

## **FORECASTING DIFFUSIVE FORMATION OF FREE-GAS METHANE LAYERS IN SEA SEDIMENTS**

**Denis S. Goldobin\***

**Department of Mathematics, University of Leicester, Leicester LE1 7RH, UK  
Institute of Continuous Media Mechanics, UB RAS, Perm 614013, Russia**

**Stephen J. Hunter, Alan M. Haywood**

**School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK**

**Nikolai V. Brilliantov, Jeremy Levesley**

**Department of Mathematics, University of Leicester, Leicester LE1 7RH, UK**

**Mike A. Lovell**

**Department of Geology, University of Leicester, Leicester LE1 7RH, UK**

**Andy J. Ridgwell**

**School of Geographical Sciences, University of Bristol, Bristol BS8 1SS, UK**

**Christopher A. Rochelle, Peter D. Jackson, John G. Rees**

**British Geological Survey, Keyworth, Nottingham NG12 5GG, UK**

### **ABSTRACT**

We study diffusive transport of aqueous methane in sea sediments, which is important for formation of methane hydrate and gas deposits and has even been claimed to be principal methane transport mechanism for some geological systems. The isothermal diffusion law (Fick's law),  $\mathbf{J} = -D\nabla X$ , which is employed in the literature for investigations on methane hydrate, is shown to significantly deviate from the actual diffusion law, accounting for the non-Fickian contributions due to (i) temperature gradient (by virtue of thermodiffusion *or* "Soret effect") and (ii) gravitational segregation. We focus our study on the mass transport in the bubbly (free-gas) zone and report that molecular diffusion (with non-Fickian contributions) can solely lead to formation of the free-gas zone. This free-gas zone can be formed independently of the presence of the hydrate stability zone and/or hydrate in it and can create bottom simulating reflector, not associated with hydrates. We calculate world maps of conditions for the formation of the free-gas zone in diffusion-dominated sediments for expected values of the thermodiffusion constant.

*Keywords:* free-gas zone, methane hydrate prospecting, thermodiffusion, sea sediments, bottom simulating reflector

### **NOMENCLATURE**

$D$  Molecular diffusion coefficient [ $\text{m}^2/\text{s}$ ]  
 $G$  Geothermal gradient [ $\text{K}/\text{km}$ ]

$g$  Gravity,  $9.8 \text{ m/s}^2$

$H$  Sea depth [ $\text{m}$ ]

$J$  Diffusive flux of  $X$  [ $\text{m}/\text{s}$ ]

---

\* Corresponding author: Phone: +44 116 252 5693 Fax +44 116 252 3915 E-mail: dg124@le.ac.uk, Denis.Goldobin@gmail.com

$M_2$  Effective molar mass of methane in water,  
 $M_2 = M_{\text{CH}_4} - N_1 M_{\text{H}_2\text{O}}$ ,  $N_1$  is the number of the  
water molecules replaced by the methane molecule  
in the solution;  $M_2 = -24.3$  g/mol

$R$  Universal gas constant, 8.31 J/(mol K)

$T$ ,  $T_{\text{sf}}$  Temperature and the seafloor temperature,  
respectively, [K]

$X$  Molar fraction of methane in aqueous solution  
[dimensionless]

$X_b$  Molar fraction of free-gas methane in the  
bubbly fluid in pores [dimensionless]

$z$  Depth in sediments, below the seafloor [m]

$\alpha$  Thermodiffusion constant [dimensionless]

BSR Bottom simulating reflector

HSZ Hydrate stability zone

FGZ Free-gas zone

## INTRODUCTION

In geological systems, one of important substance transport mechanisms is diffusion. This mechanism is widely accepted to be of particular importance for the formation of methane hydrate deposits in sea sediments [1–6]. Indeed, the methane hydrate is mechanically immobilized by porous matrix, as any solid matter, and bubbles of gaseous methane are trapped in pores by the surface tension forces (any moving bubbles experience splitting until their size becomes comparable to the pore size [7], and for the pore-sized bubbles the buoyancy force is overwhelmed by the surface tension force for the pore diameter up to 1 mm, as estimated in [8, 9]). Thus, the methane mass transfer relative to the pore matrix can be mainly associated with its aqueous solution. Transport of the solute mass is comprised by the hydrodynamic fluid flow and the diffusion. Both of them are considered to be important for marine hydrate deposits [1–6]. However, some studies suggest that for some geological systems hydrodynamic (advective) transfer is weak compared to the molecular diffusion [6].

The description of the advective transport by an ascending vertical liquid flux is straightforward and well established. However, this is not the case for the diffusive transport of mass in this system. Currently, the studies available in the literature adopt the Fick's law for the molecular diffusion

$$\vec{J} = -D\nabla X, \quad (1)$$

where  $X$  is the molar fraction of the solute,  $D$  is

the diffusivity coefficient, and  $\vec{J}$  is the flux of  $X$ . This description is valid for isothermal media in the absence of any external forces. Meanwhile, sea sediments on the spatial scale of methane-hydrate deposit are characterized by

- temperature inhomogeneity (geothermal gradient) and
- gravitational force.

The temperature gradient drives diffusive flux of molecules, because generally, in non-uniform temperature fields, the distribution of solute tends to be non-uniform as well. This so-called effect of thermodiffusion is also known as ‘‘Soret effect’’ [10, 11]. In the presence of hydrate or gas bubbles, the methane concentration equals the solubility which depends on temperature and pressure. Therefore, the inhomogeneity of concentration, which drives the Fickian diffusion, is of the same order of magnitude as the inhomogeneity of temperature, which creates the thermodiffusive flux. Hence, the Fickian and thermodiffusive fluxes should be of comparable strength.

Additionally, gravity forces methane molecules to rise because they are lighter than the water molecules in the same volume. For better intuition on this effect, we notice, that the variation of the atmosphere density with height has similar nature and similar order of magnitude. One knows that this affect is practically non-observable on the laboratory scale and does not effect laboratory experiments, while it is important on 1 km scale in the atmosphere. Therefore, we should expect the gravitational segregation to be important on the scale of methane-hydrate deposits in marine sediments and account for it in modeling.

We refer to the sum of the thermodiffusive and gravitation-induced fluxes as ‘‘*non-Fickian flux*’’, as opposed to the Fickian flux (1).

In this paper we focus our consideration on the diffusive evolution of methane-bubble layers in sediments. Consideration of methane hydrates in the hydrate stability zone (HSZ) above this layer will be addressed elsewhere. Main reasons for that are

- We find that appearance of the free-gas zone (FGZ) can be independent from hydrates but owes to the non-Fickian diffusion [8, 9, 12], while nothing qualitatively similar can be observed for simplified law (1).
- We intend to treat this phenomenon in pure form without particular complications.

- The evolution of the bubble mass in FGZ is independent of the distribution of the methane hydrate in the HSZ [12]. The information on the position of the base of HSZ is sufficient and used (for calculation of the position we utilize empirical formulae from [13]).

Unfortunately, the value of the thermodiffusion constant  $\alpha$  for the aqueous solution of methane cannot be found in the literature. This is non-surprising in light of the fact that methane is weakly soluble in water and experiments on thermodiffusion are extremely difficult on laboratory space and time scales. There is also no reliable general theory providing an analytical expression for the thermodiffusion constant. Nevertheless, some rough estimations, which yield correct values of the thermodiffusion constant for the dilute aqueous solutions of methanol ( $\alpha \approx 1.5$  [14]), ethanol ( $\alpha \approx 3.0$  [15]), and isopropanol ( $\alpha \approx 4.5$  [16]), can be performed. These estimations suggest the thermodiffusion constant for CH<sub>4</sub>–H<sub>2</sub>O system to be  $\alpha \approx 1.8$ . In this paper we report world maps of diffusive regimes calculated for  $\alpha$  in the range 0.5–2.5, which surely contains the actual value of  $\alpha$ .

Finally, we discuss implications of the reported results for detection of methane hydrates and the bottom simulating reflector (BSR).

## DIFFUSIVE TRANSPORT

Under non-isothermal conditions and gravitational force, the diffusive flux of the molar fraction  $X$  reads [8]

$$\vec{J} = -DX \left[ \frac{\nabla X}{X} + \alpha \frac{\nabla T}{T} - \frac{M_2 \vec{g}}{RT} \right], \quad (2)$$

where  $T$  is temperature;  $\alpha$  is the *thermodiffusion constant*;  $M_2 = -24.3$  g/mol is the effective molar mass of methane,  $M_2 = M_{\text{CH}_4} - N_1 M_{\text{H}_2\text{O}}$ ,  $N_1$  is the number of the water molecules replaced by the methane molecule in the solution;  $\vec{g}$  is the gravity;  $R = 8.31$  J/(mol K) is the universal gas constant. Here we have neglected the volumetric fraction of bubbles in pores which is reasonable for real systems [1–6]. Within FGZ, methane molar fraction  $X$  equals the solubility and, therefore, is not an independent value, but a function of temperature and pressure. Hence the diffusive flux is constant in time as long as temperature and pressure are constant. In Fig. 1

we plot the Fickian and non-Fickian parts of the diffusive flux for typical conditions in order to demonstrate importance of the latter.

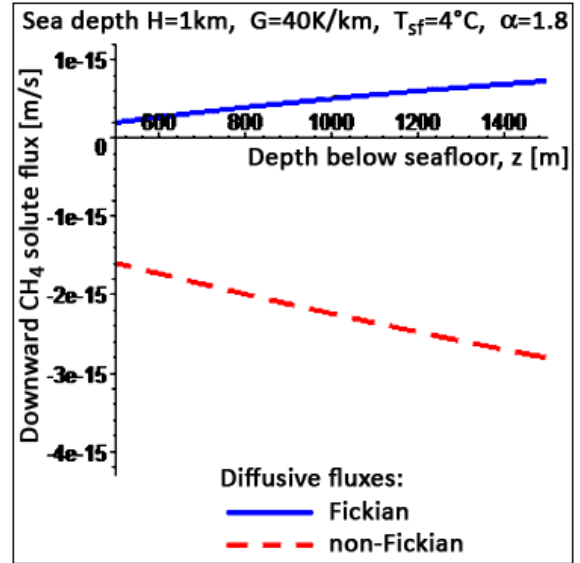


Figure 1: Comparison of the Fickian and non-Fickian parts of the diffusive flux in the free-gas zone under conditions specified in the plot

The growth/depletion of bubbles, which serves as a mass sink/source for flux (2), is described by the equation

$$\frac{\partial X_b}{\partial t} = -\frac{\partial J}{\partial z}, \quad (3)$$

where  $X_b$  is the molar fraction of methane gas in the bubbly fluid (*i.e.*, in the system bubbles and liquid) in pores and  $z$  is the depth below the seafloor.

Analysis of equations (2) and (3) [8, 12]<sup>1</sup> reveals 4 possible diffusive regimes sketched in Fig. 2:

In *regimes A1* and *A2*, methane diffuses from sediments upwards; bubbles in FGZ experience depletion and tend to disappear. In regime *A1* no HSZ is present. In regime *A2*, HSZ is enriched by methane from beneath this zone, the capacity of the methane hydrate deposit is enhanced.

In *regime B*, which is most remarkable, diffusion drives methane into the free-gas zone. The base of FGZ is the depth where the diffusive flux of the saturated solution (2) turns zero. The

<sup>1</sup> In [12] the diffusion under unsaturated conditions, in zones without hydrate and methane bubbles, is also considered.

diffusive influx of the mass to bubbles is maximal next to this base, but not next to the base of HSZ. This means that, given other solute transport mechanism are overwhelmed by diffusion, the gas BSR is stronger than the hydrate BSR.

In *regime C*, methane diffuses downwards into sediments without formation of FGZ<sup>2</sup>. Hydrate in HSZ suffers stronger depletion in comparison to the case of A2; the capacity of the hydrate deposit (if any) is diminished.

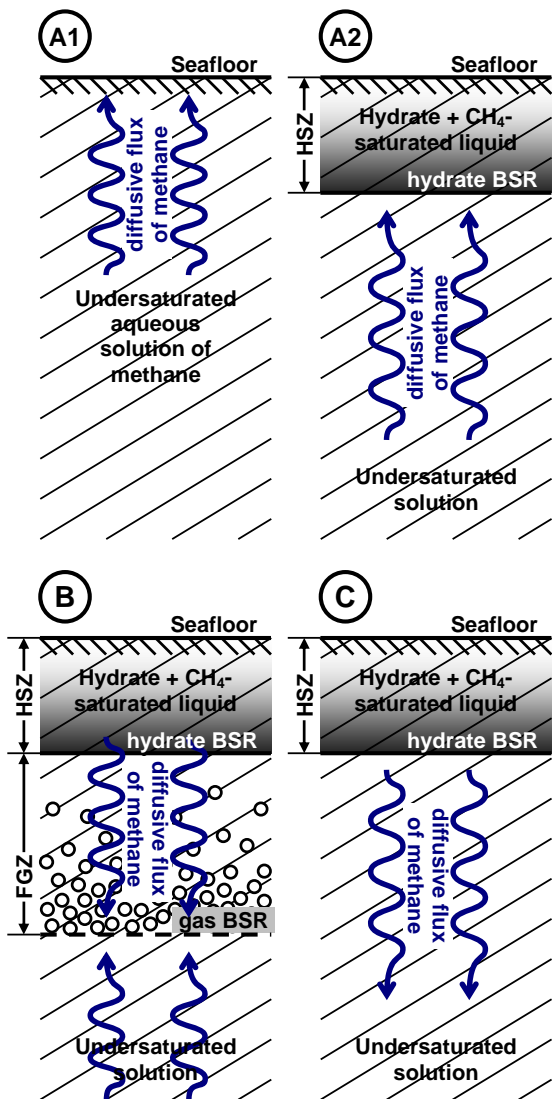


Figure 2: Regimes of diffusive transport of solute mass in free-gas stability zone

<sup>2</sup> In real geological systems, sediments are limited from below by impermeable massifs which block further diffusive transport of methane and thus may create gas accumulation zone. However, such kind phenomena are beyond the scope of our study.

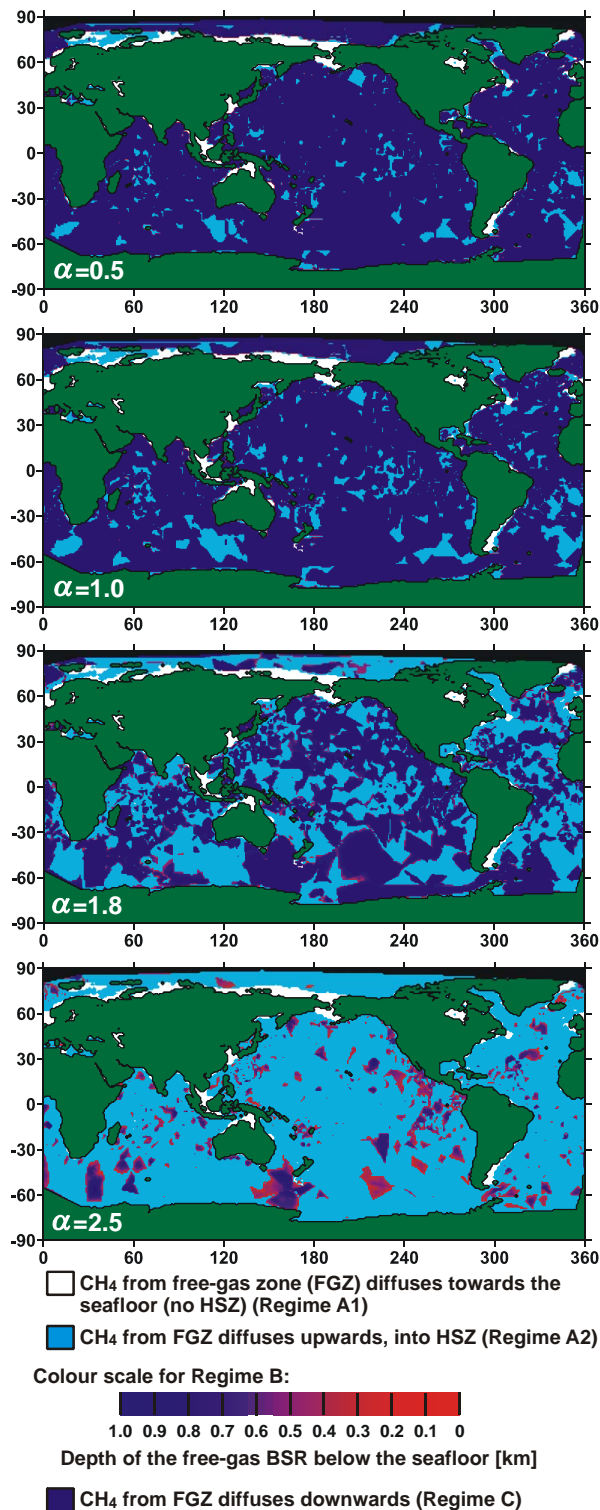


Figure 3: World maps of conditions for the formation of the free-gas zone in diffusion-dominated sediments for specified values of thermodiffusion coefficient  $\alpha$  ( $\alpha \approx 1.8$  is most expected). Regimes A1, A2, B, and C are presented in Fig. 2.

## WORLD MAP OF CONDITIONS FOR FORMATION OF FREE-GAS ZONE IN SEA SEDIMENTS

We employ equations (2) and (3) and the mathematical models for the gas solubility derived in [8] (they are also summarized in Appendix of [9]) for the global data on bathymetry, the seafloor temperature, and the geothermal gradient (see Appendix for details on these data). The resulting world maps of conditions for different regimes are presented in Fig. 3 for range of values of the thermodiffusion constant  $\alpha$ . Notice, we present the map of conditions; the corresponding regime can be really observed only when the source of methane in the site is provided.

For small  $\alpha$  regime C is dominating; methane typically diffuses deeper into sediments, with rare exceptions, regimes A1 and A2. Between the A1- and A2-areas and the C-area, there are transient areas of regime B with diffusion-formed FGZ. However, these areas are very narrow and nearly indistinguishable on the map with  $1^\circ$  resolution.

As  $\alpha$  increases, the A1- and A2-areas shrink, the C-area grows, and the B-area with diffusion-formed FGZ becomes distinguishable.

Intriguingly, the most expected value  $\alpha \approx 1.8$  yields the richest diversity of regimes: regimes A1, A2 and regime C are equally wide spread.

## CONCLUSION AND DISCUSSION

We have shown that, under conditions typical for sea sediments, Fick's law for diffusion essentially deviates from the actual law accounting for the thermodiffusion effect [10, 11] and gravitational segregation. Non-Fickian diffusion solely can result in the formation of the free-gas zone, which can be independent from the hydrate stability zone and/or the presence of hydrate in it.

Unfortunately, the value of the thermodiffusion constant for aqueous solutions of methane is not known experimentally and can be only roughly inferred theoretically. Nonetheless, any value of this constant from the admitted range of values leads to diffusive evolution which significantly differs from Fick's law.

World maps of possible diffusive regimes of the evolution of the free-gas zone are calculated for different values of  $\alpha$ .

There are important implications related to the detection of marine methane hydrates. A very small amount (*ca.* 1-2%) of gas bubbles is enough to change the sound speed in the massif and create reflection of seismic waves, bottom simulating

reflector (*e.g.*, see [17, 18]). It is typically assumed that hydrates are associated with the BSR. Indeed, for Fick's diffusion law, there are no mechanisms for formation of the free-gas zone other than contact to the zone of hydrate stability, where gas disappears having been transformed into hydrate. However, our theoretical findings suggest that for certain conditions the creation of gaseous methane horizons can be explained by thermodiffusion; formation of these horizons does not require the presence of the hydrate stability zone or the hydrates therein. This may be a reason why some BSRs seem to have no hydrate associated with them. The regime B area provides favorable conditions for thermodiffusion-formed BSRs.

Our results suggest also that some hydrate deposits may have no BSR at the bottom edge (as, *e.g.*, reported in [19]) because diffusion can lead to depletion of methane from the bubbly area as it does in regimes A2 and C. In this case, only the competition between the sedimentation rate (which creates the influx of methane mass from the hydrate zone to the free-gas one) and the diffusive depletion determines whether the BSR appears: this may happen for larger sedimentation rates.

## ACKNOWLEDGEMENTS

The work has been supported by NERC Grant no. NE/F021941/1.

## APPENDIX:

### INPUT DATA: BATHYMETRY, SEAFLOOR TEMPERATURE, AND GEOTHERMAL GRADIENT

The diffusion regime in sediments at certain location is governed by the temperature and pressure fields, which determine the solubility and govern the thermodiffusive drift. The pressure and temperature fields are determined by 3 parameters: (a) pressure at the seafloor *or* the sea depth (the pressure gradient is fixed for the hydrostatic pressure profile), (b) temperature at the seafloor, and (c) geothermal gradient.

The bathymetry and seafloor temperature data are taken from World Ocean Atlas 2005 [20] with grid  $1^\circ \times 1^\circ$  (see Fig. 4 (a) and (b)).

The data set for the geothermal gradient is taken from The Global Heat Flow Database [21]. The measurement locations providing information for calculation of the geothermal gradient are distributed inhomogeneously over the oceans (black points in Fig. 4(c)). For reconstruction of

the  $1^\circ \times 1^\circ$  grid of data, the linear interpolation was utilized; the results are presented in Fig. 4(c). Whilst more sophisticated interpolation techniques could have been used for the latter (e.g., Kriging interpolation) this was beyond the scope of this study.

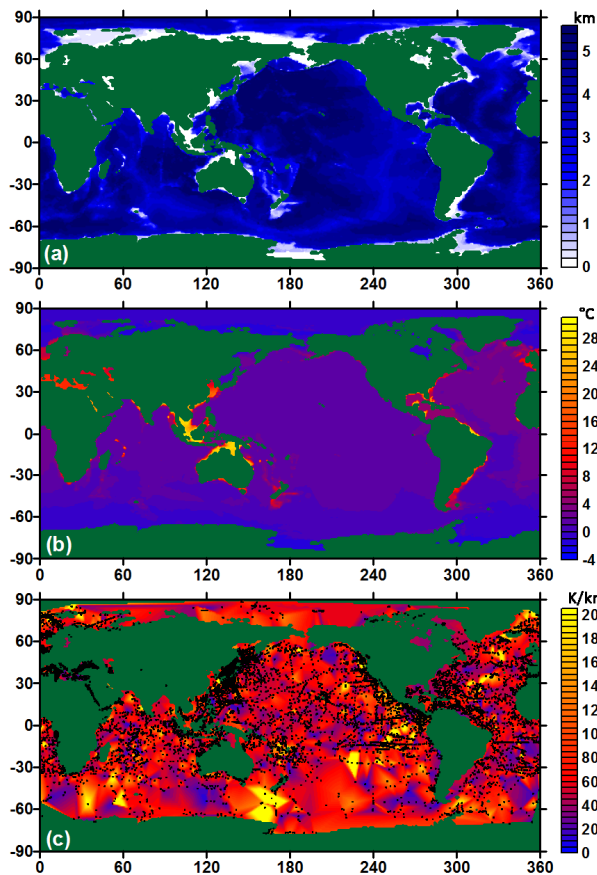


Figure 4: Maps of sea depth (a), seafloor temperature (b), and geothermal gradient (c) used for the derivation of the results presented in Fig. 3

## REFERENCES

- [1] Davie MK, Buffett BA. *A numerical model for the formation of gas hydrate below the seafloor*. J. Geophys. Res. 2001; 106:497–514.
- [2] Davie MK, Buffett BA. *A steady state model for marine hydrate formation: Constraints on methane supply from pore water sulfate profiles*. J. Geophys. Res. 2003; 108:2495.
- [3] Davie MK, Buffett BA. *Sources of methane for marine gas hydrate: inferences from a comparison of observations and numerical models*. Earth and Planetary Science Letters 2003; 206:51–63.
- [4] Archer D. *Methane hydrate stability and anthropogenic climate change*. Biogeosciences 2007; 4:521–544.
- [5] Garg SK, Pritchett JW, Katoh A, Baba K, Fujii T. *A mathematical model for the formation and dissociation of methane hydrates in the marine environment*. J. Geophys. Res. 2008; 113:B01201.
- [6] Haacke RR, Westbrook GK, Riley MS. *Controls on the formation and stability of gas hydrate-related bottom-simulating reflectors (BSRs): A case study from the west Svalbard continental slope*. J. Geophys. Res. 2008; 113: B05104.
- [7] Lyubimov DV, Shklyayev S, Lyubimova TP, Zikanov O. *Instability of a drop moving in a brinkman porous medium*, Physics of Fluids 2009; 21:014105.
- [8] Goldobin DS, Brilliantov NV, *Diffusive migration of mass in bubbly media, unpublished, 2011. E-print arxiv:1011.5140*.
- [9] Goldobin DS, et.al. *Diffusive Accumulation of Methane Bubbles in Deep-Water Sediments, unpublished, 2011. E-print arXiv:1011.6345*.
- [10] Sorét C. *Sur l'état d'équilibre que prend au point de vue de sa concentration une dissolution saaline primitivement homogène dont deux parties sont portées a des températures différentes*. Arch. Geneve 1879; 3:48.
- [11] Jones RC, Furry WH. *The separation of isotopes by thermal diffusion*. Rev. Mod. Phys. 1946; 18:151–224.
- [12] Goldobin DS, Brilliantov NV, *Non-Fickian Diffusion to Form Horizons of Weakly Soluble Substances in Earth's Crust, unpublished, 2011*.
- [13] Moridis GJ. *Numerical studies of gas production from methane hydrates*. Society of Petroleum Engineers Journal 2003; 32(8):359–370.
- [14] Tichacek LJ, Kmak WS, Drickamer HG. *Thermal Diffusion in Liquids; The Effect of Non-ideality and Association*. J. Phys. Chem. 1956; 60(5):660–665.
- [15] Kita R, Wiegand S, Luettmmer-Strathmann J. *Sign change of the Soret coefficient of poly(ethylene oxide) in water/ethanol mixtures observed by thermal diffusion forced Rayleigh scattering*. J. Phys. Chem. 2004; 121:3874.
- [16] Poty P, Legros JC, Thomaes G. *Thermal diffusion in some binary liquid mixtures by the flowing cell methods*. Z. Naturforsch. A 1974; 29A:1915.
- [17] MacKay ME, Jarrard RD, Westbrook GK, Hyndman RD. *Origin of bottom-simulating reflectors: Geophysical evidence from the Cascadia accretionary prism*. Geology 1994; 22:

459–462.

[18] Hovland M, Francis TJG, Claypool GE, Ball MM. *Strategy for scientific drilling of marine gas hydrates*. JOIDES Journal 1999; 25:20–24.

[19] Ecker C, Dvorkin J, Nur A, *Estimating the amount of hydrate and free gas from surface seismic*. SEG Technical Program Expanded Abstracts 1998; 17:566–569.

[20] Collier MA, Durack PJ. *The CSIRO netCDF version of the NODC World Ocean Atlas 2005*. In: CSIRO Marine and Atmospheric Research Papers (Series), 2006. Paper no. 15.

[21] *The Global Heat Flow Database of The International Heat Flow Commission*

<http://www.heatflow.und.edu>.