The peculiar characteristics of air-water gas transfer across a broken surface

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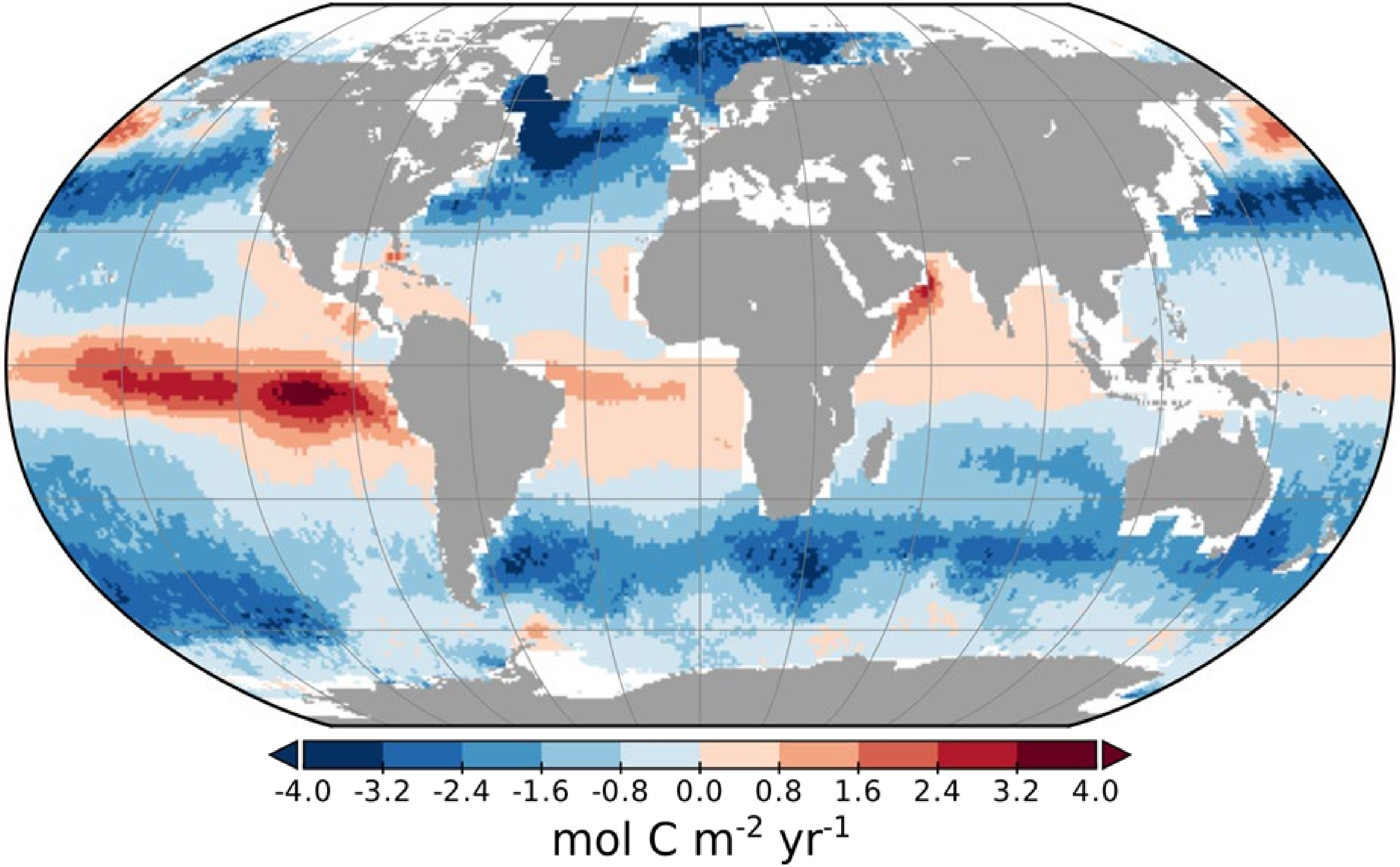
Or Why we need a thorough mechanistic understanding to get the right answer



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Overview

- Philosophy 101
- Gas Transfer Equation
- Counter-Gradient Transfer
- Asymmetric Transfer
- Transfer Velocity
- Philosophy 201
- Regional and Seasonal Transfer Velocities
- Solubility
- Wind and Sea State
- Calculating Fluxes

On the Exchange of Carbon Dioxide between the Atmosphere and the Sea

By BERT BOLIN, University of Stockholm

(Manuscript received March 3, 1960)

Abstract

The physical and chemical processes responsible for exchange of carbon dioxide between the atmosphere and the sea are analyzed. It is shown that the rate of transfer is considerably decreased due to the finite rate of hydration of CO_2 in water. This is the case both for a smooth water surface where molecular diffusion plays a rôle in the first few hundredths of a millimeter as well as for a rough sea where turbulence extends all the way to the surface. A general agreement is found between the transfer rate deduced in this way and the rate of exchange estimated on the basis of the C^{14}/C^{12} ratio in the atmosphere and the sea.

1. Introduction

Recent studies of the exchange of carbon dioxide between the atmosphere and the sea (REVELLE and SUESS, 1957; CRAIG, 1957; ARNOLD and ANDERSON, 1957; BOLIN and ERIKSSON, 1959) using measurements of radiocarbon in the atmosphere and the sea have given a residence time for carbon dioxide in the atmosphere of 3—7 years. This result has been obtained considering the atmosphere and the sea as well mixed reservoirs (the latter one divided into an upper and a lower part) and assuming the exchange between them being directly proportional to the concentrations. The value of the residence time is roughly proportional to the difference of C^{14}/C^{12} in the atmosphere and the surface layers of the ocean (after correction for fractionation). A large number of new measurements has recently become available (BROECKER et al., 1959) and they agree in general with the previous measurement reported by REVELLE and SUESS (l.c.). Considerable variations occur, however, for example between the surface waters around the Antarctica and the Northern Atlantic. We shall here accept a value for this average residence time of about 5 years but keep in mind that this is an average value applicable to the ocean as a whole.

Obviously the model of the atmosphere and the sea adopted in these studies is a gross oversimplification of actual conditions and it therefore seems desirable to investigate a little more in detail the processes that bring about this exchange. It is of particular interest to analyze the proposal by ERIKSSON (1959), that the comparatively slow rate of hydration is of importance.

2. Chemical and physical processes governing the exchange

The carbon system of the sea consists of dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate ions, which are all in approximate equilibrium. We may write (BUCH ET AL., 1932)

$$\left.\begin{array}{ll}\text{(a)} & CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H + \\ & \quad + HCO_3^- \rightleftharpoons 2H + CO_3^= \\ \text{(b)} & CO_2 + OH \rightleftharpoons HCO_3 \rightleftharpoons H + CO_3\end{array}\right\} \quad (1)$$

The first reaction is the only one of importance for $pH \leq 8$ and the latter one is the

Tellus XII (1960), 3

Shoring up the foundations

- Scientific knowledge is often taught as a cumulative process
- But it is important to inspect the foundations and occasionally they need some repair
- That thing you know
  - How do you know it?
  - Are there exceptions?

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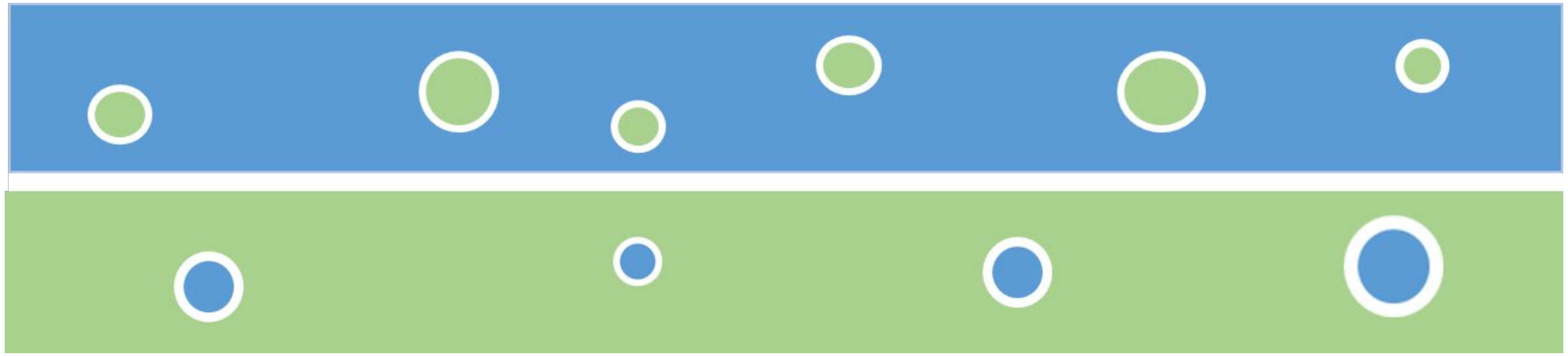
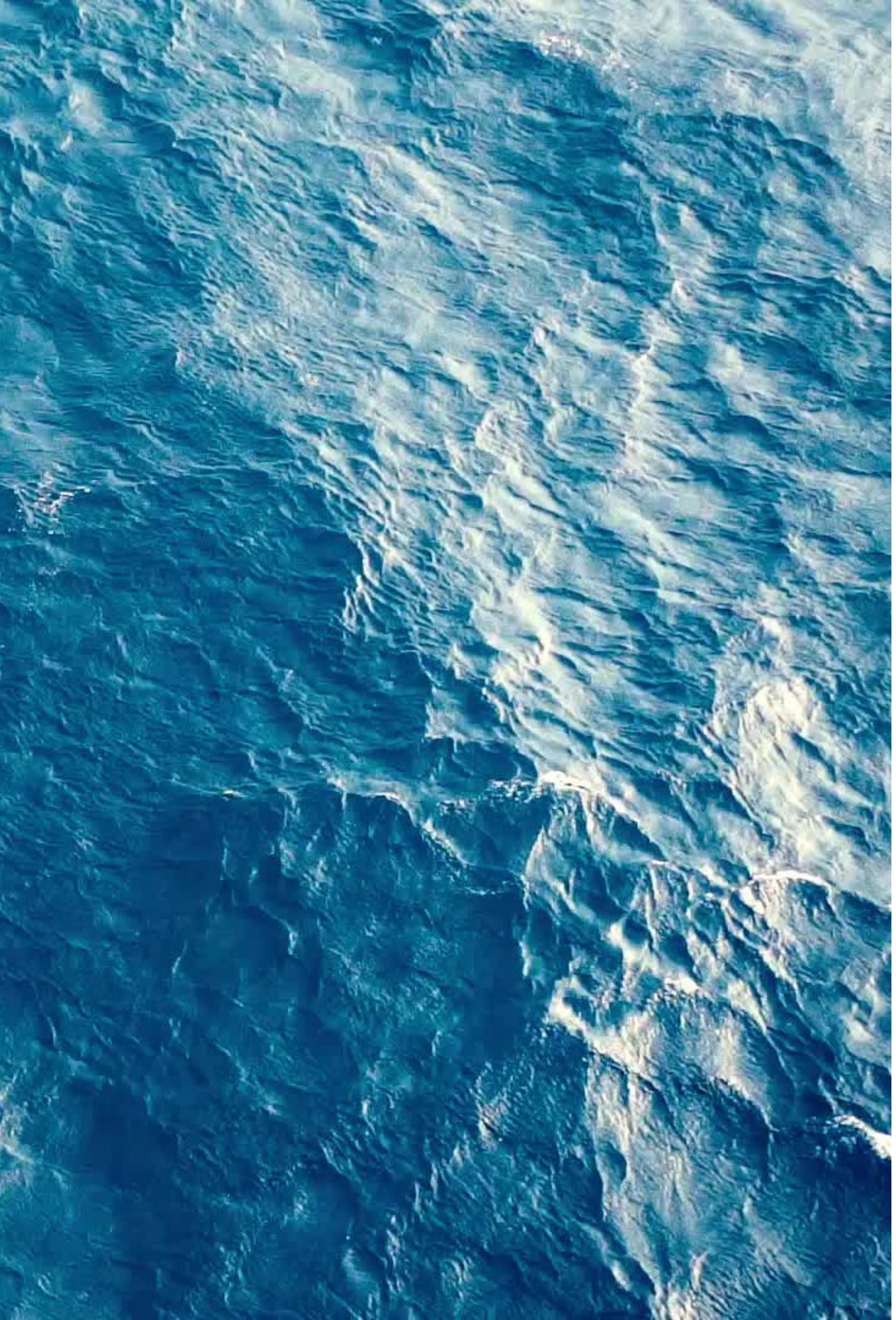
Bulk Air-Sea Gas Flux Formulae

$$\text{Sea-to-Air Flux} = K\,(C_w - SP_a)$$

Describes air-water gas transfer as a (molecular + turbulent) diffusive process. Net flux is “down gradient” and proportional to the gradient.

A broken surface



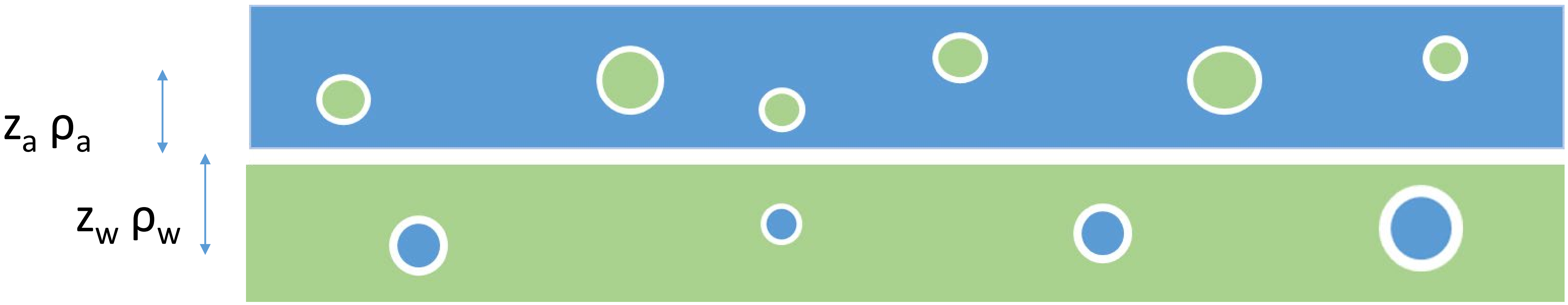


Counter gradient transport; a recipe

- Ocean is undersaturated in a highly soluble gas
- A strong dry air flow over the ocean
- Strong wind lifts sea spray from the ocean
- Sea spray droplets shrink in the dry atmosphere
- Shrinkage supersaturates the gas in the particles
- Particles return to the sea surface with less gas than they started

- Gas has been transferred from sea-to-air in an undersaturated ocean

A broken surface and asymmetry



A bubble or droplet experiences a different static pressure to the sea surface and that changes the dynamics. Changes the appropriate equation
e.g. for bubble-mediated transfer

$$\text{Bubble-Mediated Sea-to-Air Flux} = K\,(C_w - Sp_a(1 + \Delta))$$

Transfer Velocity Parametrisations

- Since Kanwisher (1963), transfer velocity for poorly soluble gases is proportional to the square of the wind speed
- Generally we are comfortable with k_w proportional to $Sc^{-1/2}$

$$k_w = 0.254\ U^2\ (660/Sc)^{1/2}$$ (Ho *et al.*, 2006)

- Why sweat the detail?

“All models are wrong but some are useful”

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We use models because they are useful

Since they are inevitably wrong, we need to understand the implications of the errors

Is the model sufficient at a regional and seasonal scale?

No!

Carbon isotope evidence for the latitudinal distribution and wind speed dependence of the air–sea gas transfer velocity

By NIR Y. KRAKAUER1∗ , JAMES T. RANDERSON2, FRANC¸ OIS W. PRIMEAU2, NICOLAS GRUBER3 and DIMITRIS MENEMENLIS4, [1]*Department of Earth and Planetary Sciences, University of California, Berkeley, CA 94720, USA;* [2]*Department of Earth System Science, University of California, Irvine, CA 92697, USA;* [3]*Environmental Physics, Institute of Biogeochemistry and Pollution Dynamics, ETH Zurich, Zurich, Switzerland;* [4]*Jet Propulsion Laboratory, Pasadena, CA 91109, USA*

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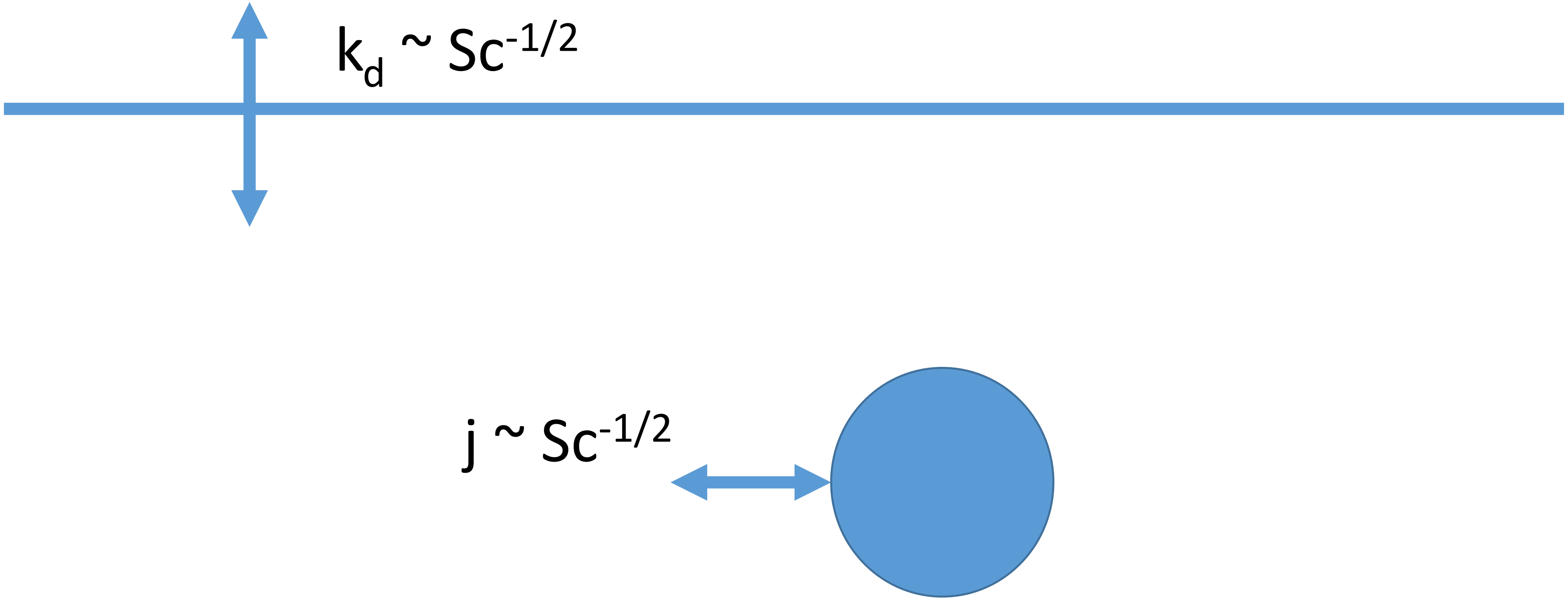
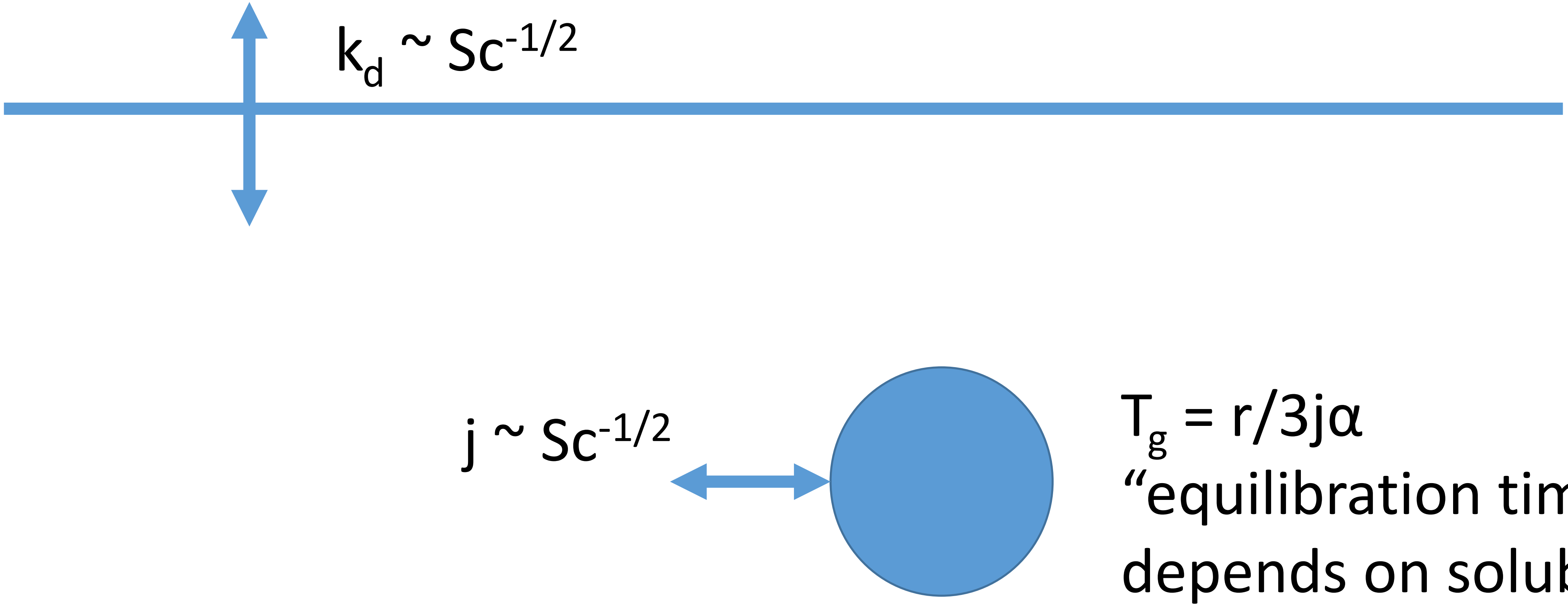
Solubility



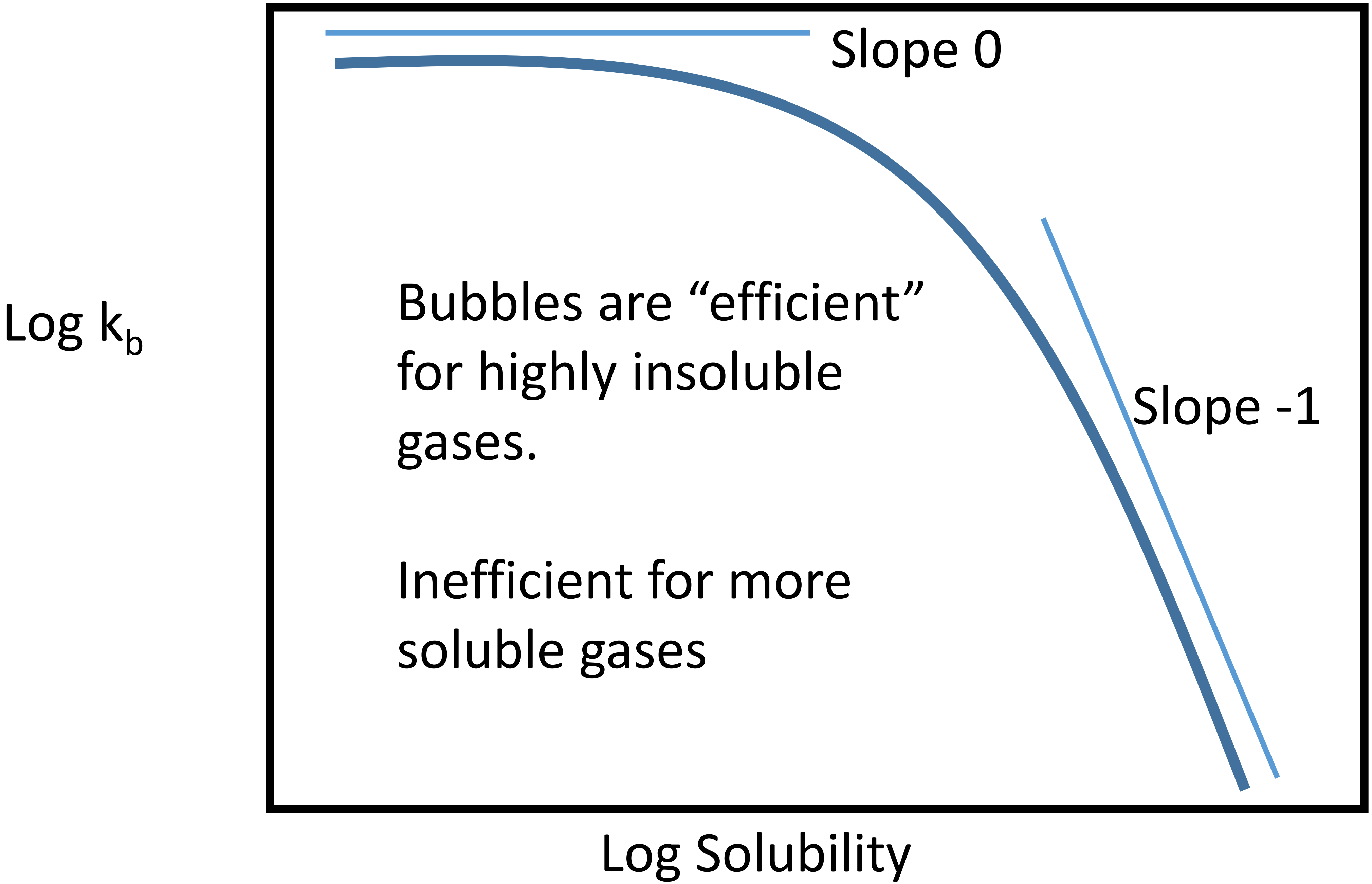
Solubility: Bubbles "lose drive" with a characteristic time scale

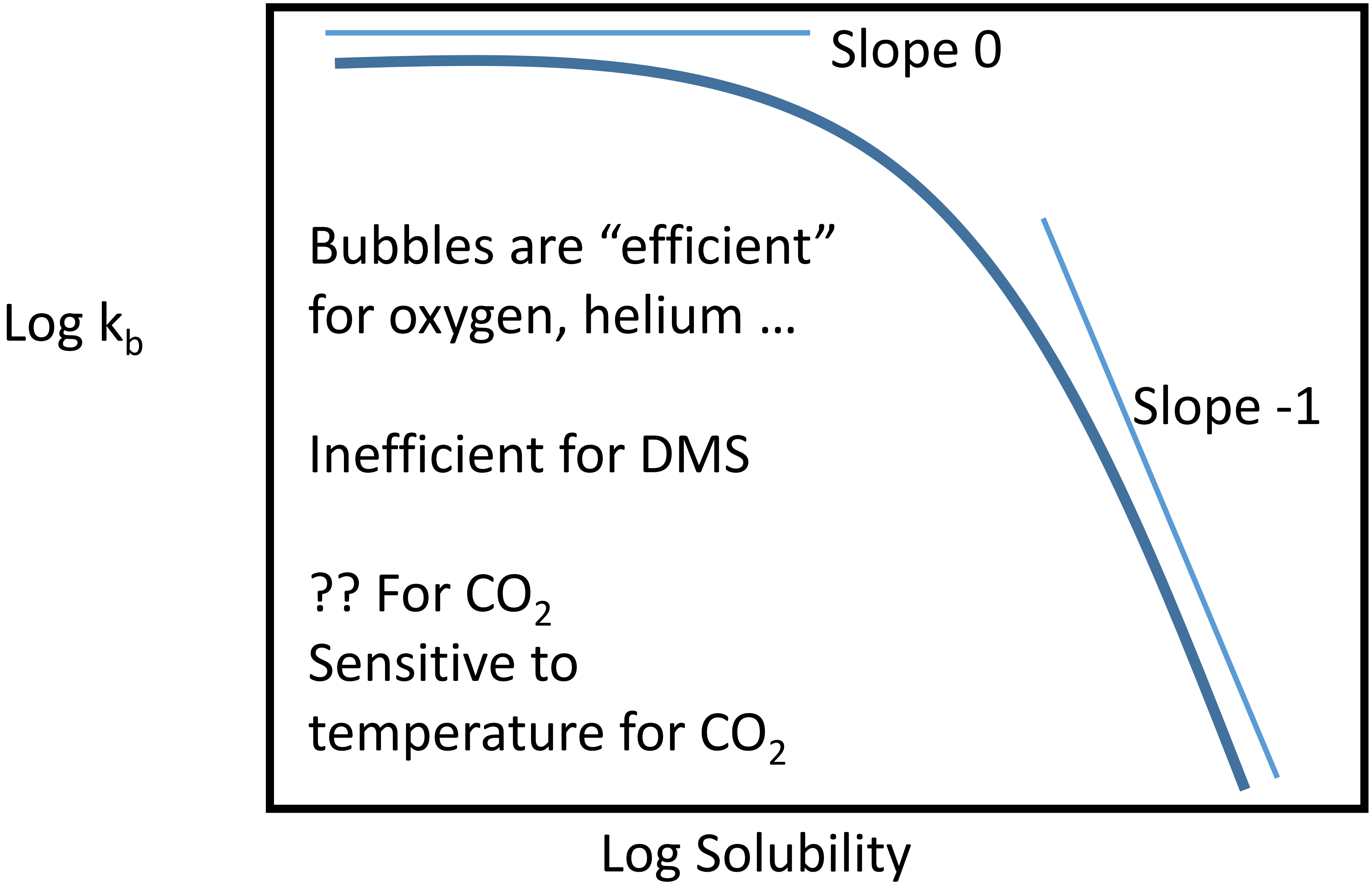


$T_g = r/3j\alpha$

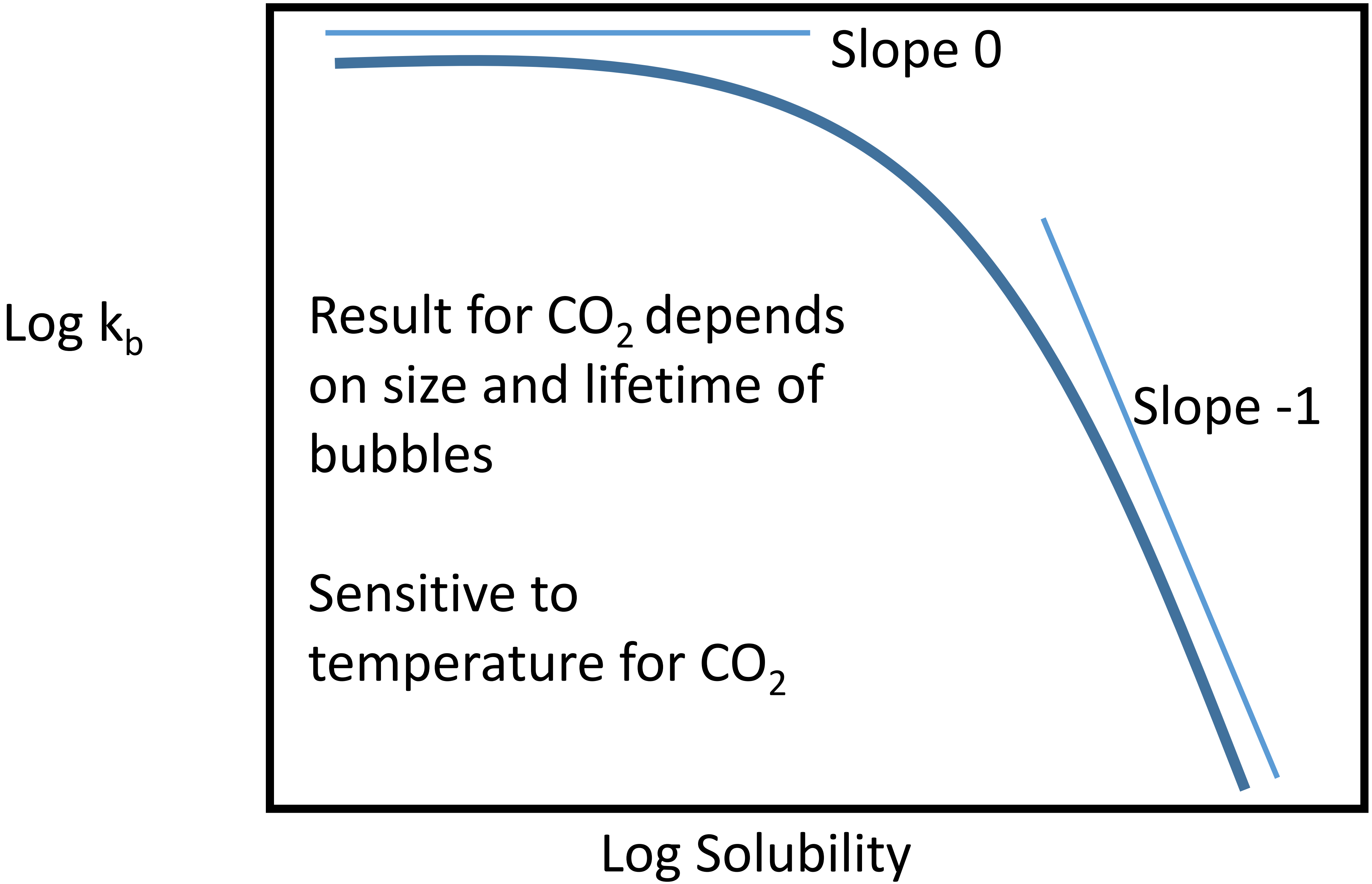
"equilibration time scale"

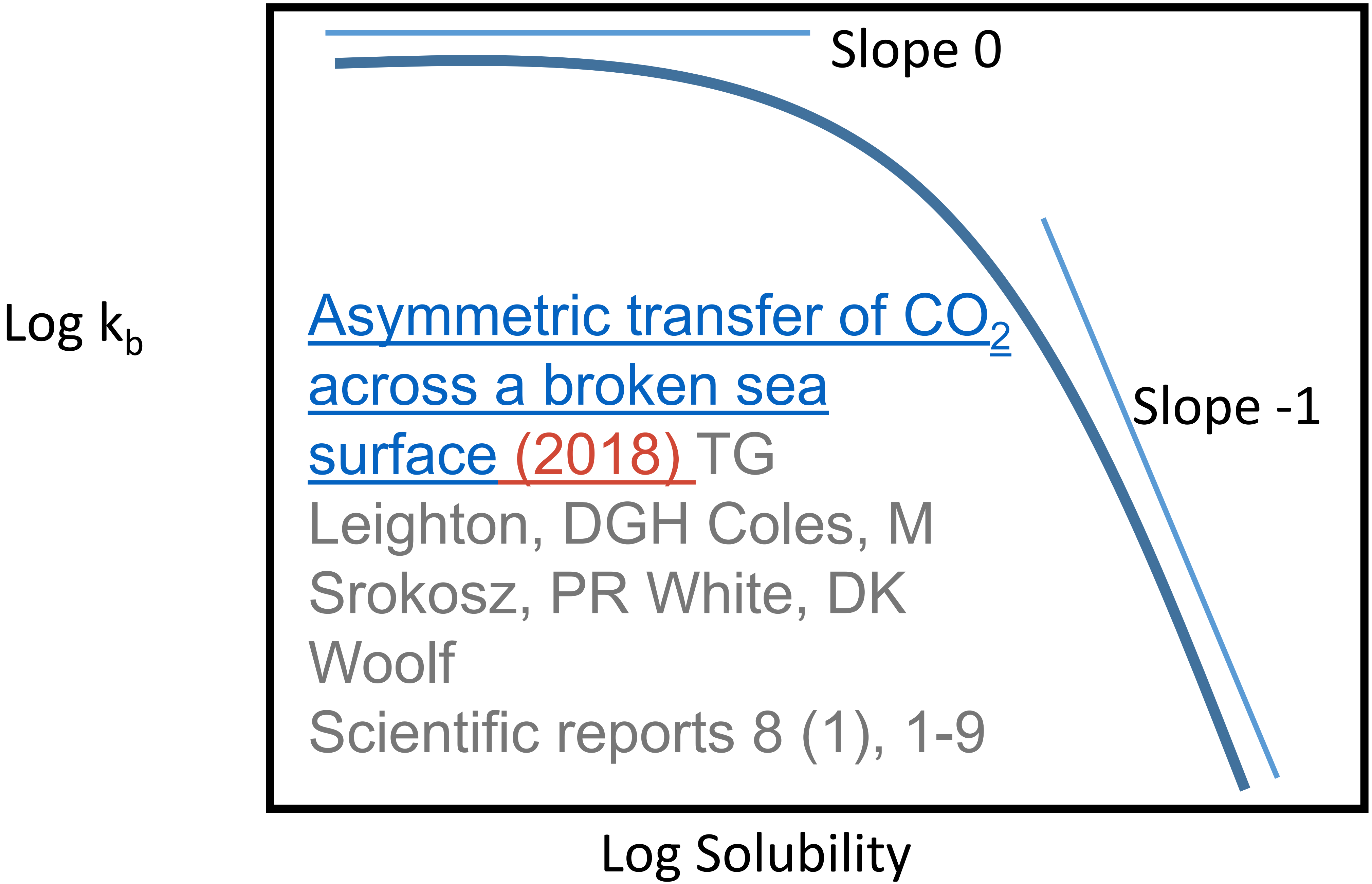
depends on solubility


Slope 0
Slope -1
Bubbles are "efficient" for highly insoluble gases.
Inefficient for more soluble gases
Log k_b
Log Solubility



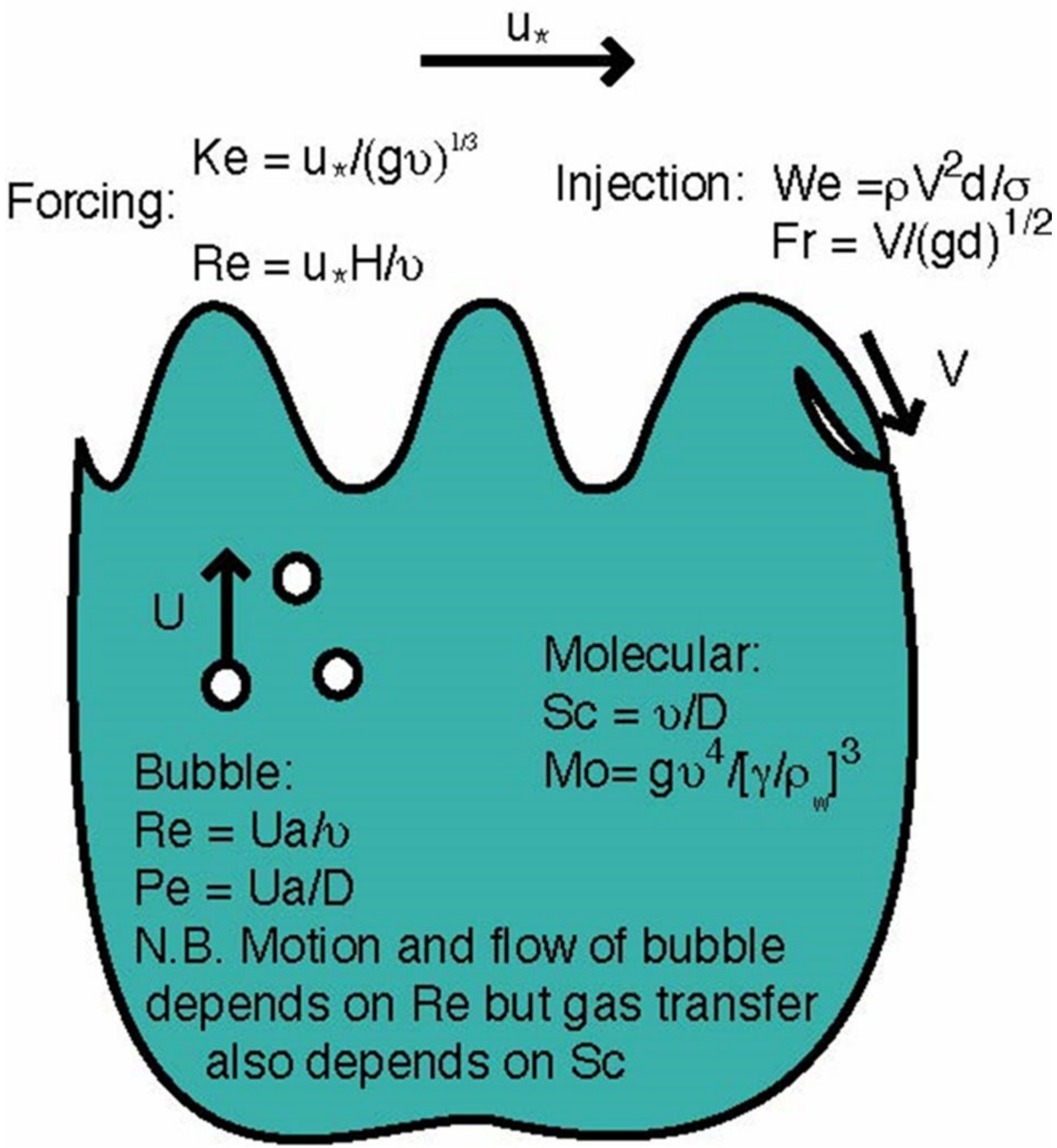
Slope 0
Bubbles are "efficient"
for oxygen, helium …
Inefficient for DMS
?? For CO_2
Sensitive to
temperature for CO_2
Slope -1
Log k_b
Log Solubility


Slope 0
Slope -1
Log k_b
Result for CO_2 depends on size and lifetime of bubbles
Sensitive to temperature for CO_2
Log Solubility



Asymmetric transfer of CO_2 across a broken sea surface (2018) TG Leighton, DGH Coles, M Srokosz, PR White, DK Woolf

Scientific reports 8 (1), 1-9



Wind and Sea State

- Wind speed, sea state and temperature influence bubble-mediated transfer at a range of scales.
- Deike and collaborators

Go Calculate!

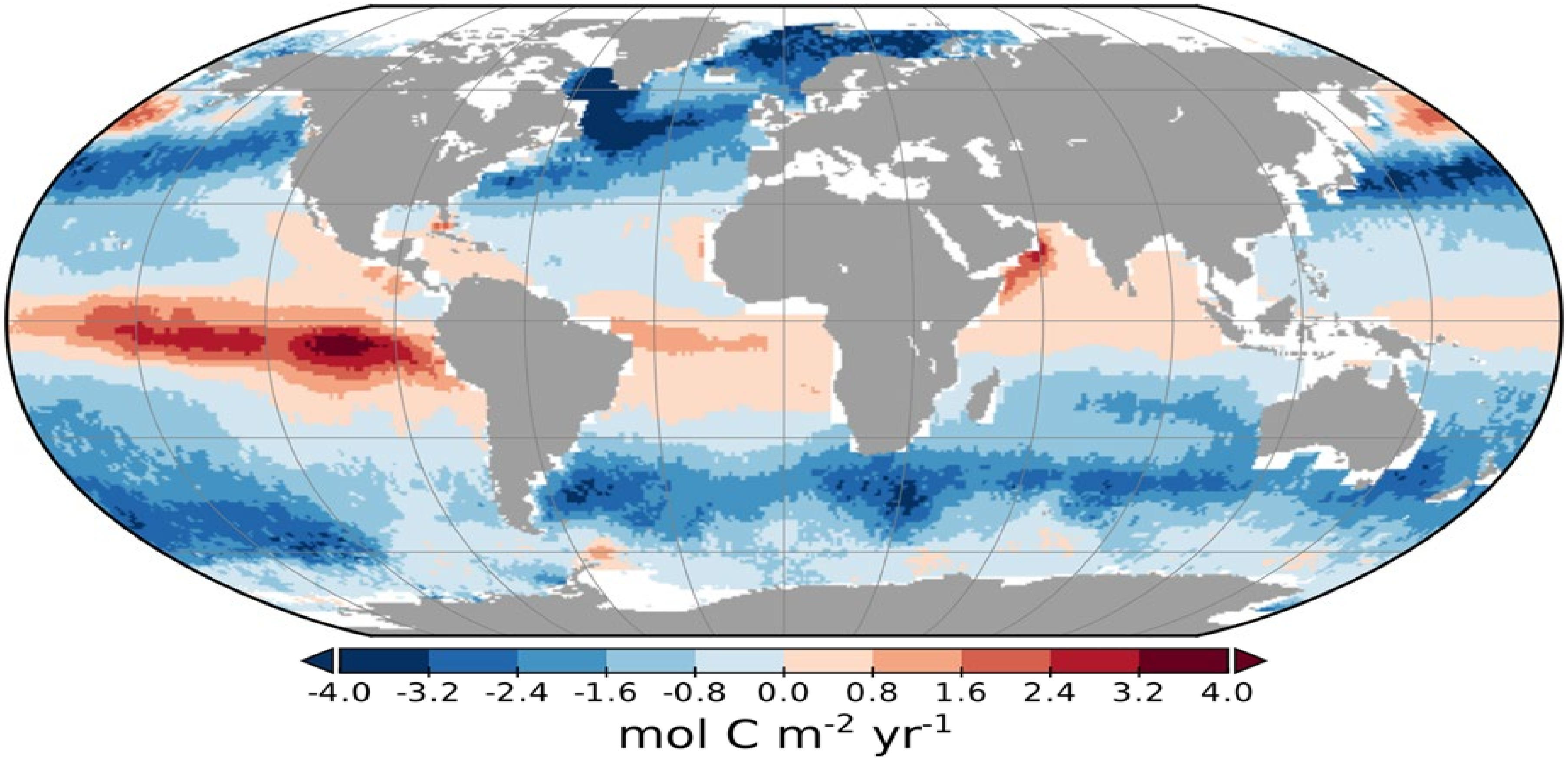
FluxEngine Python library version (v4.0.7) https://pypi.org/project/fluxengine/

Github location for all code (v4.0.7) https://github.com/oceanflux-ghg/FluxEngine

Papers

Holding et al 2019 https://os.copernicus.org/articles/15/1707/2019/

Shutler et al 2016 https://journals.ametsoc.org/view/journals/atot/33/4/jtech-d-14-00204_1.xml



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