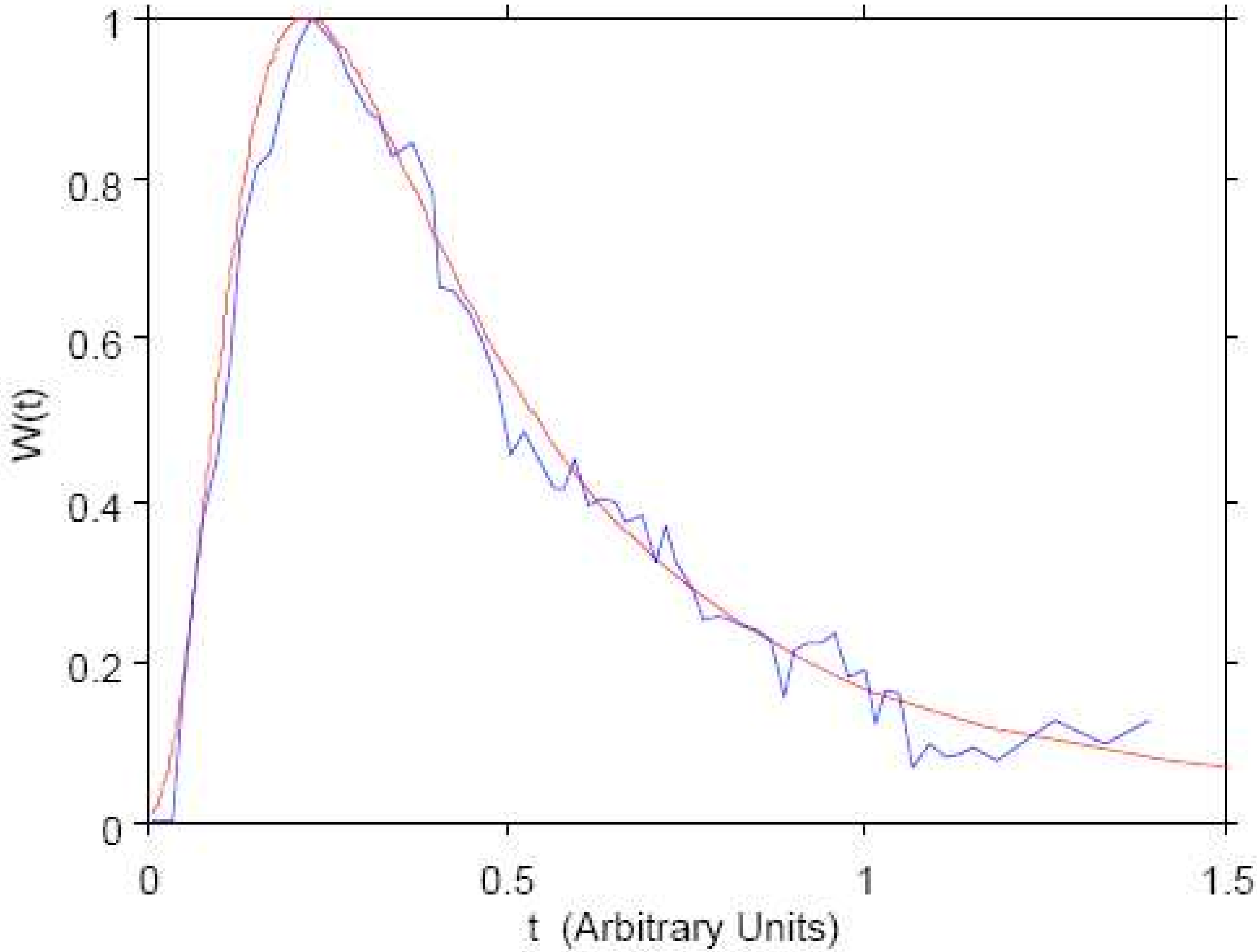
Apply $W_\mathrm{p}(t\ ; x) = g\, W_\mathrm{p}(g\ ; x)\ /\ (\ dt(g)/dg\ )$


D = 1.0
D = 2.7
W(t)
Time
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}

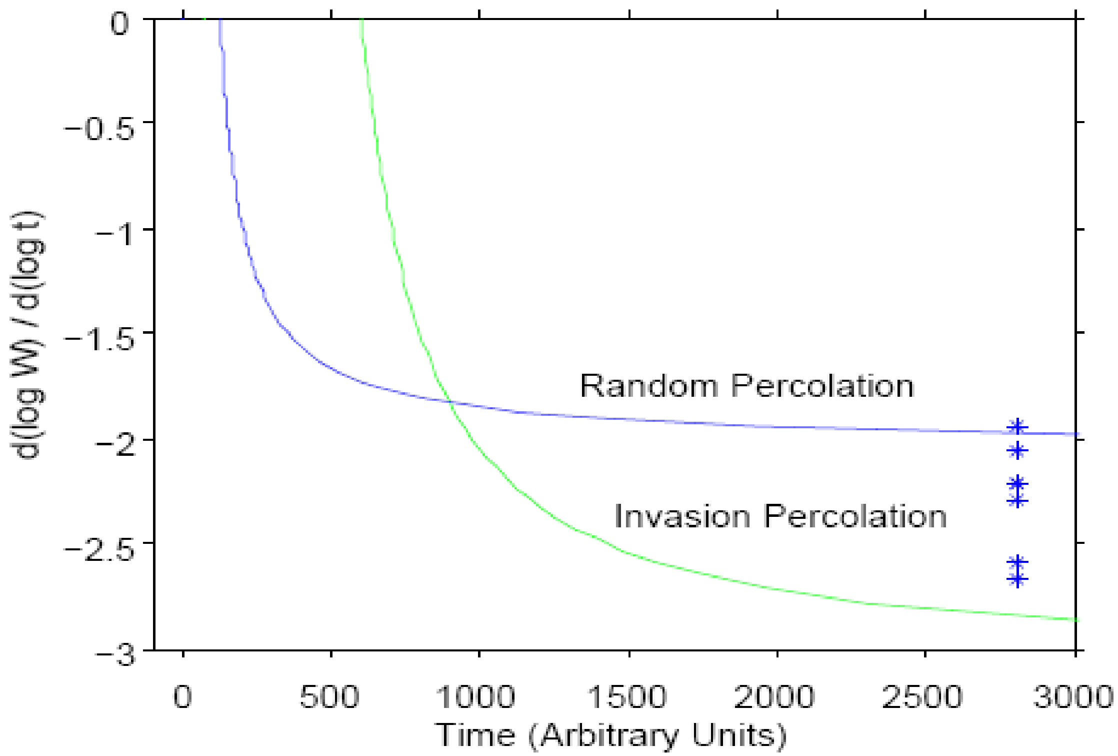


Note that we do not obtain power-law tail, but our results match such experimental results rather closely. Example given has slope -1.56, almost identical to what is seen in fracture flow experiments.

2-D flow, parameters from 2-D random percolation.
Navier-Stokes simulations on 2-D structure at Percolation threshold

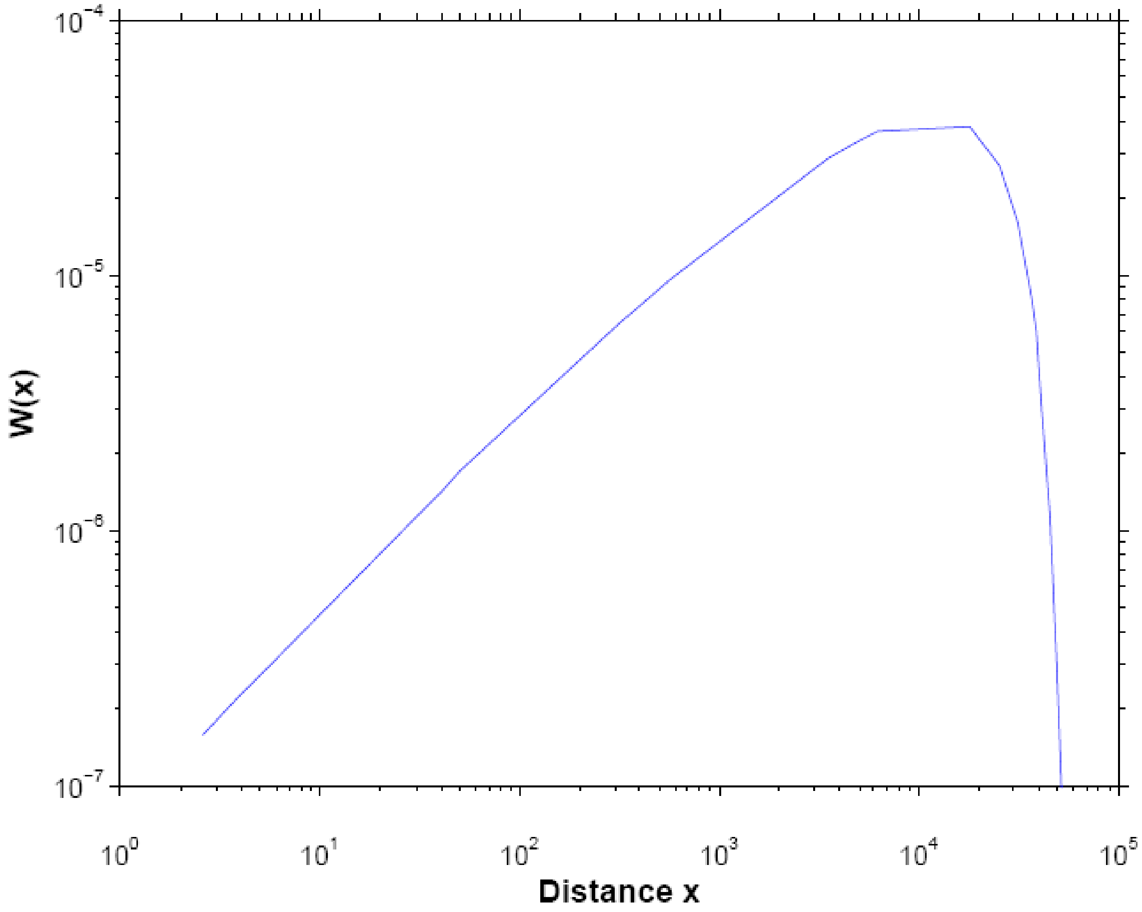


No prediction here, only a fit, but to “classic” Nielsen and Biggar experiment (cited by Cortis and Berkowitz)



0
−0.5
−1
−1.5
−2
−2.5
−3
d(log W) / d(log t)
0
500
1000
1500
2000
2500
3000
Time (Arbitrary Units)
Random Percolation
Invasion Percolation

Analogous procedure for spatial distribution at time t

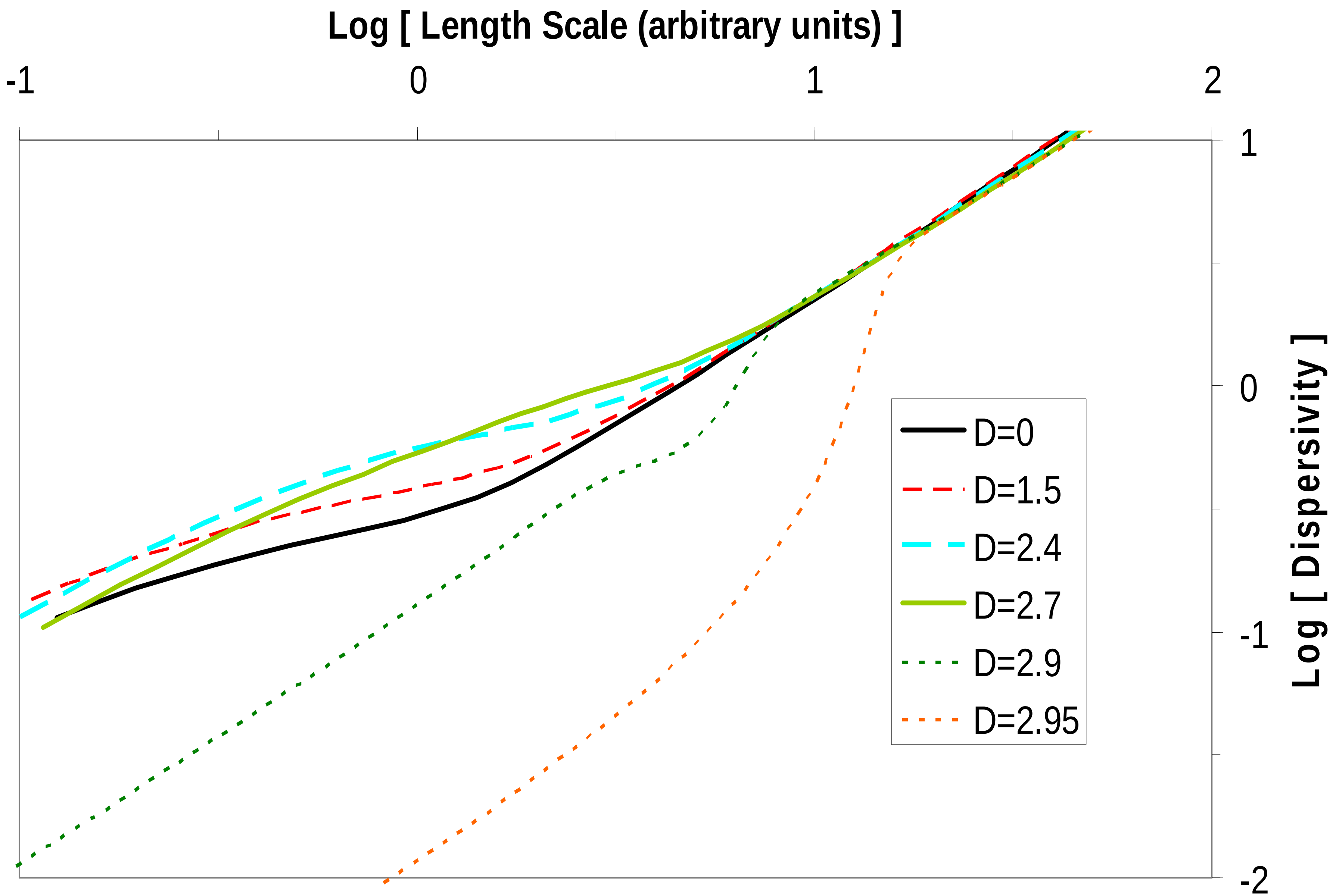


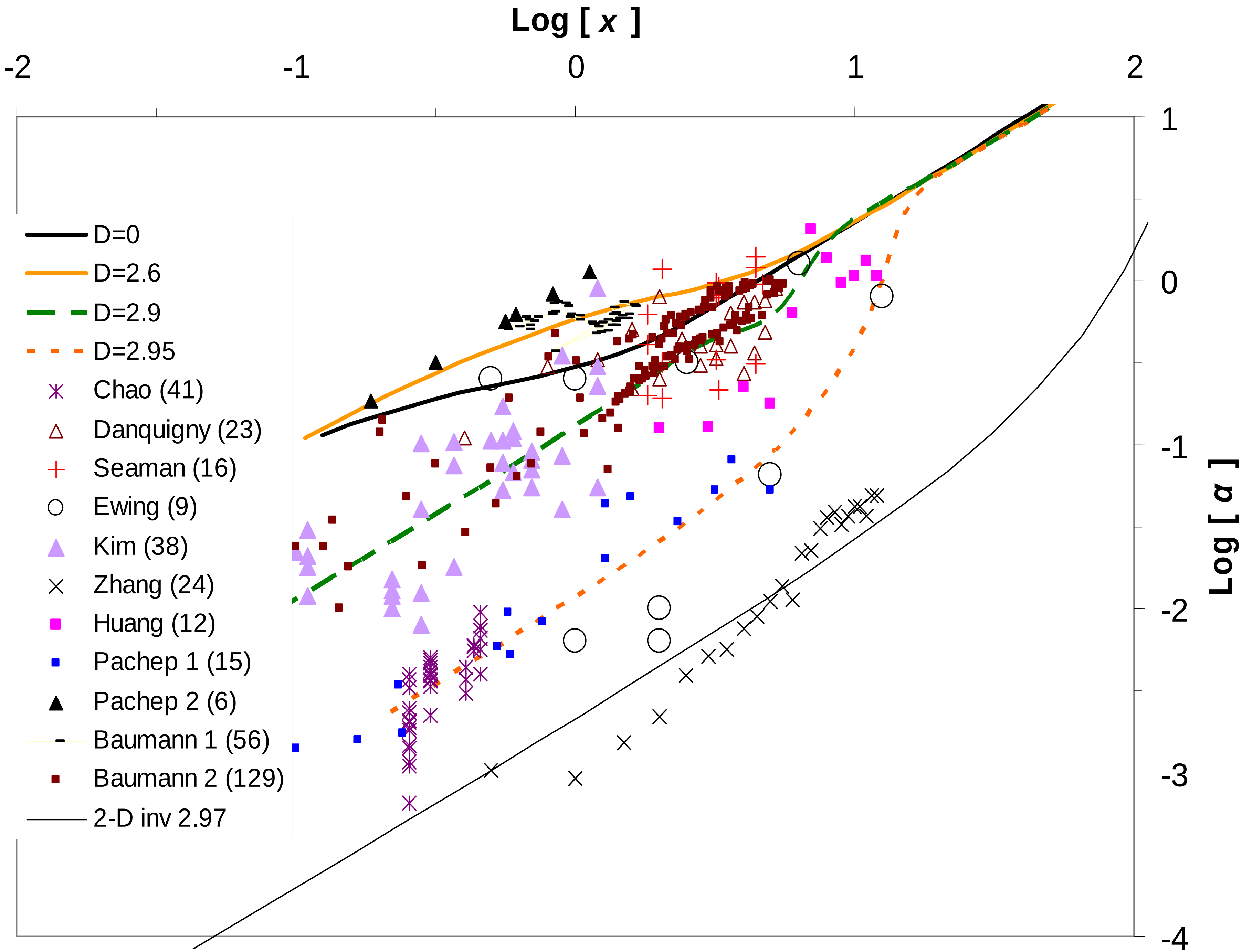
Define longitudinal dispersion coefficient and dispersivity

$$D_l(t) \equiv \tfrac{1}{2}\, d/dt\, [< x^2 > - < x > ^2] \approx [< x^2 > - < x > ^2] / \mathrm{t}.$$

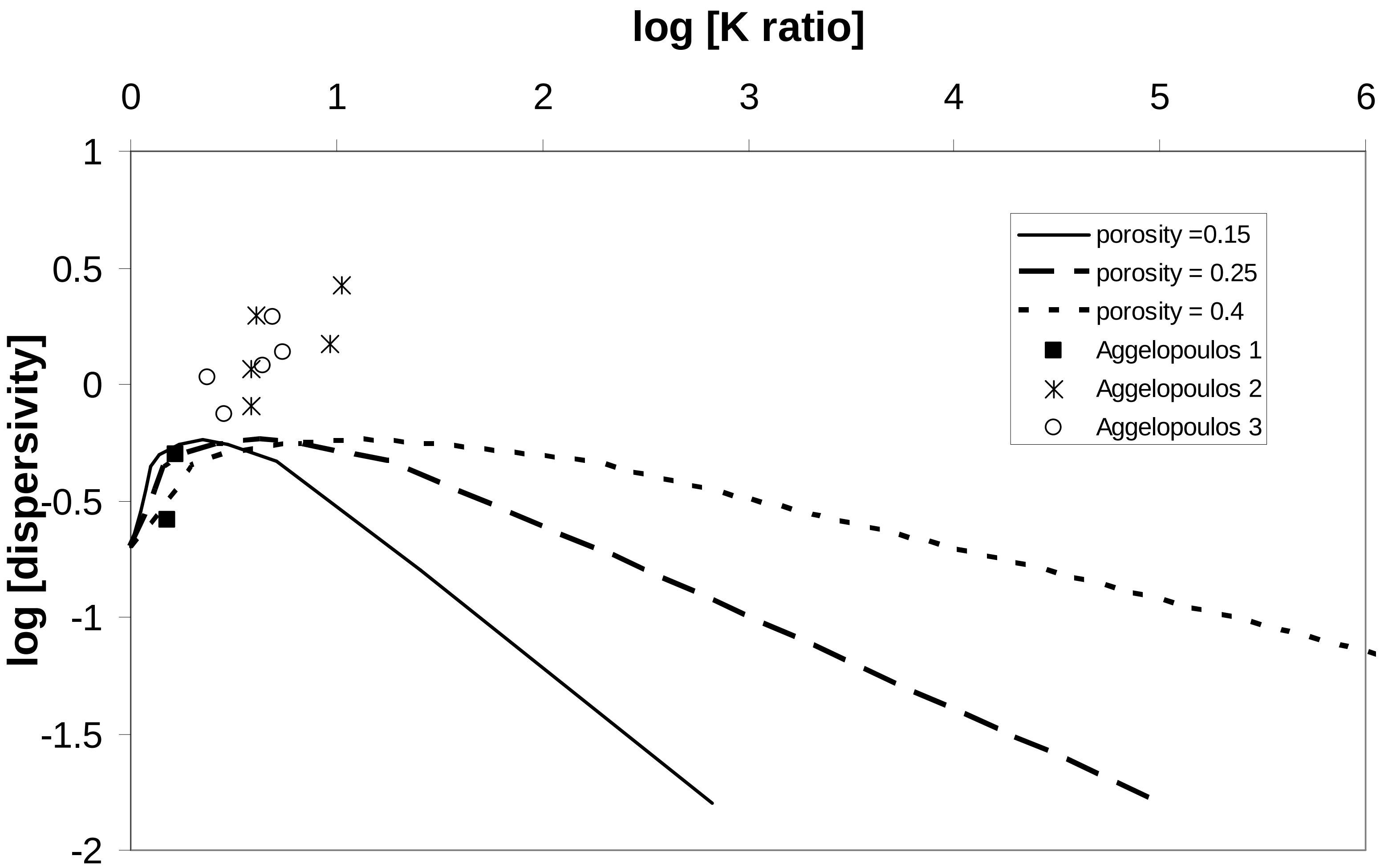
$$\alpha \equiv [< x^2 > - < x > ^2] / < x >.$$

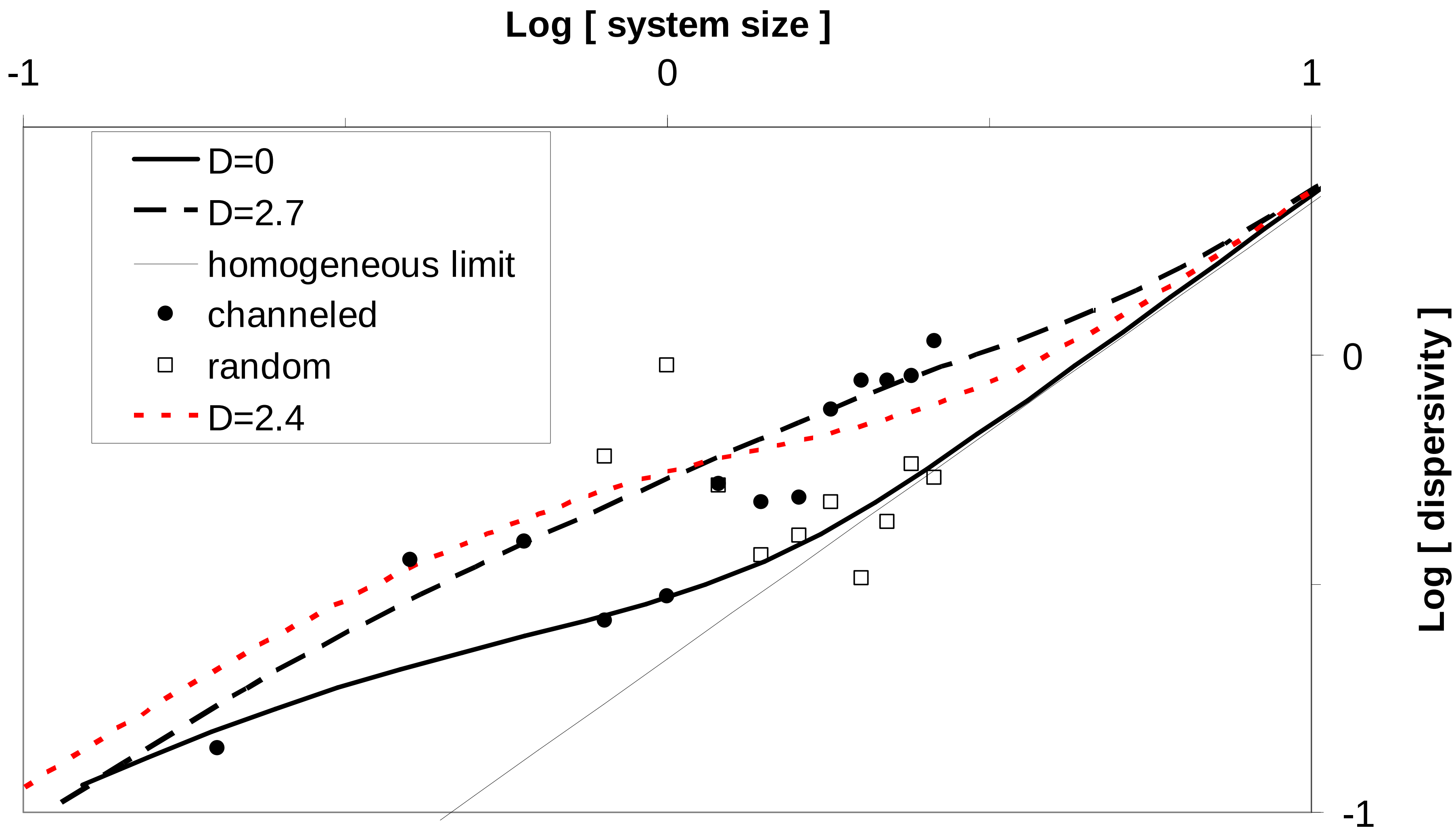
Averages performed over distributions derived above: for Gaussian spreading, $D_l(t)$ would be constant in time, making α constant in space.


Log [Length Scale (arbitrary units)]
-1
0
1
2
1
0
-1
-2
Log [Dispersivity]
D=0
D=1.5
D=2.4
D=2.7
D=2.9
D=2.95

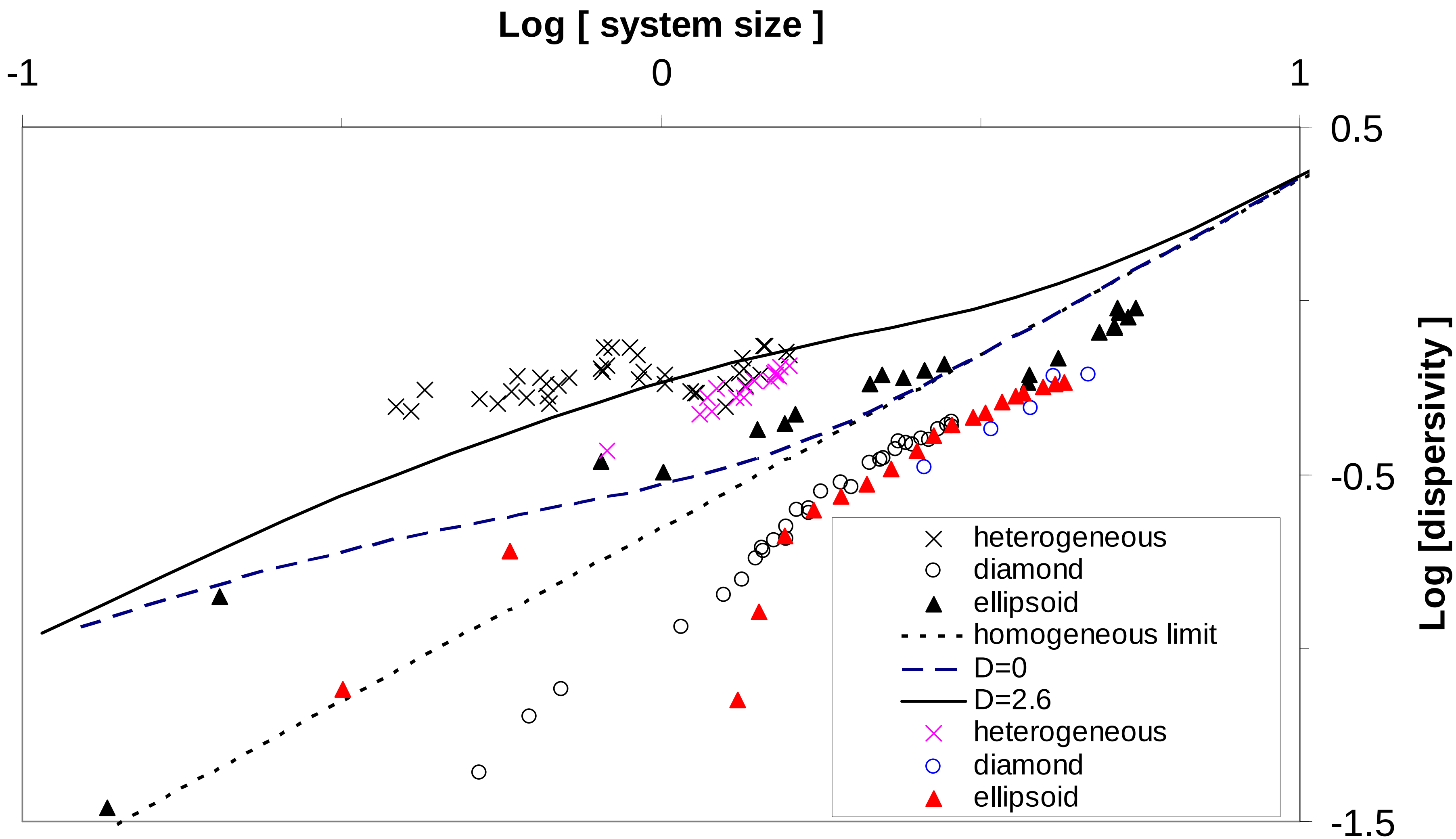


Log [x]
-2
-1
0
1
2
1
0
-1
-2
-3
-4
Log [α]
D=0
D=2.6
D=2.9
D=2.95
Chao (41)
Danquigny (23)
Seaman (16)
Ewing (9)
Kim (38)
Zhang (24)
Huang (12)
Pachep 1 (15)
Pachep 2 (6)
Baumann 1 (56)
Baumann 2 (129)
2-D inv 2.97

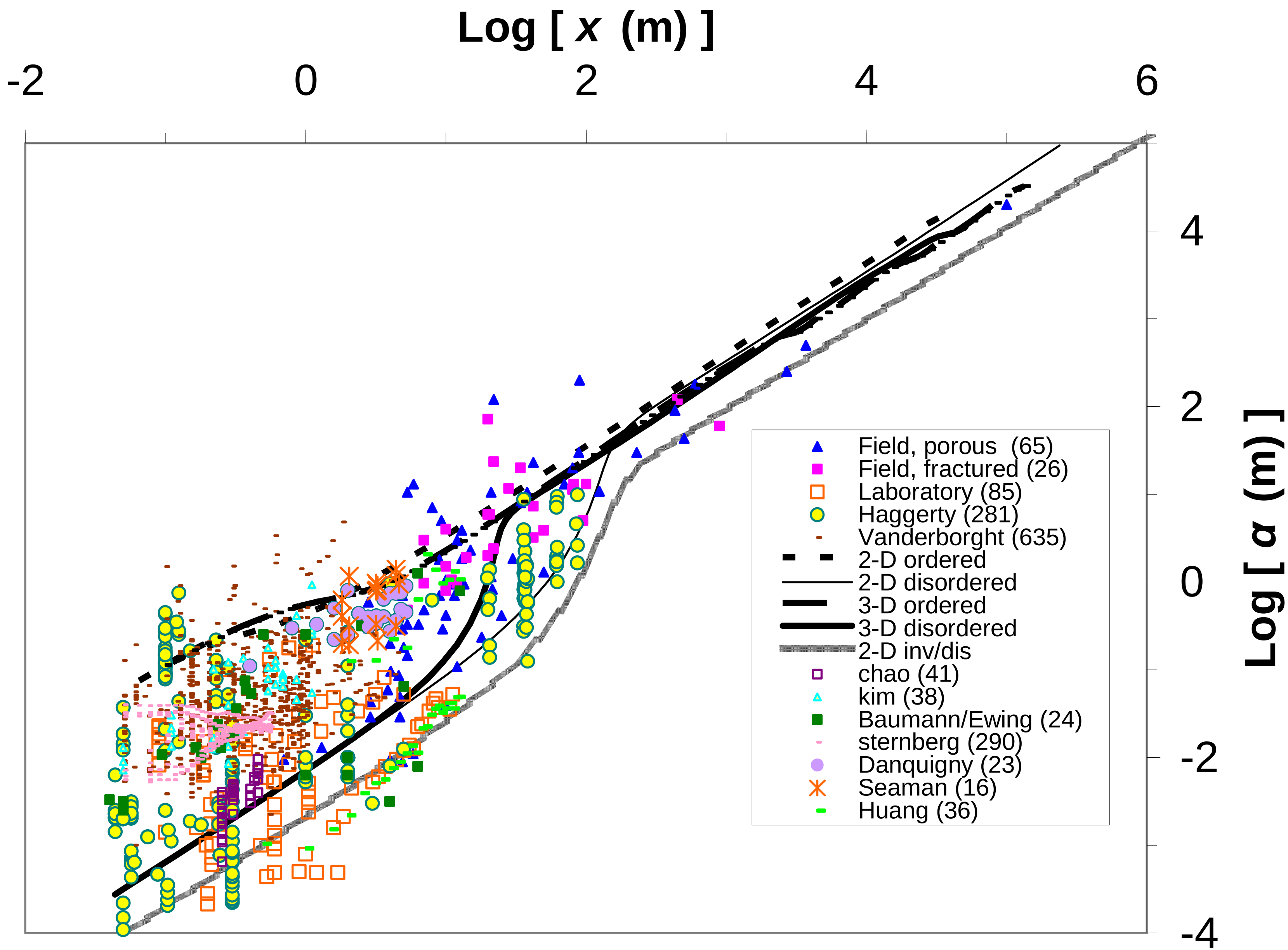

log [K ratio]
0
1
2
3
4
5
6
1
0.5
0
-0.5
-1
-1.5
-2
log [dispersivity]
porosity =0.15
porosity = 0.25
porosity = 0.4
Aggelopoulos 1
Aggelopoulos 2
Aggelopoulos 3



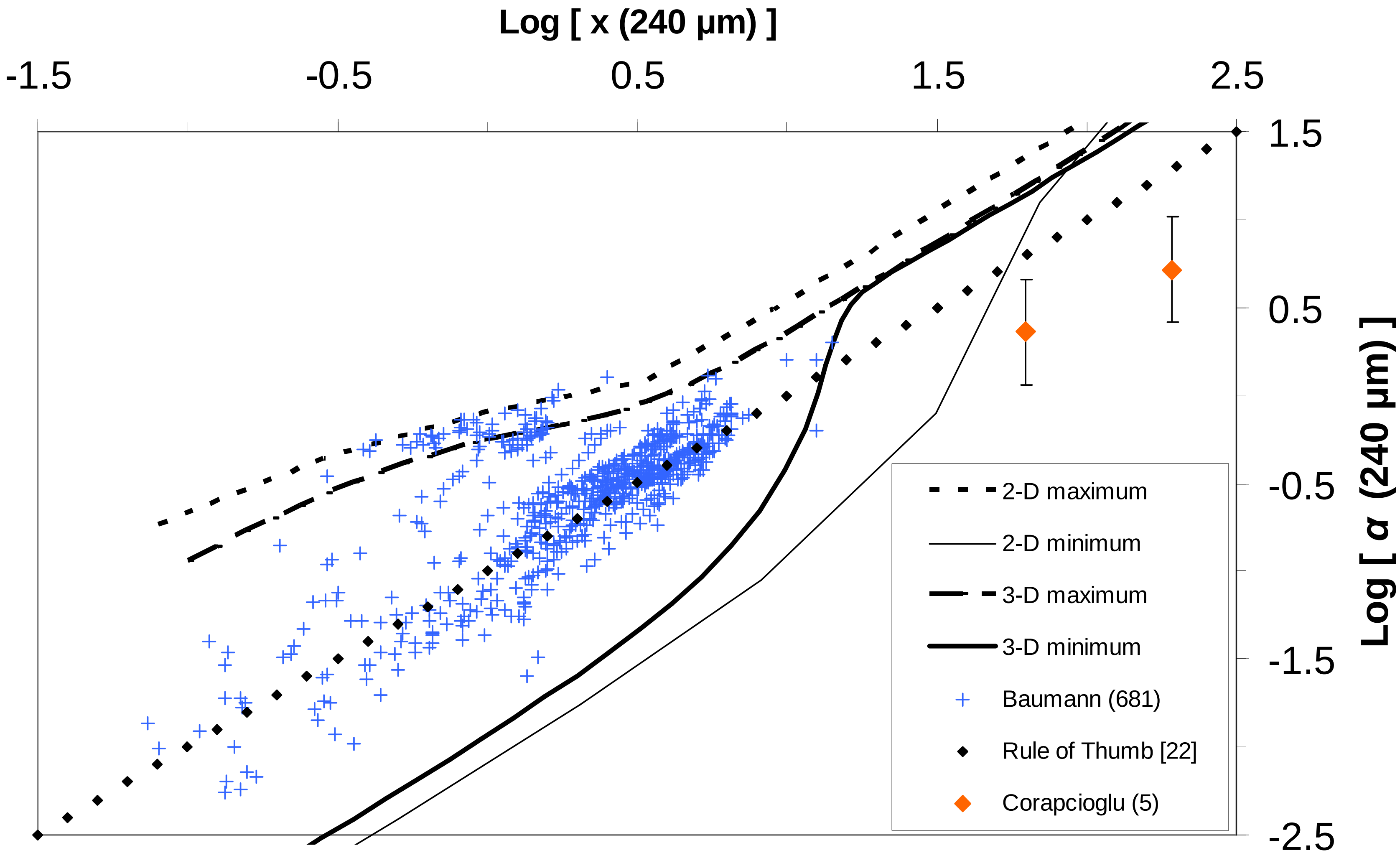
Log [system size]
-1
0
1
D=0
D=2.7
homogeneous limit
channeled
random
D=2.4
0
-1
Log [dispersivity]



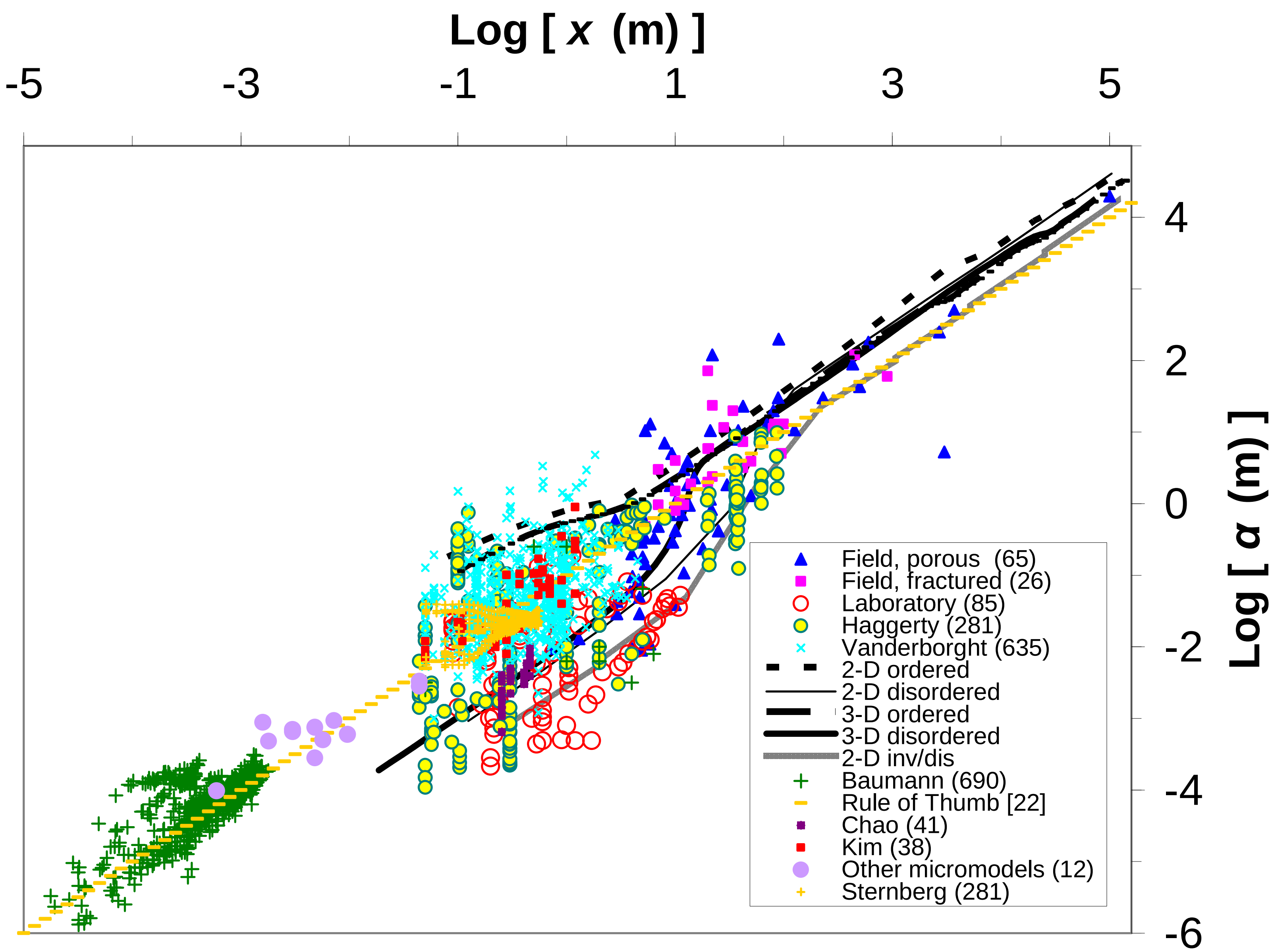
Log [system size]
-1
0
1
0.5
-0.5
-1.5
Log [dispersivity]
heterogeneous
diamond
ellipsoid
homogeneous limit
D=0
D=2.6
heterogeneous
diamond
ellipsoid



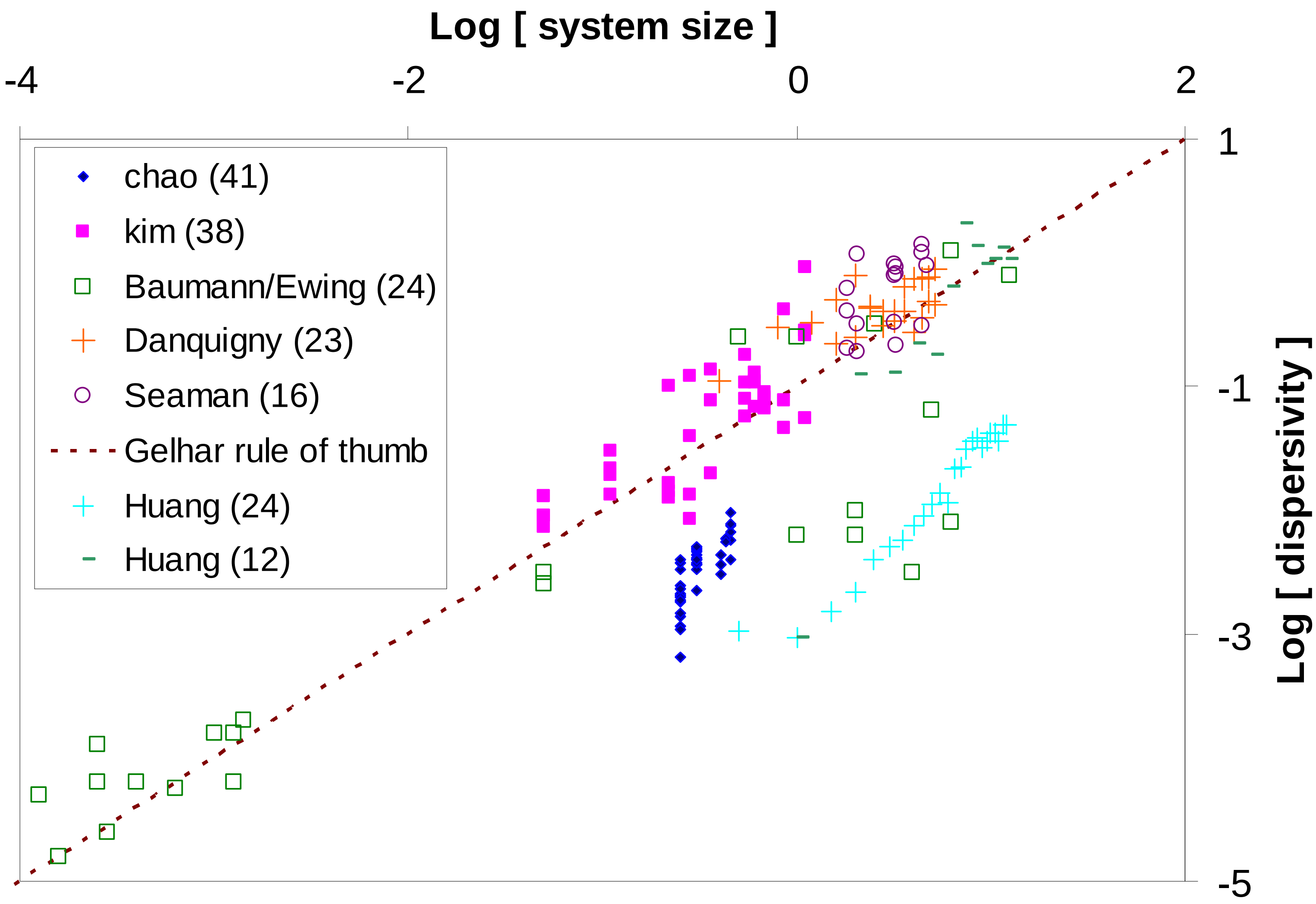
Log [x (m)]
-2
0
2
4
6
Log [α (m)]
4
2
0
-2
-4
Field, porous (65)
Field, fractured (26)
Laboratory (85)
Haggerty (281)
Vanderborght (635)
2-D ordered
2-D disordered
3-D ordered
3-D disordered
2-D inv/dis
chao (41)
kim (38)
Baumann/Ewing (24)
sternberg (290)
Danquigny (23)
Seaman (16)
Huang (36)



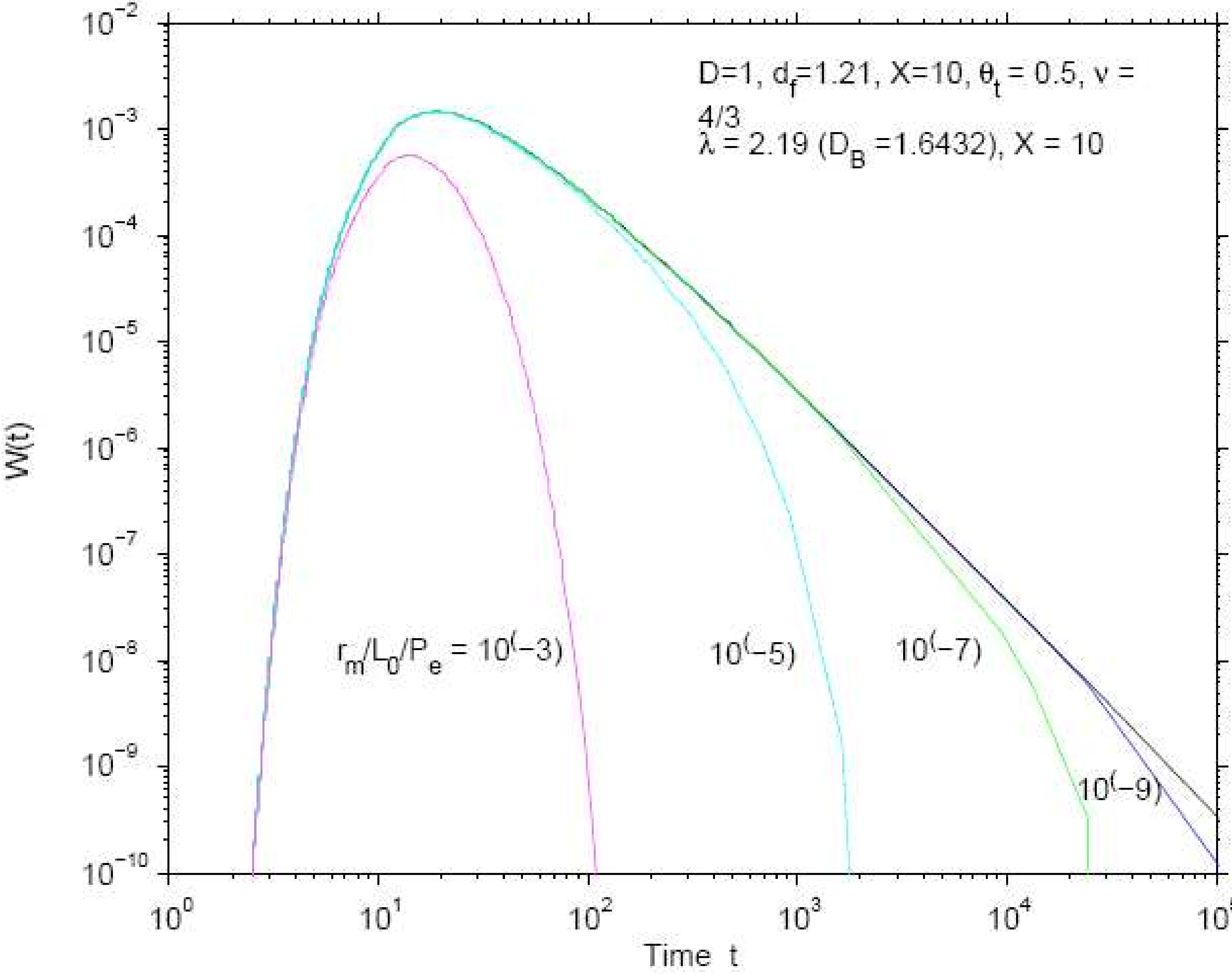
Log [x (240 μm)]
-1.5
-0.5
0.5
1.5
2.5
1.5
0.5
-0.5
-1.5
-2.5
Log [α (240 μm)]
2-D maximum
2-D minimum
3-D maximum
3-D minimum
Baumann (681)
Rule of Thumb [22]
Corapcioglu (5)



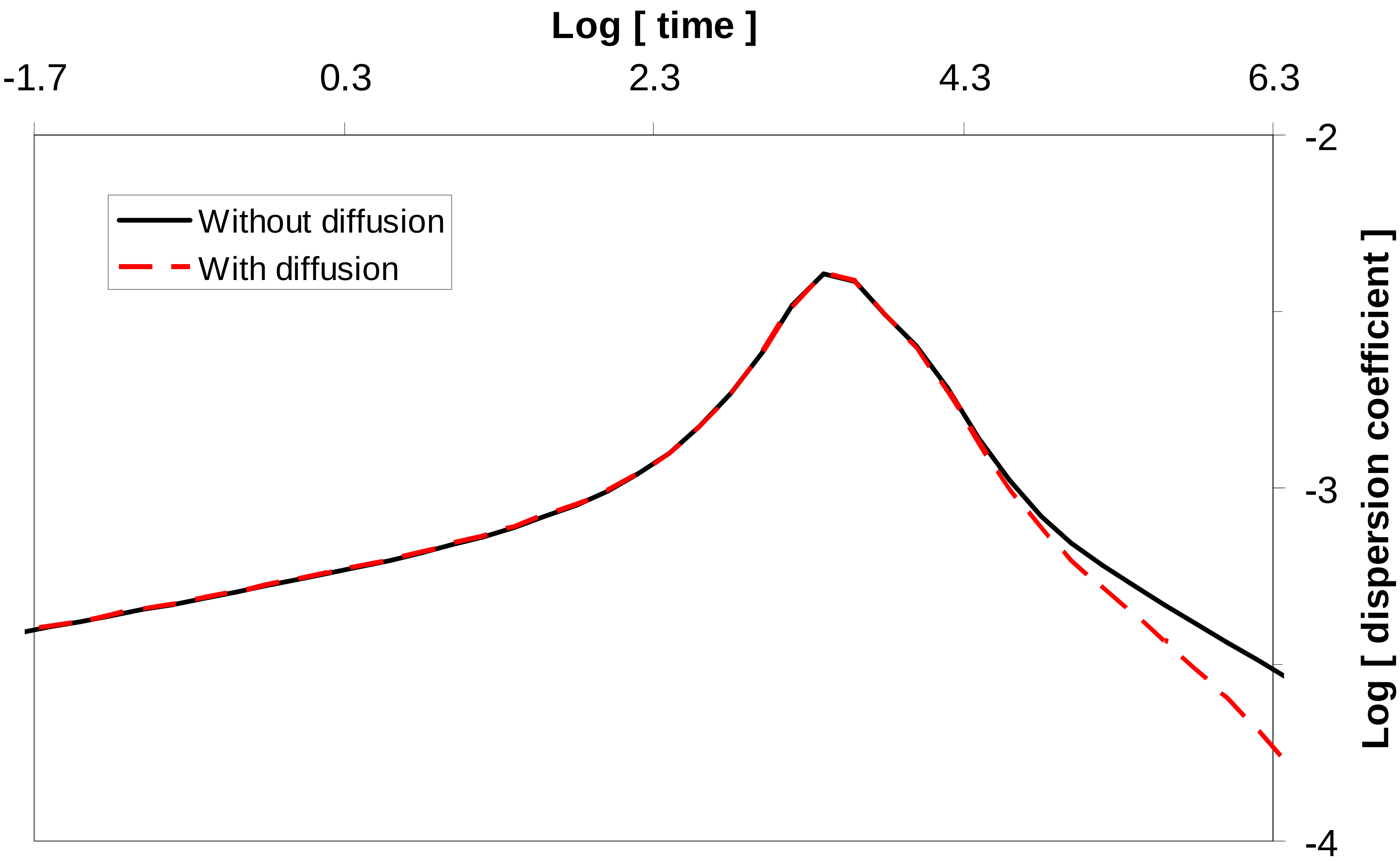
Log [x (m)]
-5
-3
-1
1
3
5
4
2
0
-2
-4
-6
Log [α (m)]
Field, porous (65)
Field, fractured (26)
Laboratory (85)
Haggerty (281)
Vanderborght (635)
2-D ordered
2-D disordered
3-D ordered
3-D disordered
2-D inv/dis
Baumann (690)
Rule of Thumb [22]
Chao (41)
Kim (38)
Other micromodels (12)
Sternberg (281)



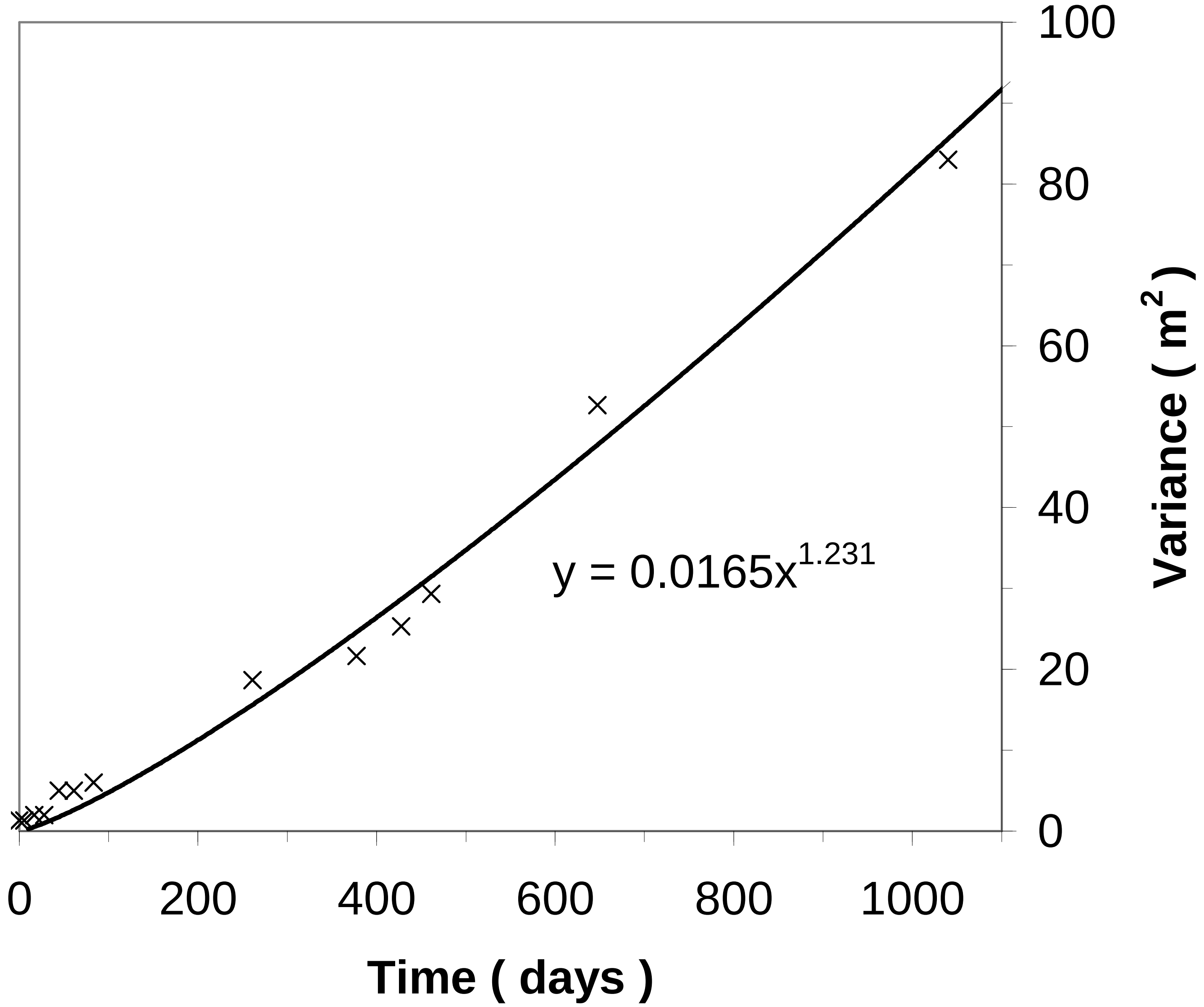
Log [system size]
-4
-2
0
2
1
-1
-3
-5
Log [dispersivity]
chao (41)
kim (38)
Baumann/Ewing (24)
Danquigny (23)
Seaman (16)
Gelhar rule of thumb
Huang (24)
Huang (12)



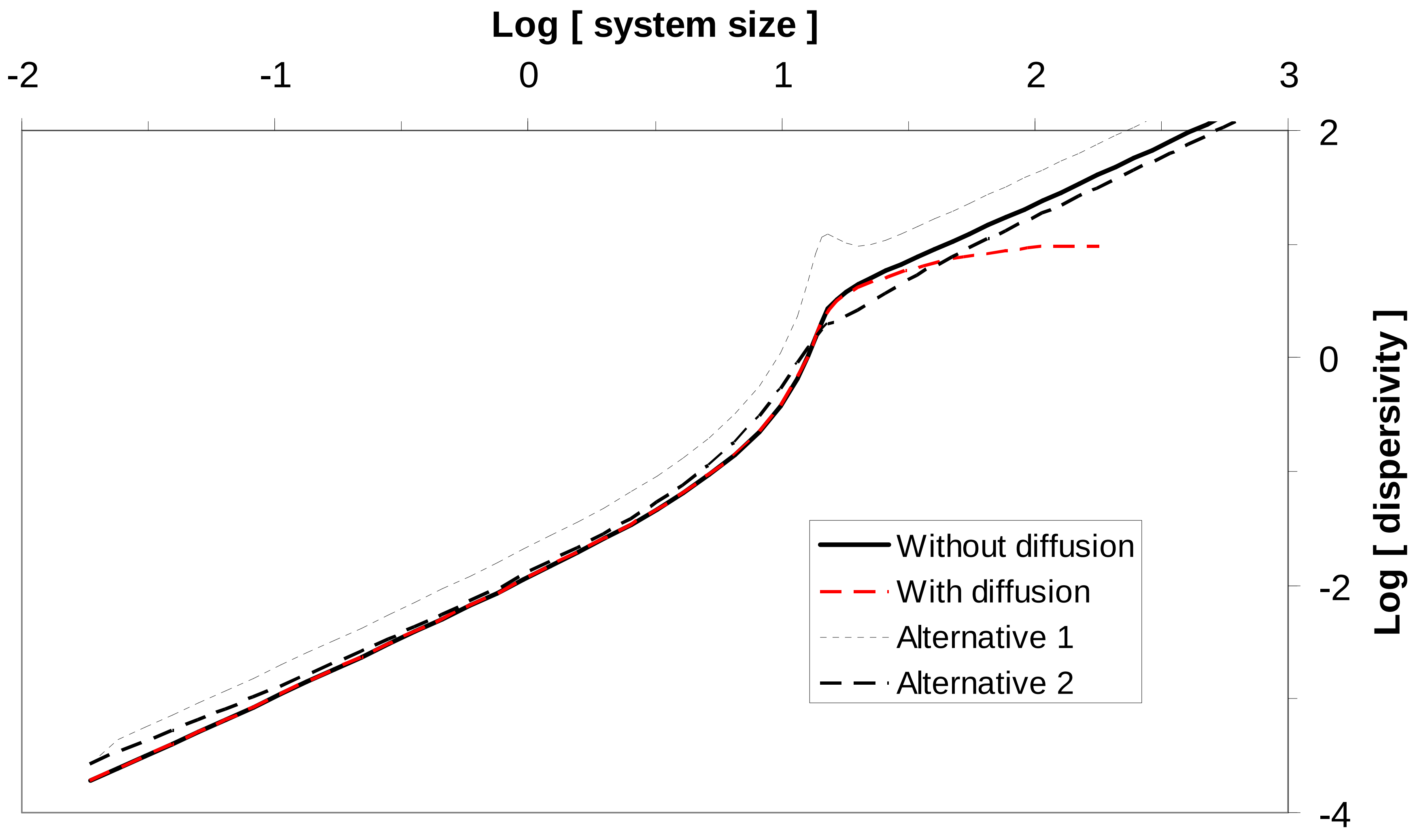
D=1, d_f=1.21, X=10, θ_t = 0.5, ν = 4/3
λ = 2.19 (D_B =1.6432), X = 10
$r_m/L_0/P_e$ = 10^(−3)
10^(−5)
10^(−7)
10^(−9)
W(t)
Time t



Log [time]
-1.7
0.3
2.3
4.3
6.3
-2
-3
-4
Log [dispersion coefficient]
Without diffusion
With diffusion



100
80
60
40
20
0
0
200
400
600
800
1000
y = 0.0165x^1.231
Time (days)
Variance (m^2)



Log [system size]
-2
-1
0
1
2
3
2
0
-2
-4
Log [dispersivity]
Without diffusion
With diffusion
Alternative 1
Alternative 2

Length Dependence of Typical System Crossing Time

Power	Predicted	Reference	Material
1.67	1.64	Pfister and Griffiths[127]	Carbazole polymers
1.72	1.64	Pfister and Griffiths[127]	Carbazole polymers
2.1	1.9	Pfister[128]	As_2Se_3
2	1.9	Tiedje[129]	a-Si:H
2.2	can't predict	Scher and Montroll[65]	not given
1.91	1.9	Pfister[130]	a-Se
1.86	1.9	Pfister[130]	a-Se
1.61	1.64	Bos et al[131]	Polyvinyl carbazole
1.82	can't predict	Pfister and Scher[132]	not given

Summary

- Straightforward derivation in terms of known quantities from percolation theory leads to:
- Arrival time distribution consistent with simulations and experiments in soils and fracture flow
- Superlinear dependence of variance on time (at short times) in accord with experimental summaries and possibly predictive for Borden aquifer
- Dependence of dispersivity on length scale in accord with over 2400 experiments over 10 orders of magnitude of length scale
- Dependence of dispersivity on heterogeneity which is in accord with experiment for small heterogeneity, but which may or may not be for large heterogeneity
- Dependence of typical transport time on system length which is observed in semiconductors/polymers.

Implications

- No need to invoke multiple scales of heterogeneity to produce continuing rise of dispersivity with length scale (trouble for stochastic subsurface hydrology and NSF).

- Tendency for all experiments at scales of centimeters and above to have same REV ($1m^3$) implies the relevance of experimental apparatus (human size on order of 2m).

- No role of diffusion means trouble both for ADE users and for proponents of matrix diffusion to explain solute transport retardation in fracture flow (nuclear regulatory issue).

- Where is the importance of geological complexity?