

Master's Thesis
Academic Year 2021

**Numerical investigation on electrical
and thermal characteristics in organic
semiconductor films from the aspect of
variable range hopping**

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School of Integrated Design Engineering,
Keio University

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Table of Contents

Acknowledgements	ii
1 Introduction	1
1.1 Organic semiconductors	1
1.1.1 Background	1
1.1.2 Organic materials	2
1.1.3 Charge carrier transport	4
1.1.4 The einstein relation	5
1.1.5 Gaussian density of states	6
1.1.6 Thermal diffusion	6
1.2 Objectives of this thesis	8
2 Julia	10
2.1 Introduction	10
2.2 Performances	10
2.3 Notebooks	10
2.4 Code implementation	11
2.4.1 Packages	11
2.4.2 Code adaptation	12
2.5 Conclusion	15
References	16
Appendix	18
A Appendix 1	18

List of Figures

1.1	Evolution of the performance for some organic semiconductors [17]	2
1.2	σ and π bonds in ethene [3]	3
1.3	$\pi - \pi^*$ bonding [3]	3
1.4	Hopping transport	4
1.5	Gaussian DOS, $\sigma = 1$	7
1.6	Gaussian DOS, $\sigma = 3$	7
2.1	Julia benchmark	11

Chapter 1

Introduction

1.1 Organic semiconductors

1.1.1 Background

For the past century, inorganic materials have been at the heart of the semiconductor industry, with elements such as silicon, germanium or gallium arsenide. But, the industry turned itself to new devices and organics semiconductors are one of them. Their different set of properties: very flexible, low cost, less polluting helped them to gain interest.

More specifically, in 1977, the first highly conducting polymer was found, chemically doped polyacetylene, was discovered [5]. Such materials can be easily processed by techniques already known in the industry: vacuum evaporation, solution casting... But a better understanding and control of the self-assembly of molecules, as well as a booming research field, have increased greatly the performances, reaching the charge carrier mobility of amorphous silicon for some of them (fig. 1.1). The high diversity of geometry within the material allows a better tuning of the characteristic of the semiconductor to the use. One greater advance is the combination of both organic and inorganic molecules, particularly with perovskite. The high mobility of inorganic material combined with the more flexible geometry of organic ones make possible the creation of devices that reaches the performances of single-crystal silicon [12, 17].

This new development has been seen through the recent appearance of organic devices in the market. The more flagrant one is OLED devices, they offer a better diversity (flexible screens) with increased performance (higher color fidelity, darker black and better contrast) as well as consumption. But it's also used in professional devices such as OTFT [11], laser diode [16], ...

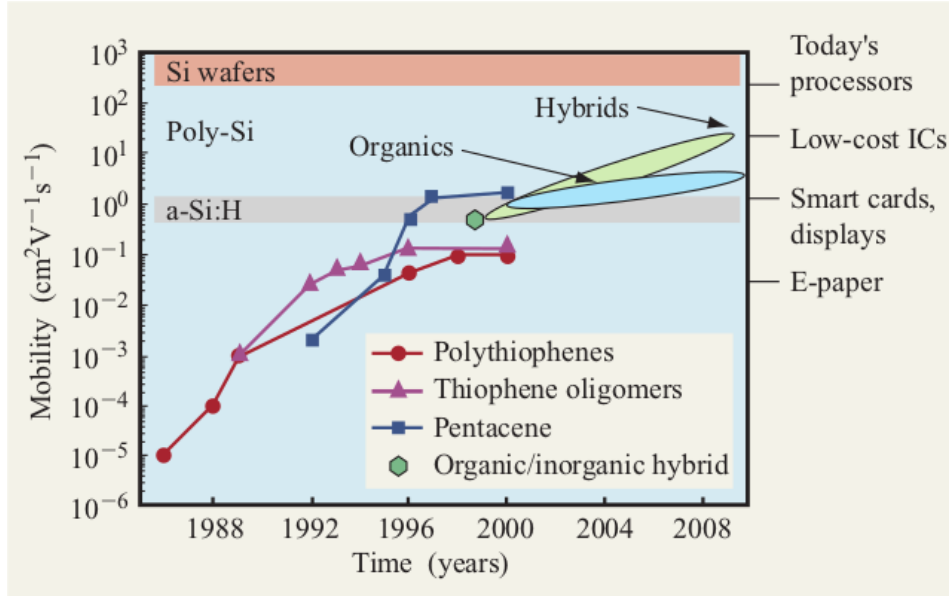
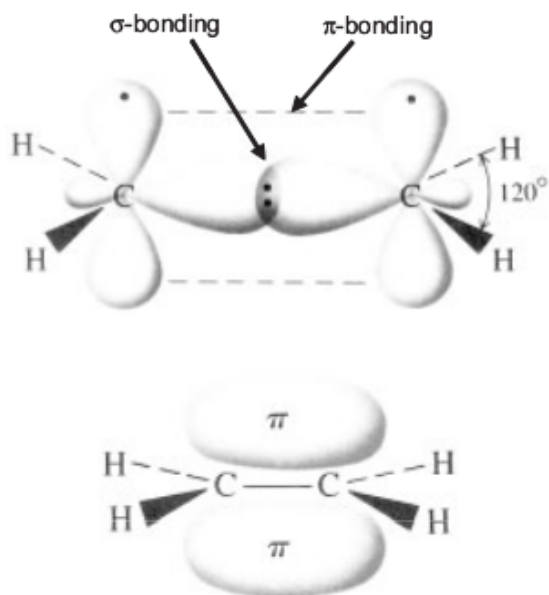
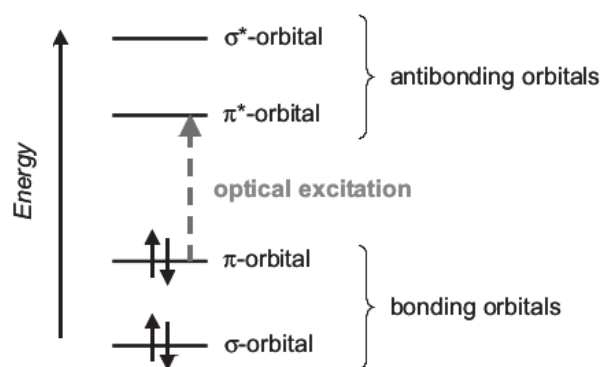


Figure 1.1: Evolution of the performance for some organic semiconductors [17]

1.1.2 Organic materials

Organic molecules are bound to each other by $\pi - \pi$ bonding which is the result of p_z -orbitals of sp^2 -hybridized C-atoms in the molecules (fig. 1.2). Such bonding is way weaker compared to the classic σ -bonding in the molecule backbone. Therefore, the $\pi - \pi^*$ transitions have a typical lower gap: around 1.5 eV–3 eV (fig. 1.3). Their crystallinity ranges from single-crystal (pentacene, rubrene crystals) [19] to completely amorphous semiconductors like α -NPD [18].

Those weaker Van der Waals bonding lead to more localized charge carrier in the material. Most of the time, charge carriers do not evolve in bands like in Si, but are subject to a HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) states. It results in a much weaker wavefunction delocalization for the neighboring molecules [3]. Instead of band transport, organic materials are subject to hopping transport: a charge carrier hop from a site to an other and thus participate to the general conduction (fig.1.4). The difference between trapping and hopping state is in the recombination and release rate. If the former one is higher than the latter one, the state is a recombination center, otherwise, it is a trap. In this model the difference between trapping states and recombination states can be thin.

Figure 1.2: σ and π bonds in ethene [3]Figure 1.3: $\pi - \pi^*$ bonding [3]

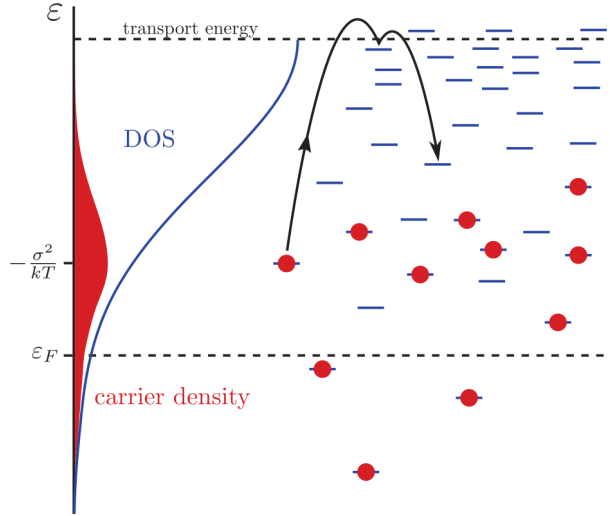


Figure 1.4: Hopping transport

Organic semiconductors are divided between polymers and small molecules. The separation occurs at 1000 molecular weights. Small molecules can achieve high crystallinity but are less soluble in solvent, requiring dry processes such as vacuum deposit, which is more difficult and more costly. On the other hand, polymers are easier to make in organic solvents. Even though small molecules show better performances, they're less stable than polymers in atmospheric conditions.

1.1.3 Charge carrier transport

As it has been said before, disordered organic semiconductors are the place of localized charge carrier transport, and in the 70's, a theory has been proposed involving tunneling between near states [1]. Such theory has been previously discovered by Mott based on the dependence of the mobility on the temperature: an increasing temperature leads to an increasing mobility. This relation has been verified in practical devices [1, 8].

In the variable range hopping theory (VRH), the displacement between two states for a charge carrier is determined only by the difference in energy W and in position R , thus highlighting the fact that our system is resolutely in 4D. On top of that, we assume that the system is so disordered that these two quantities are decoupled. The jump frequency is usually described by the Miller-Abrahams formalism [10]:

$$\nu = \nu_0 \begin{cases} \exp\left(-2\alpha R_{ij} - \frac{E_j - E_i}{k_B T}\right) : E_j - E_i \geq 0 \\ \exp(-2\alpha R_{ij}) : E_j - E_i \leq 0 \end{cases} \quad (1.1)$$

- ν_0 : base-jump frequency
- R_{ij} : distance between initial state i and final state j
- α : decay constant of the assumed hydrogen-like localized state wave functions
- E_i : energy of the state i

Depending on the position of the final state j , the formula change. If the state is on higher energy, it requires tunneling to occur on the energetic part, whereas if the reaching state is of a lower energy, only the distance is taken into account for the tunneling effect.

Using this formalism, it is possible to access the mobility and diffusivity for charge carrier.

1.1.4 The einstein relation

Classical einstein relation

$$\frac{D}{\mu} = \frac{k_B T}{q} \quad (1.2)$$

- μ : mobility
- D : diffusion
- k_B : Boltzmann constant
- T : temperature
- q : elementary charge

The einstein relation [6], is a useful equation that link two quantities, μ and D over a simple equation. D constitutes a key parameter in analyzing semiconductor but is not so easy to measure. On the contrary, the mobility is easily accessed. However, in the presence of energetic disorder, such simple equation does not seem to hold [2, 14]. In non-equilibrium cases, it also seems that we can't use this relation anymore, the relation between the diffusion and the field seems to be quadratic [13].

Generalized equation

From the limit of the eq. 1.2, a new relation has been proposed, taking into account the dependence on the carrier concentration [15]:

$$\frac{D}{\mu} = \frac{n}{q\partial n/\partial E_F} \quad (1.3)$$

- E_F : quasi-Fermi level
- n : carrier concentration

With n being the carrier concentration defined by the fermi-dirac distribution $f = \frac{1}{1+\exp\left(\frac{E-E_F}{k_B T}\right)}$ and g the gaussian density of state [15]:

$$n = \int_{-\infty}^{\infty} \frac{g(E)}{1 + \exp\left(\frac{E-E_F}{k_B T}\right)} dE \quad (1.4)$$

Such eq. 1.4 has been calculated following the hypothesis that drift and diffusion of charge carrier at fermi level are exactly compensated, meaning that there is no net current and is only valid for low electric field.

From this stating, a more suitable equation has been proposed in the following thesis.

1.1.5 Gaussian density of states

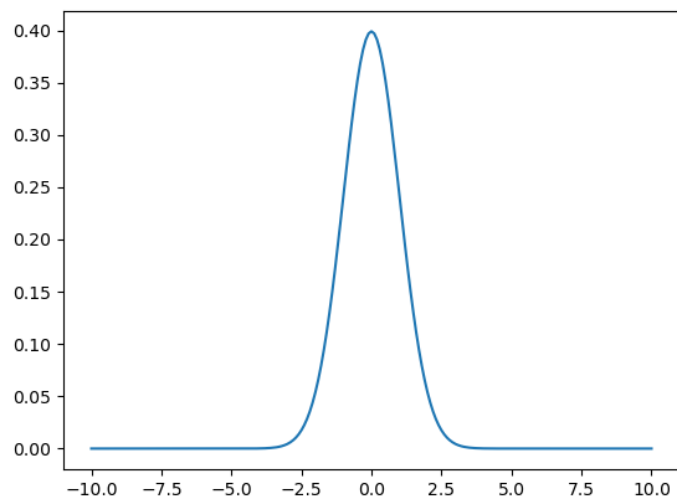
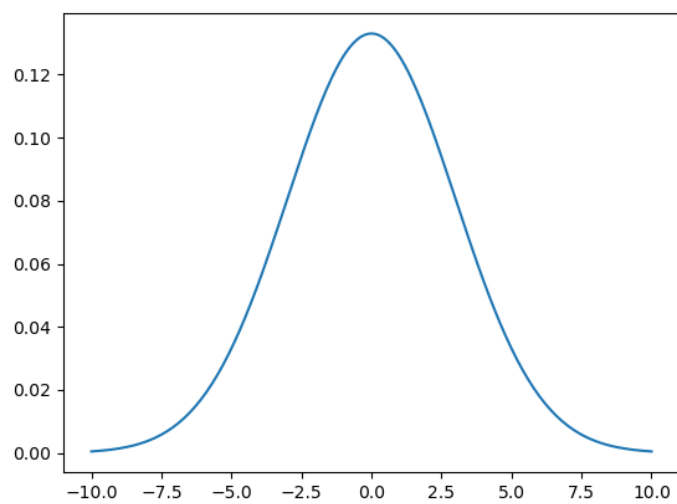
$$g(E) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right) \quad (1.5)$$

Gaussian density of states has been suggested by numerous monte-carlo simulations [4] as well by the observation of the excitonic absorption profile which is gaussian too. Besides, the intrinsic localization behavior of the gaussian density of state fit very well the observation made on real devices.

From a mathematical point of view, the disorder is directly linked to σ , which broadens the bell-shaped of the function (fig. 1.5, 1.6).

1.1.6 Thermal diffusion

Organic semiconductors have recently received much attention regarding their potential thermoelectric effect. From their figure of merit (eq. 1.6)

Figure 1.5: Gaussian DOS, $\sigma = 1$ Figure 1.6: Gaussian DOS, $\sigma = 3$

$$ZT = \frac{\sigma \cdot S^2}{\kappa} T \quad (1.6)$$

- S : Seebeck coefficient
- σ : electrical conductivity
- κ : thermal conductivity

From ZT value is representative of the electric efficiency of the device. Thus a lower thermal conductivity κ naturally leads to higher figure of merit and to an increased energetic conversion.

A better understanding of the process is key to engineering better devices, but the classical theory used on inorganic material [7] can't be applied directly to organic ones. The variety of morphology in organic semiconductors plays a great role in defining its thermal characteristics and is extremely sensitive to the spacial arrangement of the molecules within the material.

To simulate the thermal effect, one should take into account both charge carrier and phonon transport: $\kappa = \kappa_e + \kappa_p$ with a slight predominance of the phonon in the process of thermal conduction [9].

1.2 Objectives of this thesis

The overall understanding of both electric and thermal behavior of organic semiconductors is scarce. Their great diversity, which is at the heart of their recent success, makes it difficult to get an simulation of the charge carrier in the material. The goal of this thesis is to obtain, thanks to equations developed throughout the 20th century and to new hypothesis on the comportment of the charge carrier, as well as a powerful computer language, a reasonable approximation of the electric and thermal figures in doped organic semiconductors. Our objectives are:

- Estimate einstein ratio for many type of organic semiconductors
- Estimate the thermal conduction by taking into account both charge carrier and phonon participation
- Take into account the doping behavior of the semiconductor, as well as the disorder and electric effect

- Simulate the behavior in a fairly small amount of time

The novelty of this study resides in the multitude of the parameters taken into account and in new behavior for charge carrier within the material.

Chapter 2

Julia

2.1 Introduction

Julia is a recent open-source language (MIT) which has been developed specifically for scientific purposes. Syntax is also very similar to what can be done with Python, meaning that it's easy to read and write efficient code. Of course the syntax is also optimized for mathematics purpose, and the expressions are straightforwardly converted into the computer language. Even though it is a compiled language like Matlab, his use of REPL makes it quite easy to beta test code and run simple programs. The huge community involved around the language makes it easier to find useful package that are already optimized for fast computation in Julia. The support of other languages within the Julia language allows an even greater access to simple and user friendly tools: it is very easy to use the Python graphic renderer to plot and easily visualize data.

2.2 Performances

One key argument in choosing Julia over Matlab was its performances. According to the officials data (fig. 2.1), for this specific benchmark, Julia language reaches the performances of static-compiled languages such as C and is even better performing than Matlab.

2.3 Notebooks

The communication and presentation of data and code is a key part in making a scientific work. To help smoothing out the process, we intensively used Jupyter notebooks. They put in the same document programming language code, as well



Figure 2.1: Julia benchmark

as plain text (rendered through markdown) to help clarify and improve the overall lisibility.

2.4 Code implementation

2.4.1 Packages

One of the key aspect of the modelisation that has been performed, was to perform easily and quickly complex integral over multiple dimension. The computation of 1D expression such as σ (TODO: add ref) has been realized using QUADGK package:

```
kp(semiconductor, T) = k * T * quadgk(
    r -> DOSp(semiconductor, r, T) * C(r, T) * Dp(semiconductor, r,
        T),
    semiconductor.omega_min * hbar / (k * T),
    +Inf
)[1]
```

The multidimensional integrals have been computed using HCubature:

```

# Number of free state within a sphere of radius R
N(semiconductor::Semiconductor, U::Real, T::Real, R::Real)::Float64
= (k * T) / (8 * semiconductor.alpha^3) * 2 * pi * hcubature(
  x -> DOS(semiconductor, var1(U, semiconductor.beta(T), R, x[1],
    x[2], x[3]), T) * (1 - F(semiconductor, var1(U,
    semiconductor.beta(T), R, x[1], x[2], x[3]), T)) * 1 / (1 -
    x[1])^2 * x[2]^2 * sin(x[3]),
  [0, 0, 0],
  [1, R, pi],
  rtol=1e-6)[1]

```

2.4.2 Code adaptation

However, concerning the multi-dimensional integrals, they can't be used as they were presented in the thesis. The parameters presented in the born have to be some constant and not depend on an other integral parameters.

Number of free states

The formula for the number of free state is taken from TODO:REF :

$$\mathcal{N}(u, T, \beta, \mathcal{R}) = \int_0^\pi \int_0^{\mathcal{R}} \int_{-\infty}^{\mathcal{R}+u-r(1+\beta \cos \theta)} N(v) [1 - F(v)] \frac{kT}{8\alpha^3} \times 2\pi r^2 \sin \theta dv dr d\theta \quad (2.1)$$

For the dv integrals, the superior born is defined by $\mathcal{R} + u - r(1 + \beta \cos \theta)$, where θ and R' are already parameters for the first and second integral. In order to get rid of such born, we've made the change of variable:

$$v = \mathcal{R} + u - r(1 + \beta \cos \theta) - \frac{t}{1-t} = a - \frac{t}{1-t} \quad (2.2)$$

It results in the change from eq. 2.1 to:

$$\mathcal{N}(u, T, \beta, \mathcal{R}) = \int_0^\pi \int_0^{\mathcal{R}} \int_0^1 N\left(a - \frac{t}{1-t}\right) \left[1 - F\left(a - \frac{t}{1-t}\right)\right] \frac{kT}{8\alpha^3} \times 2\pi r^2 \sin \theta \frac{1}{(1-t)^2} dt dr d\theta \quad (2.3)$$

With this simple change of variable, the time of computation has been reduced from several minutes depending on the initial conditions, to a few seconds.

Real hopped distance

From the equation of the real hopper distance TODO:REF:

$$\begin{aligned}
I_1 &= \int_0^\pi \int_{u-\overline{r_{nn}}\beta \cos \theta}^{u+\overline{r_{nn}}} N(v) [1 - F(v)] \left[\frac{\overline{r_{nn}} - v + u}{1 + \beta \cos \theta} \right]^3 \times \sin \theta \cos \theta dv d\theta \\
I_2 &= \int_0^\pi \int_{-\infty}^{u-\overline{r_{nn}}\beta \cos \theta} N(v) [1 - F(v)] \overline{r_{nn}}^3 \sin \theta \cos \theta dv d\theta \\
I_3 &= \int_0^\pi \int_{u-\overline{r_{nn}}\beta \cos \theta}^{u+\overline{r_{nn}}} N(v) [1 - F(v)] \left[\frac{\overline{r_{nn}} - v + u}{1 + \beta \cos \theta} \right]^2 \sin \theta dv d\theta \\
I_4 &= \int_0^\pi \int_{-\infty}^{u-\overline{r_{nn}}\beta \cos \theta} N(v) [1 - F(v)] \overline{r_{nn}}^2 \sin \theta dv d\theta
\end{aligned} \tag{2.4}$$

Similarly to the section 2.4.2, the area of integrals contain integrated variable θ . By the change of variable for I_1 and I_3 :

$$v = f_1(t) = \overline{\mathcal{R}_{nn}} \left[\frac{1 + \beta \cos \theta}{t} - \beta \cos \theta \right] + u \tag{2.5}$$

And by doing the change of variable for I_2 and I_4 :

$$v = f_2(t) = u - \overline{\mathcal{R}_{nn}}\beta \cos \theta - \frac{t}{1-t} \tag{2.6}$$

We obtain the following formulas:

$$\begin{aligned}
I_1 &= 0.5 * \overline{r_{nn}} \int_0^\pi \int_0^1 N(f_1(t)) [1 - F(f_1(t))] \frac{[\overline{r_{nn}} - f_1(t) + u]^3}{[1 + \beta \cos \theta]^2} \sin(2\theta) dt d\theta \\
I_2 &= 0.5 * \overline{r_{nn}}^3 \int_0^\pi \int_0^1 N(f_2(t)) [1 - F(f_2(t))] \sin(2\theta) \frac{1}{(1-t)^2} dt d\theta \\
I_3 &= \overline{r_{nn}} \int_0^\pi \int_0^1 N(f_1(t)) [1 - F(f_1(t))] \frac{[\overline{r_{nn}} - f_1(t) + u]^2}{[1 + \beta \cos \theta]} \sin(\theta) dt d\theta \\
I_4 &= \overline{r_{nn}}^2 \int_0^\pi \int_0^1 N(f_2(t)) [1 - F(f_2(t))] \sin(\theta) \frac{1}{(1-t)^2} dt d\theta
\end{aligned} \tag{2.7}$$

Stochastic time of trap

From the equation of the stochastic time of trap TODO:REF:

$$\begin{aligned}
J_1(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_{u-r\beta \cos \theta}^{\bar{r}_{nn}+u-r(1+\beta \cos \theta)} du \\
&\quad \times \frac{\tau(u, u_F)}{v_0} \exp((1 + \beta \cos \theta)r + u - u), \\
J_2(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_{-\infty}^{u-r\beta \cos \theta} du \frac{\tau(u, u_F)}{v_0} \\
&\quad \times \exp((1 + \beta \cos \theta)r), \\
J_3(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_{u-r\beta \cos \theta}^{\bar{r}_{nn}+u-r(1+\beta \cos \theta)} du \tau(u, u_F), \\
J_4(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_{-\infty}^{u-r\beta \cos \theta} du \tau(u, \epsilon_F)
\end{aligned} \tag{2.8}$$

By doing the change of variable for J_1 and J_3 :

$$v = g_1(t) = t(\bar{r}_{nn} - r) + u + r\beta \cos \theta \tag{2.9}$$

And by doing the change of variable for J_2 and J_4 :

$$g_2(t) = \frac{t}{t-1} + u - r\beta \cos \theta \tag{2.10}$$

We obtain the following formulas:

$$\begin{aligned}
I_1(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_0^1 dt \frac{\tau(g_1(t), u_F)}{v_0} \exp((1 + \beta \cos \theta)r + g_1(t) - u) \\
I_2(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_0^1 dt \frac{\tau(g_2(t), u_F)}{v_0} \exp((1 + \beta \cos \theta)) \\
I_3(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_0^1 dt \tau(g_1(t), u_F) \\
I_4(u) &= \int_0^\pi d\theta \sin \theta \int_0^{\bar{r}_{nn}} dr 2\pi r^2 \int_0^1 dt \tau(g_2(t), u_F)
\end{aligned} \tag{2.11}$$

2.5 Conclusion

Thanks to the possibilities of Julia and to numerous package, we could optimize the code to obtain a final computation of einstein ratio in the order of several minutes/hours depending on the initial conditions.

Optimization is a key point to computational simulation as we need to get a result in a fair amount of time in order to work by iteration and tune our model to real data: we may want to fit a certain numerical value for instance.

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Appendix

A Appendix 1