



**HAL**  
open science

# Probabilistic Interpretation for the Nonlinear Poisson-Boltzmann Equation in Molecular Dynamics

Nicolas Perrin

► **To cite this version:**

Nicolas Perrin. Probabilistic Interpretation for the Nonlinear Poisson-Boltzmann Equation in Molecular Dynamics. 2011. hal-00648180v1

**HAL Id: hal-00648180**

**<https://inria.hal.science/hal-00648180v1>**

Preprint submitted on 5 Dec 2011 (v1), last revised 1 Mar 2012 (v3)

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## PROBABILISTIC INTERPRETATION FOR THE NONLINEAR POISSON-BOLTZMANN EQUATION IN MOLECULAR DYNAMICS.

NICOLAS PERRIN<sup>1</sup>

**Abstract.** The Poisson-Boltzmann (PB) equation describes the electrostatic potential of a biomolecular system composed by a molecule in a solvent. The electrostatic potential is involved in biomolecular models which are used in molecular simulation. In consequences, finding an efficient method to simulate the numerical solution of PB equation is very useful. In this paper, we establish a probabilistic interpretation of the nonlinear PB equation with Backward Stochastic Differential Equations (BSDEs). This interpretation requires an adaptation of existing results on BSDEs.

**Résumé.** En dynamique moléculaire, l'équation de Poisson-Boltzmann (PB) permet de décrire le potentiel électrostatique d'un système moléculaire composé d'une molécule dans un solvant. Ce potentiel électrostatique intervient dans les modèles de simulation numérique permettant de comprendre la structure, la dynamique et le fonctionnement des protéines. La résolution numérique de l'équation de PB est donc une étape importante de ces simulations. Aussi, nous proposons une interprétation probabiliste de l'équation de PB non-linéaire à l'aide des Equations Différentielles Stochastiques Rétrogrades (EDSR). Cette interprétation nécessite une adaptation des résultats d'existence et d'unicité des solutions d'EDSR.

### INTRODUCTION

In this paper, we establish a probabilistic interpretation for the solution of the nonlinear Poisson-Boltzmann (PB) equation

$$-\nabla \cdot (\epsilon(x)\nabla u(x)) + \kappa^2(x) \sinh \{u(x)\} = g(x), \quad x \in \mathbb{R}^3,$$

where  $\epsilon$  and  $\kappa$  are piecewise constant functions from  $\mathbb{R}^3$  to  $(0, +\infty)$ , and  $g$  is a singular function. Our probabilistic interpretation consists in the sum of a singular known function and the solution of a particular Backward Stochastic Differential Equation (BSDE). We prove an existence and uniqueness result for this BSDE by extending to our situation the methodology developed in [BDH<sup>+</sup>03] or [Par99].

In Section 1, we introduce the Poisson-Boltzmann equation in molecular dynamics and underline three difficulties we have to face to get a probabilistic interpretation of the nonlinear Poisson-Boltzmann equation.

In Section 2, we recall the probabilistic interpretation of divergence-form operators with discontinuous coefficients in term of SDE with weighted local time.

In Section 3, we very briefly introduce BSDEs theory, before giving a general result for the existence and the uniqueness of the solution of BSDEs with time-dependent monotonicity (Theorem 3.5), which we apply in order to get a probabilistic interpretation theorem (Theorem 3.7) of the solution of the corresponding Partial Differential Equation (PDE).

---

<sup>1</sup> TOSCA project-team, INRIA Sophia Antipolis, France. nicolas.perrin@inria.fr

In Section 4, we state our main result (Theorem 4.1). In order to prove it, we state an existence, uniqueness and regularity theorem (Theorem 4.2) for the solution  $v$  in  $H^1(\mathbb{R}^d)$  to the regularised Poisson-Boltzmann equation. Then we conclude in Section 4.3 by giving the steps of proof for our main result.

## 1. THE POISSON-BOLTZMANN EQUATION IN MOLECULAR DYNAMICS

The electrostatic potential of a biomolecular system in a medium of electric permittivity  $\epsilon$  generated by a charge distribution  $\rho_c$  is given by the Poisson equation (cf. [BBC06])

$$-\nabla \cdot (\epsilon(x) \nabla u(x)) = 4\pi \rho_c(x), \quad x \in \mathbb{R}^3.$$

We consider a molecule immersed in an aqueous solvent. The contribution of the molecule to the charge distribution is modelled by a finite system of charges centred in the positions of the  $N$  atoms of the molecule

$$\rho_m(x) = \sum_{i=1}^N q_i \delta_{x_i}, \quad x \in \mathbb{R}^3,$$

where  $q_i \in \mathbb{R}$  and  $x_i \in \mathbb{R}^3$  are respectively the charge and the position of the  $i$ th atom and where  $\delta_x$  is the Dirac distribution at  $x \in \mathbb{R}^3$ . The solvent contribution is modelled by:

$$\rho_s(x) = e_c \sum_{j=1}^m \bar{n}_j z_j \exp \{ -e_c z_j u(x) / k_B T_e - V_j(x) / k_B T_e \}, \quad x \in \mathbb{R}^3,$$

where  $m$  is the number of different types of ions in the solvent,  $\bar{n}_j$  is the number of ions of the type  $j$ ,  $z_j$  is the valence of ions of the type  $j$ ,  $e_c$  is the elementary charge,  $k_B$  is the Boltzmann constant,  $T_e$  is the system temperature and  $V_j$  models the steric interaction between the ions of the type  $j$  and the molecule.

For an electrolyte as NaCl where  $q_1 = 1$  et  $q_2 = -1$ , the Poisson equation simplifies to give the nonlinear Poisson-Boltzmann equation

$$-\nabla \cdot (\epsilon(x) \nabla u(x)) + 8\pi e_c \bar{n} e^{-V(x)/k_B T_e} \sinh \{ e_c u(x) / k_B T_e \} = g(x), \quad x \in \mathbb{R}^3 \quad (1)$$

where the term source  $g$  is given by

$$g(x) = 4\pi \sum_{i=1}^N q_i \delta_{x_i}.$$

Let  $\Omega_{\text{int}}$  and  $\Omega_{\text{ext}}$  be two disjoint open subsets of  $\mathbb{R}^3$ , which model the molecule and the solvent respectively, such that  $\bar{\Omega}_{\text{int}} \cup \bar{\Omega}_{\text{ext}} = \mathbb{R}^3$ ;  $\Omega_{\text{int}}$  is supposed to be bounded with boundary  $\Gamma$ .

The dielectric permittivity  $\epsilon$  is represented by a discontinuous function taking two values inside the molecule  $\Omega_{\text{int}}$  (vacuum permittivity) and outside  $\Omega_{\text{ext}}$  (solvent permittivity):

$$\epsilon(x) = \begin{cases} \epsilon_{\text{int}} > 0 & \text{si } x \in \Omega_{\text{int}}, \\ \epsilon_{\text{ext}} > 0 & \text{si } x \in \Omega_{\text{ext}}. \end{cases}$$

In the following, we study the nonlinear Poisson-Boltzmann equation

$$-\nabla \cdot (\epsilon(x) \nabla u(x)) + \kappa^2(x) \sinh \{ u(x) \} = g(x), \quad x \in \mathbb{R}^3. \quad (2)$$

where the modified Debye-Hückel parameter

$$\kappa^2(x) = \begin{cases} 0 & \text{si } x \in \Omega_{\text{int}}, \\ \bar{\kappa}^2 > 0 & \text{si } x \in \Omega_{\text{ext}}. \end{cases} \quad (3)$$

approximates  $e^{-V(\cdot)/k_B T_e} \frac{8\pi e^2 I}{k_B T_e} \frac{1}{2} \sum_s \bar{n}_s z_s^2$ .

The probabilistic interpretation for the nonlinear PB equation we propose in this paper requires to handle three difficulties:

- (1) the singularity of the source term (cf. Section 2.1);
- (2) the discontinuity of the coefficient in the divergence form operator (cf. Section 2.2);
- (3) the non-linearity of the equation (cf. Section 3).

We should emphasize that if we suppose  $e_{cu}(\cdot)$  much smaller than  $k_B T_e$ , we obtain a linear version of the Poisson-Boltzmann equation

$$-\nabla \cdot (\epsilon(x) \nabla u(x)) + \kappa^2(x) u(x) = g(x), \quad x \in \mathbb{R}^3. \quad (4)$$

## 2. A PROBABILISTIC INTERPRETATION IN TERMS OF SDEs WITH WEIGHTED LOCAL TIME

In this section, we present the probabilistic interpretation of the linear Poisson-Boltzmann equation ( Eq. (4)) established in [BCMT10].

### 2.1. The regularised Poisson-Boltzmann equation

The singular source term is handled by writing the solution as a sum of a known singular function and the solution of a regularised equation.

The following regularisation is introduced in [BCMT10]. Let  $\chi$  be a function  $C^\infty$  with a compact support embedded in  $\Omega_{\text{int}}$ , such that  $\chi(x) = 1$  for  $x$  close to  $\{x_1, \dots, x_N\}$  and  $G = \sum_i G_i$  where

$$G_i(x) = \frac{q_i}{\epsilon_{\text{int}}} \frac{1}{|x - x_i|} \quad x \in \mathbb{R}^3,$$

satisfying

$$-\nabla \cdot (\epsilon_{\text{int}} \nabla G_i) = q_i \delta_i.$$

We then study the function  $v = u - \chi G$  which is the solution of

$$-\nabla \cdot (\epsilon(x) \nabla v(x)) + \kappa^2(x) \sinh(v(x)) = \tilde{g}(x), \quad x \in \mathbb{R}^3 \quad (5)$$

The regularised source term is then expressed as  $\tilde{g}(x) = \epsilon_{\text{int}} (G(x) \Delta \chi(x) + \nabla G(x) \cdot \nabla \chi(x))$ , for  $x \in \mathbb{R}^3$  since the support of  $\chi G$  is in  $\Omega_{\text{int}}$  while  $\kappa$  is null on  $\Omega_{\text{int}}$ . In particular, the function  $\tilde{g}$  is  $C^\infty$ .

### 2.2. The martingale problem associated with the linear Poisson-Boltzmann equation

In [BCMT10], a probabilistic interpretation is introduced for divergence-form operators in  $\mathbb{R}^d$ ,  $d \geq 1$  with discontinuous coefficients of the form

$$\mathcal{L} = \nabla \cdot (\epsilon(x) \nabla),$$

where  $\epsilon$  is a piecewise constant function from  $\mathbb{R}^d$  to  $(0, \infty)$  with a smooth discontinuity manifold  $\Gamma$ .

We suppose that  $\Omega_{\text{int}}$  is a simply connected set with a boundary  $\Gamma$  of class  $C^\infty$ , and that  $\Omega_{\text{ext}} = \mathbb{R}^d \setminus (\Omega_{\text{int}} \cup \Gamma)$ . The smoothness of  $\Gamma$  allows us to construct a mapping  $\pi$  of class  $C_b^2$  from a neighborhood  $\mathcal{N}$  of  $\Gamma$  to  $\Gamma$  such that

$$|x - \pi(x)| = d(x, \Gamma), \quad \forall x \in \mathcal{N},$$

where  $d(x, \Gamma)$  denotes the distance of  $x$  to  $\Gamma$ . Let  $n(x)$  be the unit vector normal to  $\Gamma$  at  $x \in \Gamma$  pointing in direction of  $\Omega_{\text{ext}}$ . Finally, let  $\rho$  be the signed distance to  $\Gamma$  positive in  $\Omega_{\text{ext}}$  and negative in  $\Omega_{\text{int}}$  for all  $x \in \mathcal{N}$

$$\rho(x) = (x - \pi(x)) \cdot n(\pi(x)), \quad x \in \mathcal{N},$$

which can be extended to the whole Euclidean space  $\mathbb{R}^d$  in a function  $C_b^2$  still denoted  $\rho$  (cf. Figure 1).

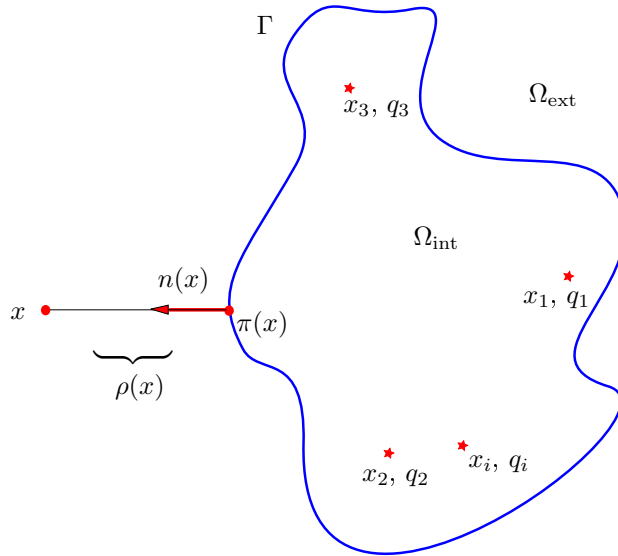


FIGURE 1

The probabilistic interpretation of elliptic and parabolic PDEs driven by the operator  $\mathcal{L}$  relies on the following martingale problem.

**Definition 2.1.** Let  $(\mathcal{C}, \mathcal{B})$  be the set  $\mathcal{C}$  of continuous function  $w$  from  $[0, \infty)$  to  $\mathbb{R}^d$  endowed with the Borel cylindrical  $\sigma$ -field  $\mathcal{B}$  and the canonical filtration  $(\mathcal{B}_t, t \geq 0)$ . A family of probability measures  $\mathbb{P}_x$  on  $(\mathcal{C}, \mathcal{B})$  solves the *martingale problem for the operator  $\mathcal{L}$*  if, for all  $x \in \mathbb{R}^d$ , one has

$$\mathbb{P}_x \{w \in \mathcal{C} : w(0) = x\} = 1,$$

and, for all  $\phi$  satisfying

$$\begin{aligned} \phi &\in \mathcal{C}_b^0(\mathbb{R}^d) \cap \mathcal{C}_b^2(\mathbb{R}^d \setminus \Gamma), \\ \epsilon \nabla \phi \cdot (n\pi) &\in \mathcal{C}_b^0(\mathcal{N}), \end{aligned}$$

one has the process

$$M_t^\phi(w) := \phi(w(t)) - \phi(w(0)) - \int_0^t \mathcal{L}\phi(w(s)) ds$$

is a  $\mathbb{P}_x$ - $(\mathcal{B}_t)$  martingale.

It is shown in [BCMT10] that the unique solution of this martingale problem is the law  $\mathbb{P}_x$  of all weak solution  $(\Omega, \mathcal{F}^x, (\mathcal{F}_t^x)_{t \geq 0}, \mathbb{P}_x, \{B_t; t \geq 0\}, \{X_t^x; t \geq 0\})$  of the Stochastic Differential Equation (SDE)

$$\begin{cases} X_t^x &= x + \int_0^t \sqrt{2\epsilon(X_s^x)} dB_s + \frac{\epsilon_{\text{ext}} - \epsilon_{\text{int}}}{2\epsilon_{\text{ext}}} \int_0^t n(X_s^x) dL_s^0(D^x), \\ D_t^x &= \rho(X_t^x), \end{cases} \quad (6)$$

where  $B$  is a  $\mathcal{F}_t^x$ -standard  $d$ -dimensional Brownian motion, and  $L_s^0(D)$  is the local time at 0 of the continuous semimartingale  $D^x$ . It is actually shown in [BCMT10] that all weak solutions to the SDE (6) are identical in law. The above process  $X$ , is used in the new probabilistic interpretation that we develop in next section.

### 3. A PROBABILISTIC INTERPRETATION IN TERMS OF BSDEs

One of probabilistic methods to handle nonlinear Partial Differential Equations (PDEs) is based on Backward Stochastic Differential Equations (BSDEs) (cf. [BDH<sup>+</sup>03] or [Par99]). We briefly present BSDEs theory before giving a result for BSDEs with a time-dependent monotonicity condition. Then we conclude by applying the above result to BSDEs driven by a SDE with weighted local time.

#### 3.1. Reminders on BSDEs

Let  $B$  be a standard  $d$ -dimensional Brownian motion defined on a probability space  $(\Omega, \mathcal{F}, \mathbb{P})$ , where  $\{\mathcal{F}_t\}$  is the natural augmented filtration of  $B$ . Let  $\tau$  be a  $\mathcal{F}_t$ -measurable stopping time,  $\xi$  a  $\mathcal{F}_\tau$ -measurable random variable and  $f$  an application from  $\Omega \times \mathbb{R}^+ \times \mathbb{R}^k \times \mathbb{R}^{k \times d}$  to  $\mathbb{R}^k$ .

**Definition 3.1.** A solution of the BSDE  $(\tau, \xi, f)$  is a couple of progressively measurable processes  $(Y, Z)$  with values in  $\mathbb{R}^k \times \mathbb{R}^{d \times k}$ , which satisfies following properties

- (1)  $t \rightarrow \mathbf{1}_{\{t \leq \tau\}} f(t, Y_t, Z_t)$  is in  $L^1_{\text{loc}}(0, \infty)$ , and  $t \rightarrow Z_t$  is in  $L^2_{\text{loc}}(0, \infty)$ ;
- (2)  $Y_{t \wedge \tau} = Y_{T \wedge \tau} + \int_{t \wedge \tau}^{T \wedge \tau} f(s, Y_s, Z_s) ds - \int_{t \wedge \tau}^{T \wedge \tau} Z_s dB_s$  for all  $0 \leq t \leq T$ ;
- (3)  $Y_t = \xi$  et  $Z_t = 0$  on the event  $\{t \geq \tau\}$ .

The application  $f$  is called the *generator* of the BSDE.

The regularised PB equation (Eq. (5)), for  $d = 3$ , is associated to the BSDE  $(\infty, 0, f)$  with generator given by

$$f(t, y) = \tilde{g}(X_t^x) - \kappa^2(X_t^x) \sinh y, \quad x \in \mathbb{R}^3, y \in \mathbb{R}, t \in [0, \infty),$$

where  $X_t$  is the solution of the SDE given by Eq. (6),

$$Y_t^x = Y_T^x + \int_t^T \tilde{g}(X_s^x) - \kappa^2(X_s^x) \sinh Y_s^x ds - \int_t^T Z_s^x dB_s, \quad (7)$$

for all  $t, T$  as  $0 \leq t \leq T$ .

Let us recall the hypothesis of [BDH<sup>+</sup>03]: let

- (h1) a  $\mathcal{F}_t$ -measurable stopping time  $\tau$ , which need not be bounded;
- (h2) a generator  $f$  which maps  $\Omega \times \mathbb{R}^+ \times \mathbb{R}^k \times \mathbb{R}^{k \times d}$  in  $\mathbb{R}^k$  such that for some real constants  $\mu, \lambda, K, K'$  satisfying  $K, K' > 0, 2\mu + K^2 < \lambda$  and such that
  - (a)  $f(\cdot, y, z)$  is progressively measurable for all  $y$  and  $z$ ;
  - (b) for all  $r > 0$ , for all  $n \in \mathbb{N}^*$ ,  $\sup_{|y| \leq r} |f(t, y, 0) - f(t, 0, 0)| \in L^1([0, n[ \times \Omega, dt \otimes \mathbb{P})$ ;
  - (c) **Lipschitz continuity** :  $f$  is  $K$ -Lipschitz in  $z$  for all  $t$  and  $y$  a.s.;
  - (d) **monotonicity** :  $f$  satisfies the monotonicity condition

$$\langle y - y', f(t, y, z) - f(t, y', z) \rangle \leq \mu |y - y'|^2$$

for all  $t, y, y', z$  a.s.;

- (e) **integrability** :  $\mathbb{E} \int_0^T e^{\lambda t} |f(t, 0, 0)|^2 dt$  bounded ;
- (f)  $y \rightarrow f(t, y, z)$  is continuous for all  $t, z$  a.s.;
- (h3) there exists a  $k$ -dimensional  $\mathcal{F}_\tau$ -measurable random variable  $\xi$ , such that

$$\mathbb{E} \left[ \int_0^T e^{\lambda t} ds |f(t, \omega, e^{-\tilde{\lambda}t/2} \bar{\xi}_t, e^{-\tilde{\lambda}t/2} \bar{\eta}_t)|^2 dt \right] < \infty$$

where  $\tilde{\lambda} := 2\mu + K^2$ ,  $\bar{\xi} = e^{\tilde{\lambda}\tau}\xi$ ,  $\bar{\xi}_t = \mathbb{E}[\bar{\xi}|\mathcal{F}_t]$  and  $\bar{\eta}$  are predictable processes such that

$$\begin{aligned}\bar{\xi} &= \mathbb{E}[\bar{\xi}] + \int_0^\infty \bar{\eta}_t dB_t, \\ \mathbb{E}\left[\int_0^\infty |\bar{\eta}_t|^2 dt\right] &< \infty.\end{aligned}$$

**Theorem 3.2** (Briand et al.). *Under Assumptions (h1-h3), there exists a unique solution to the BSDE  $(\tau, \xi, f)$ .*

However, results of [Par99] and [BDH<sup>+</sup>03] do not directly apply to the regularised PB equation (Eq. (5)), on the one hand because of the discontinuities of  $\epsilon$  and on the other hand because of Assumptions (h2d) and (h2e) which essentially require a positive constant  $\mu$ . For the generator  $f$  of the regularised PB equation the best choice of  $\mu$  is null (due to the nullity of  $\kappa^2$  on the compact  $\Omega_{\text{int}}$ ) which makes difficult the verification, for  $\lambda > 0$ , of the integrability hypothesis that  $\mathbb{E} \int_0^\infty e^{\lambda t} |\tilde{g}(X_s)|^2 dt$  is finite.

Furthermore, we emphasize that the function  $\kappa^2$  is positive outside a compact. Then, the transience of the process  $X$  incites us to weaken the assumptions by allowing monotonicity constants to depend on the time and, particularly in case of Poisson-Boltzmann, to depend on the position of the process  $X$ .

**Remark 3.3.** We should emphasize that a result for monotone BSDEs (with constant  $\mu = 0$ ) is obtained in [Roy04], under the strong hypothesis on the generator,  $f(t, 0, 0) \equiv 0$  a.s., which is not satisfied in the case of the regularised Poisson-Boltzmann equation.

### 3.2. BSDEs with time-dependent monotonicity condition

Let us weaken Assumptions (h2c), (h2d), (h2e) and (h3)

- (h'2) (c) **Lipschitz continuity** :  $|f(t, y, z) - f(t, y, z')| \leq K(t)\|z - z'\|$  for all  $t, y, y'$  a.s., where  $K$  is a progressively measurable process which is bounded by a constant  $\bar{K}$ ,  
(d) **monotonicity** : for all  $t, y, y', z$  a.s.,

$$\langle y - y', f(t, y, z) - f(t, y', z) \rangle \leq \mu(t)|y - y'|^2$$

where  $\mu$  is a progressively measurable process which is bounded by a constant  $\bar{\mu}$ , and

- (e) **integrability** :

$$\mathbb{E} \int_0^\tau e^{\int_0^t \lambda(s) ds} |f(t, 0, 0)|^2 dt < \infty$$

where the progressively measurable process  $\lambda$  is such that  $2\mu(t) + K^2(t) < \lambda(t)$  for all  $t$  in  $\mathbb{R}^+$ ,

- (h'3) the final condition  $\xi$  is a  $\mathcal{F}_\tau$ -measurable random variable such that

$$\mathbb{E}_\nu \left[ \int_0^T e^{\int_0^t \lambda(s, \omega) ds} |f(t, e^{-1/2 \int_0^t \tilde{\lambda}(s) ds} \bar{\xi}_t, e^{-1/2 \int_0^t \tilde{\lambda}(s) ds} \bar{\eta}_t)|^2 dt \right] < \infty$$

where  $\tilde{\lambda}(t) := 2\mu(t) + K^2(t)$ ,  $\bar{\xi} = e^{\int_0^T \tilde{\lambda}(s) ds} \xi$ ,  $\bar{\xi}_t = \mathbb{E}_\nu[\bar{\xi}|\mathcal{F}_t]$  and  $\bar{\eta}$  are predictable processes such that

$$\begin{aligned}\bar{\xi} &= \mathbb{E}_\nu[\bar{\xi}] + \int_0^\infty \bar{\eta}_t dB_t \\ \mathbb{E} \left[ \int_0^\infty |\bar{\eta}_t|^2 dt \right] &< \infty.\end{aligned}$$

**Definition 3.4.** For a given progressively measurable process  $\lambda$ , the solution  $(Y, Z)$  of BSDE  $(\tau, \xi, f)$  is said to be in  $L^2_{\lambda(\cdot)}$  if

$$\|(Y, Z)\|_{\lambda(\cdot)}^2 := \mathbb{E} \left[ \sup_{0 \leq t \leq \tau} e^{\int_0^t \lambda(s) ds} |Y_t|^2 + \int_0^\tau e^{\int_0^t \lambda(s) ds} (|Y_t|^2 + \|Z_t\|^2) dt \right] < \infty.$$

We prove in [Per12] the following existence and uniqueness result of the solution to BSDEs.

**Theorem 3.5.** *If Assumptions (h1-h2b-h'2c-h'3) are true, there exists a unique solution  $(Y, Z)$  to the BSDE  $(\tau, \xi, f)$  such that, for all progressively measurable process  $\lambda$  such that  $\lambda(\cdot) - 2\mu(\cdot) - K^2(\cdot) > \bar{\lambda} > 0$ ,*

$$\|(Y, Z)\|_{\lambda(\cdot)}^2 \leq C \mathbb{E} \left[ e^{\int_0^\tau \lambda(s) ds} |\xi|^2 + \int_0^\tau e^{\int_0^t \lambda(s) ds} |f(t, 0, 0)|^2 dt \right]. \quad (8)$$

The proof of this theorem follows closely the steps of the proof in [Par99] adapting them to time dependent coefficients.

### 3.3. BSDEs driven by SDEs with weighted local time

Let  $(\Omega, \mathcal{F}^x, (\mathcal{F}_t^x)_{t \geq 0}, \mathbb{P}_x, \{B_t; t \geq 0\}, \{X_t^x; t \geq 0\})$  be an arbitrary weak solution of the SDE (6). Consider the Forward-Backward SDE  $(\infty, 0, f)$ , for all  $t, T$ , such that for all  $0 \leq t \leq T$ ,

$$Y_t^x = Y_T^x + \int_t^T f(X_s^x, Y_s^x, Z_s^x) ds - \int_t^T Z_s^x dB_s. \quad (9)$$

where  $f$  is a generator from  $\mathbb{R}^d \times \mathbb{R}^k \times \mathbb{R}^{k \times d}$  to  $\mathbb{R}^k$  such that

- (H1)  $f(\cdot, y, z)$  is measurable for all  $y$  and  $z$ ;
- (H2)  $y \rightarrow f(x, y, z)$  is continuous for all  $x, z$ ;
- (H3) **Lipschitz continuity** :  $|f(x, y, z) - f(x, y, z')| \leq K(x) \|z - z'\|$  for all  $x, y, y'$  a.s., where  $K$  is measurable and bounded by a constant  $\bar{K}$ ,
- (H4) **monotonicity** : for all  $x, y, y', z$  a.s.,

$$\langle y - y', f(x, y, z) - f(x, y', z) \rangle \leq \mu(x) |y - y'|^2$$

where  $\mu$  is measurable and bounded by a constant  $\bar{\mu}$ ,

- (H5) **integrability** :

$$\mathbb{E} \int_0^\infty e^{\int_0^t \lambda(X_s^x) ds} |f(X_t, 0, 0)|^2 dt < \infty$$

where  $\lambda$  is measurable and such that  $2\mu(x) + K^2(x) < \lambda(x)$  for all  $x$  in  $\mathbb{R}^d$ ,

- (H6)  $\sup_{|y| \leq r} |f(X_t^x, y, 0) - f(X_t^x, 0, 0)| \in L^1([0, n] \times \Omega, dt \otimes \mathbb{P}), \forall n \in \mathbb{N}^*$  and  $\forall r > 0$ .

The following existence and uniqueness theorem for Eq. (9) is a corollary of Theorem 3.5.

**Theorem 3.6.** *The BSDE (9) has a unique solution in the sense of Definition 3.1 such that*

$$\begin{aligned} & \mathbb{E} \left[ \sup_{0 \leq t} e^{\int_0^t \lambda(X_s^x) ds} |Y_t^x|^2 + \int_0^\infty e^{\int_0^t \lambda(X_s^x) ds} \left( |Y_t^x|^2 + \|Z_t^x \sqrt{2\epsilon(X_s^x)}\|^2 \right) dt \right] \\ & \leq C \mathbb{E} \left[ \int_0^\infty e^{\int_0^t \lambda(X_s^x) ds} |f(X_t^x, 0, 0)|^2 dt \right]. \end{aligned}$$

*Sketch of the proof.* The key arguments of the proof are the following:

- The uniform ellipticity of  $\epsilon$  allows one to change  $Z_t^x$  in  $\tilde{Z}_t^x \sqrt{2\epsilon(X_t^x)}$ .



- The weak uniqueness of the solution  $(\Omega, \mathcal{F}^x, (\mathcal{F}_t^x)_{t \geq 0}, \mathbb{P}_x, \{B_t; t \geq 0\}, \{X_t^x; t \geq 0\})$  to the SDE (6) allows one to use Theorem 4.29 in [JS03] to represent  $(\Omega, \mathcal{F}^x, (\mathcal{F}_t^x)_{t \geq 0}, \mathbb{P}_x)$  local martingales as stochastic integrals w.r.t.  $\int_0^\cdot \sqrt{\epsilon(X_t^x)} dB_t$ .

□

The BSDE (9) provides a probabilistic interpretation to elliptic semilinear PDEs driven by the differential operator  $\mathcal{L}$ :

$$-\mathcal{L}u(x) + f(x, u(x), (\nabla u \sqrt{2\epsilon})(x)) = 0, \quad x \in \mathbb{R}^d. \quad (10)$$

**Theorem 3.7.** *Let  $u$  belongs to  $\mathcal{C}^2(\mathbb{R}^d \setminus \Gamma)$  a solution of Eq.(10), such that for all  $x$  in  $\mathbb{R}^d$*

$$\mathbb{E} \left[ \int_0^\infty e^{\int_0^t \lambda(X_s^x) ds} \|(\nabla u \sqrt{2\epsilon})(X_s^x)\|^2 dt \right] < \infty. \quad (11)$$

*Suppose there exists a function  $r$  in  $\mathcal{C}^2$ , such that  $\forall x \in \mathcal{N}$ ,*

$$r(x) = \left( \frac{\epsilon_{int}}{\epsilon_{ext}} - 1 \right) \nabla^{int} u(\pi(x)) \cdot n(\pi(x)),$$

*and such that  $\hat{u}$  belongs to  $\mathcal{C}^2(\mathbb{R}^d \setminus \Gamma) \cap W_{loc}^{2,\infty}(\mathbb{R}^d)$ , where*

$$\hat{u}(x) := u(x) - r(x)[\rho(x)]_+.$$

*Then, for all  $x$  in  $\mathbb{R}^d$ , the couple  $\{u(X_t^x), (\nabla u \sqrt{2\epsilon})(X_t^x)\}$  is the solution of BSDE (9); in particular  $u(x) = Y_0^x$ .*

The proof consists in using a generalised Itô formula proved by Theorem 2.8 in [BCMT10].

## 4. APPLICATION TO THE NONLINEAR POISSON-BOLTZMANN EQUATION

### 4.1. Main result

It is then possible to give the following probabilistic interpretation to the nonlinear Poisson-Boltzmann equation.

**Theorem 4.1.** *The nonlinear Poisson-Boltzmann equation (Eq. (2)) admits the probabilistic interpretation*

$$u(x) = \chi(x)G(x) + Y_0^x, \quad \forall x \in \mathbb{R}^3,$$

*where  $Y_0^x$  denotes the solution  $(Y^x, Z^x)$  of the BSDE (7) corresponding to the regularised Poisson-Boltzmann equation (Eq. (5)).*

To prove this result, we need to verify that the unique solution to the regularised Poisson-Boltzmann equation (Eq. (5)) satisfies the assumptions of Theorem 3.7.

### 4.2. Existence and uniqueness of the solution

In [Per12] we show the following existence and uniqueness theorem of a weak solution in the subset  $M$  of  $H^1(\mathbb{R}^d)$ ,

$$M := \{v \in H^1(\mathbb{R}^d) \mid \sinh v \in L^2(\mathbb{R}^d)\}.$$

**Theorem 4.2.** *The regularised Poisson-Boltzmann equation (Eq. (5)) has a unique weak solution  $v$  in the subset  $M$  of  $H^1$ . This solution belongs to  $\mathcal{C}_b^0(\mathbb{R}^d) \cap \mathcal{C}^2(\mathbb{R}^d \setminus \Gamma)$ , its restriction  $v|_\Gamma$  belongs to  $\mathcal{C}^\infty(\Gamma)$ . And there exists a function  $r$  in  $\mathcal{C}^2$  such that  $\forall x \in \mathcal{N}$*

$$r(x) = \left( \frac{\epsilon_{\text{int}}}{\epsilon_{\text{ext}}} - 1 \right) \nabla^{\text{int}} v(\pi(x)) \cdot n(\pi(x)), \quad (*)$$

and such that

$$\hat{v}(x) := v(x) - r(x)[\rho(x)]_+ \quad (**)$$

is in  $\mathcal{C}^2(\mathbb{R}^d \setminus \Gamma) \cap W_{\text{loc}}^{2,\infty}$ . Furthermore, the Laplacian  $\nabla v$  of  $v$  belongs to  $L^\infty$ .

*Sketch of the proof.* (1) The existence and uniqueness of the solution in  $H^1(\mathbb{R}^d)$  are obtained by an energy minimisation.

- (2) The continuity of the solution is proved by using a Hölder continuity result with respect to the initial condition of the semigroup corresponding to the uniformly elliptic divergence form operators given in [Str88] (Corollary II.1.9 p. 334).
- (3) Properties  $v$  in  $\mathcal{C}_b^0(\mathbb{R}^d) \cap \mathcal{C}^2(\mathbb{R}^d \setminus \Gamma)$  and  $\hat{v}$  in  $W_{\text{loc}}^{2,\infty}$  are proved using similar arguments as in [BCMT10], Appendix A.
- (4) The bounded condition of  $\nabla v$  is shown in a similar way as for the proof of Theorem IX.27 by H. Brezis in [Bre83].

□

### 4.3. Proof of Theorem 4.1

The proof follows the following steps.

- (1) In Section 4.2, we have stated an existence and uniqueness result (Theorem 4.2) for solutions  $v$  in  $H^1$  to the regularised Poisson-Boltzmann equation.
- (2) The following lemma (proved in [Per12]) allows us to verify the integrability Hypothesis (**H5**) for the generator  $f(x, y) = \kappa^2(x) \sinh(y) + \tilde{g}(x)$  of the nonlinear PB equation.

**Lemma 4.3.** *Let  $X^x$  be a solution of the SDE (6) associated to the operator  $\mathcal{L} := \nabla(\epsilon \nabla)$ . There exists a choice of  $p$  and  $q$  positive, such*

$$\mathbb{E} \left[ \int_0^\infty \exp \left\{ \int_0^t \lambda(X_s^x) ds \right\} |f(X_t^x, 0)|^2 dt \right] < \infty$$

where  $\lambda(X_s^x) = p \mathbf{1}_{X_s^x \in \Omega_{\text{int}}} - q \mathbf{1}_{X_s^x \in \Omega_{\text{ext}}}$ .

So the generator  $f$  satisfies Assumptions (**H1-H6**).

- (3) Furthermore, the solution  $v$  satisfies the assumptions of Theorem 3.7 which makes the link between PDEs solutions and BSDEs solutions. In particular, Lemma 4.3 and the property  $\nabla v \in L^\infty$  allow us to verify Assumption (11). We can then apply it to  $v$  and conclude.

## CONCLUSION

With this probabilistic interpretation, it should be possible to implement new numerical methods for the Poisson-Boltzmann equation. To this aim, an efficient way to simulate the forward process given by Eq. 6 has to be implemented. With more regularities hypothesis, simulation of a Forward-Backward SDE system can be done by quantification (cf. [DM06]). However the adaptation to the PB equation has to be done.

Furthermore, this BSDEs interpretation seems to be favourable to get estimates for the solution to the Poisson-Boltzmann equation. These estimates should be useful to study the convergence rate of numerical methods.

## REFERENCES

- [BBC06] Nathan A. Baker, Donald Bashford, and David A. Case. Implicit solvent electrostatics in biomolecular simulation. In *New algorithms for macromolecular simulation*, volume 49 of *Lect. Notes Comput. Sci. Eng.*, pages 263–295. Springer, Berlin, 2006.
- [BCMT10] Mireille Bossy, Nicolas Champagnat, Sylvain Maire, and Denis Talay. Probabilistic interpretation and random walk on spheres algorithms for the Poisson-Boltzmann equation in molecular dynamics. *M2AN Math. Model. Numer. Anal.*, 44(5):997–1048, 2010.
- [BDH<sup>+</sup>03] Philippe Briand, Bernard Delyon, Ying Hu, Etienne Pardoux, and Lucrétiu Stoica.  $L^p$  solutions of backward stochastic differential equations. *Stochastic Process. Appl.*, 108(1):109–129, 2003.
- [Bre83] Haïm Brezis. *Analyse fonctionnelle*. Collection Mathématiques Appliquées pour la Maîtrise. [Collection of Applied Mathematics for the Master's Degree]. Masson, Paris, 1983. Théorie et applications. [Theory and applications].
- [DM06] François Delarue and Stéphane Menozzi. A forward-backward stochastic algorithm for quasi-linear PDEs. *Ann. Appl. Probab.*, 16(1):140–184, 2006.
- [JS03] Jean Jacod and Albert N. Shiryaev. *Limit theorems for stochastic processes*, volume 288 of *Grundlehren der Mathematischen Wissenschaften [Fundamental Principles of Mathematical Sciences]*. Springer-Verlag, Berlin, second edition, 2003.
- [Par99] Étienne Pardoux. BSDEs, weak convergence and homogenization of semilinear PDEs. In *Nonlinear analysis, differential equations and control (Montreal, QC, 1998)*, volume 528 of *NATO Sci. Ser. C Math. Phys. Sci.*, pages 503–549. Kluwer Acad. Publ., Dordrecht, 1999.
- [Per12] Nicolas Perrin. Stochastic methods in molecular dynamics. *PhD in progress*, 2012.
- [Roy04] Manuela Royer. BSDEs with a random terminal time driven by a monotone generator and their links with PDEs. *Stoch. Stoch. Rep.*, 76(4):281–307, 2004.
- [Str88] Daniel W. Stroock. Diffusion semigroups corresponding to uniformly elliptic divergence form operators. In *Séminaire de Probabilités, XXII*, volume 1321 of *Lecture Notes in Math.*, pages 316–347. Springer, Berlin, 1988.