Master of Physics

M1 General Physics

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Temperature at different scales - Toward measurement on nanostructures

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Abstract

The main goal of this work, is to give a definition of the temperature of a system that can be hold at several scales and directly link to a dynamic and a local description of the system. For this purpose, we try to build a model to approach temperature, based on local quantities starting from thermodynamics properties of a system. We used lagrangian formalism to give meaning to dynamics of a system, and then we formalise further, asserting that temperature can be computed through the contribution of all particles in an ensemble (motion and rest). This approach, can be extended to diffusion and mobility of particles on surface that can described for instance, clusters deposition on substrate. Brownian motion and DLA model will describe, respectively, one particle mobility, and an ensemble of particles behaviour, leading to self-organisation. The temperature can than be approached through this diffusion process. A link to experimental measurement can then be achieved, as an example application, through zeta potential measurement on solution on substrate.

Contents

1 Motivation

Temperature is one of the most important concepts in physics. This comes because we find it everywhere and at different scales. Every thing that has a rest mass has a temperature. However the temperature is always defined as a mean value of an ensemble of particles behavior, depending on models (canonical, microcanonical, ...) or through equivalency (cold atoms are slow atoms for exemple). From this point of view, my motivation came along how to define a temperature for a single particle to be able to extend the concept. An other motivation is linked to the research activities of Nano^3 group in laboratoire Aime Cotton. They work on self-organisation of nanoparticles on a surface and they have a great interest on more direct link between temperature definition and mobility description.

Temperature is almost always measured through its effects on physical properties (dilatation of a liquid or a gas, change of resistivity, spectrum of radiation, potential change, ...) and quiet never directly linked to its definition. Temperature is defined as the measure of average translational kinetic energy of particles and since this is a statistical concept, we should have an ensemble to determine it. Another opened question is how to discretize (”quantize”) it and define a quantum operator for temperature. One of the connection that can be usefull to do that, is the link between principle of least action (general, multisacle concept) and entropy. We have learnt from quantum mechanics lectures for example that we can quantify angular momentum from action, and from entropy we can quantify information. This appears so, very promising and in this project that is the main goal to achieve. We shall emphasize that defining S, T for systems with discrete energy levels is still an **open problem**. For such a task one may have to redefine at the end the concept of temperature. We will further have also to discuss the importance of intensive parameters that has to be studied to achieve such a goal. This approach, can be extended to diffusion and mobility of particles on surface that can desctribed for instance, clusters deposition on substrate.

Brownian motion and DLA model will describe, respectively, one particle mobility, and an ensemble of particles behavior, leading to self-organisation. The temperature can than be approached through this diffusion process. A link to experimental measurement can then be achieved, as an exemple application, throw zeta potential measurement on solution on substrate.

2 Statistical definition

We have seen in thermodynamics, that temperature is an intensive parameter and is a key concept to define properties of our system. Temperature is the average value of translational kinetic energy of each particle in ensemble divided by a constant (Boltzmann constant) :

$$T = \frac{<E>}{k_B} \tag{1}$$

if we want to be more general we then must link it to the definition due to entropy:

$$T = \left(\frac{\partial U}{\partial S}\right)_i$$

where temperature is defined, now, as partial derivate of internal energy $U(S, V, N)$ with respect to entropy S, over some parameter we defined by the ensemble that we choose to describe, from which in most cases $i = V, N$. With N representing the number of particles and V representing the volume of the ensemble in study.

3 The model

In this study the model is very simple and here we can start by introducing the tools that will be used. Starting with canonical ensemble in thermal equilibrum with a heat bath at fixed temperature.

As we know, we have to describe this canonical ensemble by determining thermodynamic potentials, and for this we just focus on internal energy $U(S, V, \{N\}, \{x_i\})$ and Helmoltz free energy $F(T, V, \{N\}, \{x_i\})$ defined using Temperature T, Volume V, Entropy S and $X_i dx_i$ for any external forces:

$$dU = TdS - pdV + \Sigma\{\mu_i dN_i\} + \Sigma\{X_i dx_i\} \tag{2}$$

$$F = U - TS \tag{3}$$

$$dF = -SdT - pdV + \Sigma\{\mu_i dN_i\} + \Sigma\{X_i dx_i\} \tag{4}$$

The reason of presenting this here is pointed out from de Broglie and Helmoltz's Theory.

From this definitions, one may easily write the Euler - Lagrange equation for the system:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_i}\right) - \frac{\partial L}{\partial x_i} = X_i \tag{5}$$

writing simply $L = E_{kin} - U_{pot}$ subject to x_i and $\dot{x}_i$ where we have in an implicit form of the energy for our canonical ensemble.

Therefore is simple from here to build an Hamiltonian representation of our system by a Legendre transformation, and therefore having a hamiltonien for Schrodinger equation:

$$\hat{H}|\psi\!> = (E_{kin} + U_{pot})|\psi\!> \tag{6}$$

In this model, we will focus first in kinetic energy and we will suppose that particles do not interact with each other and have no potential energy. Entropy soon will appear as a function of density or as a function of wavefunction for a particle. We may recall:

$$S = k_B \ln W \qquad S = -k_B \Sigma \rho_i \ln \rho_i$$

Boltzmann entropy formula deduced from H-theorem, W being the number of microstates and the second representation of entropy is the one called Shanon Entropy. They have both equivalent meaning but they are used in different frameworks. Reminding that entropy is zero in revesible processes and increases in irreversible processes. Moments later we shall see the link.

4 Analogy and Lagrangian formalism

Starting with a very basic analogy (Helmoltz canonical schema) which consists of linking temperature and 'velocity' $\dot{x}$, for x, generalized coordinated, being a cyclic variable, we can write:

$$\dot{x} = \frac{dx}{dt} = T \tag{7}$$

From (2) by only considering external forces and the pdV term, we can write:

$$dU = Xdx - pdV$$

and with (7):

$$dU = X\dot{x}dt - pdV \tag{8}$$

From 1st and 2nd laws of thermodynamics :

$$TdS = dU + pdV$$

inferring heat:

$$X\dot{x}dt = TdS \tag{9}$$

where now from (7) and (9) we deduce:

$$X = \dot{S} = \frac{dp_x}{dt}$$

From model, keeping volume constant, we know that $\dot{V}$ will have no contribution to the lagrangian and hence:

$$\frac{\partial L}{\partial x} = 0, \qquad \frac{d}{dt}\frac{\partial L}{\partial \dot{x}} = X, \qquad \frac{\partial L}{\partial \dot{x}} = p$$

Easily one finds back that, entropic momenta:

$$\vec{p}_x = S \tag{10}$$

This is self-consistent, and establish in this model canonical link between temperature and entropy, there are conjugated through Legendre transformation. Applying Legendre transform for $\hat{L}$, we get :

$$\hat{L} = \dot{x}\frac{\partial L}{\partial \dot{x}} + \dot{V}\frac{\partial L}{\partial \dot{V}} - L = \dot{x}\frac{\partial L}{\partial \dot{x}} - L = TS - L \tag{11}$$

Denoting $\hat{L}$ as energy one will have:

$$U = TS - L \qquad <=> \qquad L = TS - U$$

from equation (3):

$$L = -F \tag{12}$$

This is a strong deduction which tells us that Helmoltz free energy plays a deep role in lagrangian formalism for this system, and hence one should consider this to build a framework.

5 Introducing locality

All quantities studied in our experiment are functions of position and time. In this part of the report we will introduce locality for temperature, entropy, energy and their behaviour to the model(1d). One may to write it, is :

$$T = T(x,t), \qquad S = S(x,t), \qquad U = U(x,t)$$

Our situation now becomes local, and in few words we went from global analysis, as we are used to in usual thermodynamics to local approach, to consider only part of the space inside the canonical ensemble.

Therefore is strongly important to present the following observables:

$$dS = \left(\frac{\partial S}{\partial x}\right) dx + \left(\frac{\partial S}{\partial t}\right) dt \qquad dT = \left(\frac{\partial T}{\partial x}\right) dx + \left(\frac{\partial T}{\partial t}\right) dt$$

$$dU = \left(\frac{\partial U}{\partial x}\right) dx + \left(\frac{\partial U}{\partial t}\right) dt \qquad dF = \left(\frac{\partial F}{\partial x}\right) dx + \left(\frac{\partial F}{\partial t}\right) dt$$

that therefore leads to :

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial x}\right) dx + \frac{1}{T}\left(\frac{\partial U}{\partial t}\right) dt \tag{13}$$

Internal energy remains conserved, so $\partial U/\partial t = 0$, same for $F(x,t)$.

It should be pointed out that time derivative of temperature will be also zero, $\partial T/\partial t = 0$. Thus one can easily prove that entropy stays the same as $dS = dU/T$. For the gradient of temperature, we can easily check that:

$$\boldsymbol{\nabla} T = -\frac{1}{S}\left(\frac{\partial F}{\partial x}\right)$$

Gradient of temperature plays an important role as driving force of many phenomena from diffusion to environmental and climatic behavior. In our study we kept temperature locally constant, so the gradient will be of no use for this model but we have there a tool for generalisation. Having gone as strictly as possible, now we would like to rewrite formula (1) to emphase it for the following. Since our system will have constant temperature, we assume that we can sum all temperatures of the particles hof the ensemble.

$$T(x,t) = \sum_{i=1}^{n} T_i = \frac{1}{2k_b}\sum_{i=1}^{n}\frac{p_i^2}{m_i} \tag{14}$$

for $i = 1, 2, ..., n$ particles, and we may write for entropy:

$$S = -k_b \sum_{i}^{n} \rho_i(x,t) \ln \rho_i(x,t) \tag{15}$$

6 New equation

From eq (12) we clearly see that kinetic energy will be subject to $T\dot{S}$. One may easily write from a Legendre transform that our hamiltonian is given by:

$$H = TS + U_{pot}$$

With eq (14), (15) and for no potential energy we find our hamiltionian to be like:

$$H = \frac{1}{2k_b}\sum_i^n \frac{p_i^2}{m_i}\sum_j^k S_j$$

now proposing that $i = j$ finding kinetic energy for same particle and defining minor entropy s_i, dimensionless variable, we find the final hamiltonian expression:

$$H = \frac{1}{2}\sum_i^n \frac{p_i^2}{m_i} s_i \tag{16}$$

from first quantization rule and Heisenberg's uncertainty principle, we know that:

$$\hat{p}|\psi\!> = -i\hbar\frac{\partial|\psi\!>}{\partial x} \qquad \hat{x}\psi = x\psi$$

With eq (6), (16) it comes :

$$\hat{H}|\psi_i\!> = \frac{1}{2}\sum_i^n \frac{p_i^2}{m_i} s_i|\psi_i\!> \tag{17}$$

from $\hat{p}^2(...) = -\hbar^2\Delta(...)$:

$$\hat{H}\psi_i = -\frac{\hbar^2}{2}\sum_i^n \frac{\Delta(s_i\psi_i)}{m_i}$$

and from the linearity of laplacian operator $\Delta(fg) = g\Delta f + f\Delta g + 2\boldsymbol{\nabla} f\boldsymbol{\nabla} g$, one can write:

$$\hat{H}\psi_i = -\frac{\hbar^2}{2}\sum_i^n \frac{1}{m_i}(\psi_i\Delta s_i + s_i\Delta\psi_i + 2\boldsymbol{\nabla} s_i\boldsymbol{\nabla}\psi_i) \tag{18}$$

and (18) will be the modified Schrodinger equation for free particles.

It is easy get classical expression by sending local entropy $s(x,t)$, to global $s(U,V,\{N\})$. Thus, entropy will have no laplacian, no gradient and kinetic part will be just $F(T,V,\{N\})$ retrieving the Schrodinger equation (6).

7 Entropic Source

In equation (18) there are new concepts to deal with. Question arises now are : 'What is the gradient and laplacian of local entropy ?' 'Is it possible to define entropy as a field ?' or 'Is it possible to determine entropy sources ?'

Before we get into the framework of these concepts, let us remind a few concepts from electrodynamic theory and Poission's law or Newtonian gravitation field.

$$\boldsymbol{\nabla}\vec{g} = -4\pi G\rho \qquad <=> \qquad \vec{g} = -\boldsymbol{\nabla}\phi$$

Retrieving Poission's equation for a gravitational field:

$$\Delta\phi(r) = 4\pi G\rho$$

The left hand side has the laplacian of a potential function, and right hand side its source. Another example is found in electrostatics:

$$\Delta\phi(r) = -\frac{\rho}{\epsilon_0}$$

For left hand side being the potential function, and right hand side being charge density which is the source

Now it is important to point out, that by analogy there must exist a source for local entropy too :

$$\Delta s(x) = f(x)$$

For $f(x) = 0$ the equation will be called a Laplace equation for entropic source.

Which might solve eq (18) for stationary cases very well and hence one may result to the temperature for one particle.

One can think of entropic source as the basis of general temperature-entropy relation.

By using the Green function for the Poission's equation we find:

$$s(x) = -\int_{x'} \frac{f(x')}{4\pi|x - x'|} dx' \tag{19}$$

For which we might be able to retrieve the solution, as it will be seen below.

8 Single and many particles Problem

Let us now study, as an example, the behaviour of one particle, stationary, for which eq (18) becomes:

$$\Delta s + (2\frac{\nabla\psi}{\psi})\nabla s + (\frac{\Delta\psi}{\psi})s = 0 \tag{20}$$

This is a second order linear homogeneous differential equation for which can be solved with characteristic polynomial:

$$a\lambda^2 + b\lambda + c = 0$$

for $a \neq 0$, $b = 2\frac{\nabla\psi}{\psi}$, $c = \frac{\Delta\psi}{\psi}$; for which it has two roots respectively:

$$\lambda_1 = \frac{\nabla\psi}{\psi}(-1 + \sqrt{1-\psi})$$

$$\lambda_2 = \frac{\nabla\psi}{\psi}(-1 - \sqrt{1-\psi})$$

and the general solution for eq (19):

$$s(x) = Ae^{[\frac{\nabla\psi}{\psi}(-1+\sqrt{1-\psi})]x} + Be^{-[\frac{\nabla\psi}{\psi}(1+\sqrt{1-\psi})]x}$$

We can see that local entropy depends upon length and not from mass of the body. Therefore, we have entropy dependent on the size of subject in study!

To calibrate our A and B coefficients, we can see for their values at extremities, proposing $s(0) = 0$ we find $A = -B$ therefore:

$$s(x) = A\left[e^{[\frac{\nabla\psi}{\psi}(-1+\sqrt{1-\psi})]x} - e^{-[\frac{\nabla\psi}{\psi}(1+\sqrt{1-\psi})]x}\right]$$

This equation is the solution to eq(18) and eq(19) for which we may say that entropic source is coming from. Further, asserting $A = s_0$ at initial time $t = t_0$.

$$\boxed{s(x) = s_0\left[e^{[\frac{\nabla\psi}{\psi}(-1+\sqrt{1-\psi})]x} - e^{-[\frac{\nabla\psi}{\psi}(1+\sqrt{1-\psi})]x}\right]} \tag{21}$$

8.1 Two particle Problem

The problem may easily presented as ratios:

$$\begin{aligned} \frac{1}{m_1}\Delta(s_1\psi_1) + \frac{1}{m_2}\Delta(s_2\psi_2) = 0 \\ \frac{m_2}{m_1} + \frac{\Delta(s_2\psi_2)}{\Delta(s_1\psi_1)} = 0 \end{aligned} \tag{22}$$

It is important to emphasize that these two particles will have a constant mass ratio and this shall be also the same for laplacians.

8.2 Three particle Problem

Let us see the problem for three different particles,

$$\frac{1}{m_1}\Delta(s_1\psi_1) + \frac{1}{m_2}\Delta(s_2\psi_2) + \frac{1}{m_3}\Delta(s_3\psi_3) = 0$$

Clearly, is seen that local entropy will be dependent of size, and thus can be represented as mass ratios.

$$\frac{m_3}{m_1 m_2}\left[m_2\Delta(s_1\psi_1) + m_1\Delta(s_2\psi_2)\right] + \Delta(s_3\psi_3) = 0$$

We can generalize these equations in a second need.

8.3 N-Particle Problem

Let us generalize these equations for N-Particle system,

$$\frac{m_n}{\Pi_{i=1}^{n-1} m_i}\left[\Pi_{j\in N=1\ldots sup(n-1)}^{n-1} m_j \bigotimes \sum_{g=1}^{n-1} \Delta(s_g\psi_g)\right] + \Delta(s_n\psi_n) = 0$$

This expression can be linked to find the nth particle local entropy, thus finding its temperature.

9 Mobility of particles on a substrate or solution

The experimental activities of Nano^3 group in Laboratoire Aimé Cotton, deal with clusters deposition on substrate and the use of their self organisation for nanostructured materials engineering. One of the problem encountered is how to link diffusion and mobility of particles deposited on a substrate to a local definition of the temperature. Being able to define temperature and entropy, will enable us to determine phase transition that can describe the change from diffusion to nucleation process.

9.1 Brownian motion and Einstein model

One of the model commonly used to describe the motion of a particle on a substrate are in a solution is brownian motion, known also as raandom walk. If the interaction between the particle and the substrate or the solution is weak enough, then the particle is free to move randomly in its environment. Even if the starting and ending points are given, it is impossible to predict every intermediate steps traveled by a particle. Its movements are completely randomized. Moreover, when several particles move at the same time, they are exposed to unpredictable random collisions and as there is no privileged direction, it makes more complicated to guess the trajectory. This is so called Brownian Motion, generally defined as random motion of particles suspended in a fluid resulting from their collision. The name has been given by Robert Brown who observed, in the early 19th century, under a microscope, that particles trapped in cavities inside pollen grains in water where in a constant state of agitation. About a century after Brown's discovery, Einstein explained the reason, why pollen grains agitate constantly in water: their movements are influenced by every single water molecules. Einstein was interested in the kinetic part of the Brownian Motion. He predicted that the diffusion coefficient is related to Brownian particle's displacement by a simple law. $D = \sqrt{\frac{k_B.T}{6\pi\eta Rt}}$ where η corresponds to the viscosity of fluid; R the size of particle and t time; D is called the Diffusion coefficient. Nowadays, this theory is applied to all kind of diffusion phenomenas. One of the main result of the Einstein's theory on the Brownian Motion predicts that the mean value of the displacement of the particles is proportional to $\sqrt{t}$ where t is time: $\lambda = \sqrt{2Dt}$, λ corresponds to the mean value of the displacement of the particles; t time; D the Diffusion coefficient. We implemented a numerical simulation of this random walk where the time t has been replaced by N which is the number of steps. This numerical experience will enable us to predict the behavior of particle's movement, to demonstrate through this numerical experiment, Einstein model prediction, and to verify that the extension of the definition of the temperature as described previously will show that brownian motion is a phenomena with constant temerature and entropy.

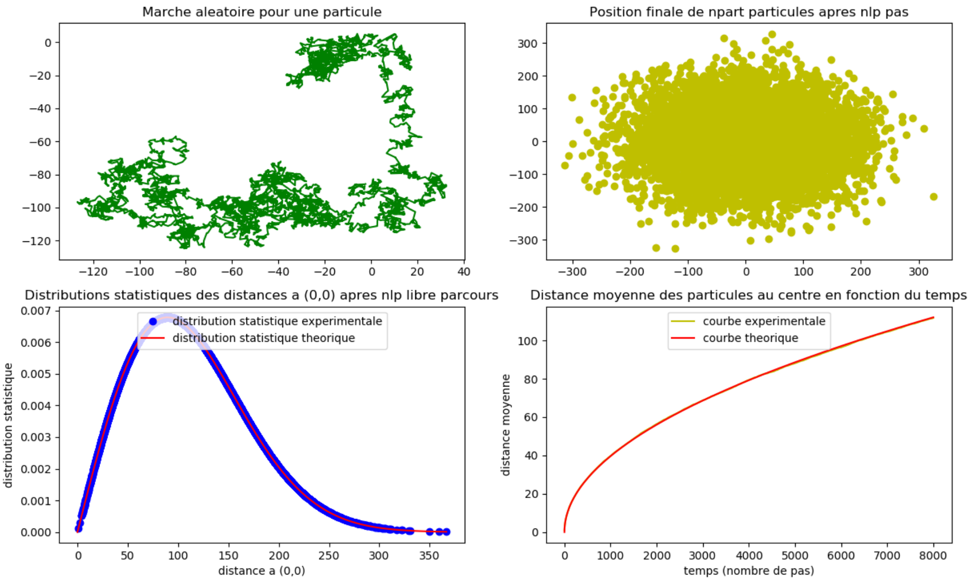

Figure 1: Main result obtained by random walk simulation.

The figure above show the main result of the random walk simulation on trajectories (random aspect), statistics of distribution of distances (stochastic phenomena) and mean value of the displacement (Einstein model). This simulation done for diffusion on a substrate (2D) can be easily extended to motion on a solution (3D).

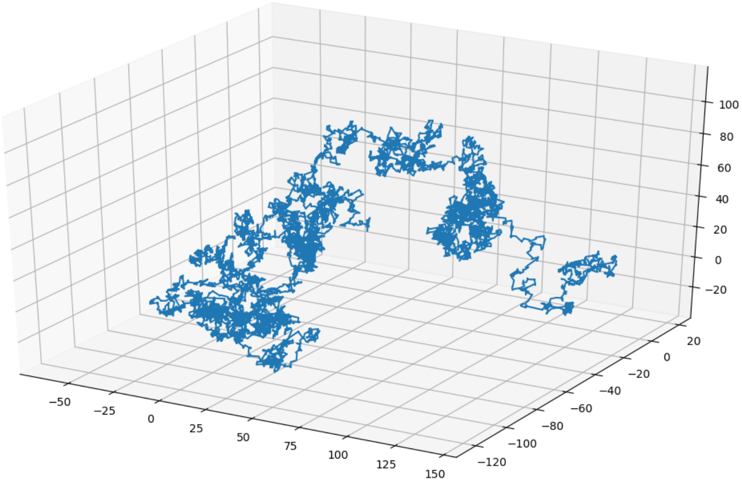

Figure 2: 3D simulation of a random walk in a solution.

9.2 Diffusion Limited Aggregation

What happen now if you allow a diffusing particle to nucleate, i.e. to stop and stick on a nucleation site (defect on a substrate for instance). Such process is known as diffusion-limited aggregation, or DLA, that produces fractal branching structures using random motion for particles (diffusion) and particles sticking (nucleation). Evidence of this process can be found at multiple scales in nature in both organic and inorganic systems. First described by Thomas Witten and Leonard Sander in their 1981 article Diffusion-Limited Aggregation, a Kinetic Critical Phenomenon, diffusion-limited aggregation is a process in which particles of matter stick together (aggregate) as they chaotically move (diffuse) through a medium that provides some sort of resistive (limiting) force. As these particles clump together over time they form characteristic fractal branching structures known as Brownian dendrites or trees. We implemented this process in a simulation (particle by particle step deposition) and we could demonstrate the dendritic nature of the obtain nanostructures.

We will have to extend that simulation to many particle motion and to calculate with our framework particle temperature. The expected results are constant temperature during motion and a drop of temperature on nucleation. The many particle

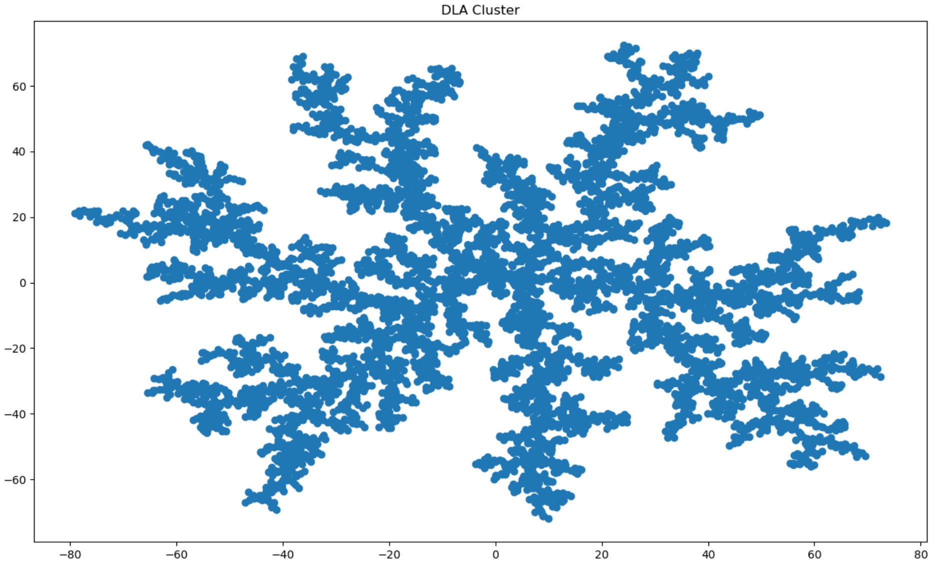

Figure 3: Fractal structure produced by particle by particle deposition.

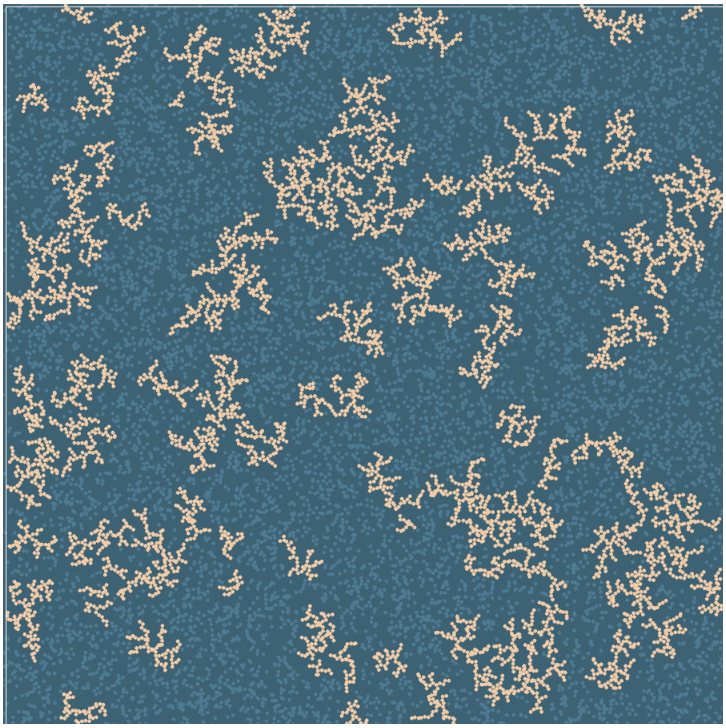

Figure 4: Multiple particle motion with heterogeneous nucleation (on a nucleation site (defect)) and homogeneous nucleation (particle collision).

simulation should also give us access to drastic change on temperature and entropy as a signature of phase transition from gas phase (free particle on motion) to solid phase (nucleation and nanostructures formation).

10 Implementation of ζ Potential

To be able to link an experimental measurement to our concept of temperature, we should find a physical variable that can be measured with good resolution and directly ling to particles motion. A very important object which really matters to colloidal science is ζ potential. This object is a physical property that is found in all particles in suspension.

We would like to emphasize two descriptions, ζ potential is the electrical potential at the slipping plane, and, ζ potential is a scientific term for electrokinetic potential in colloidal dispersions.

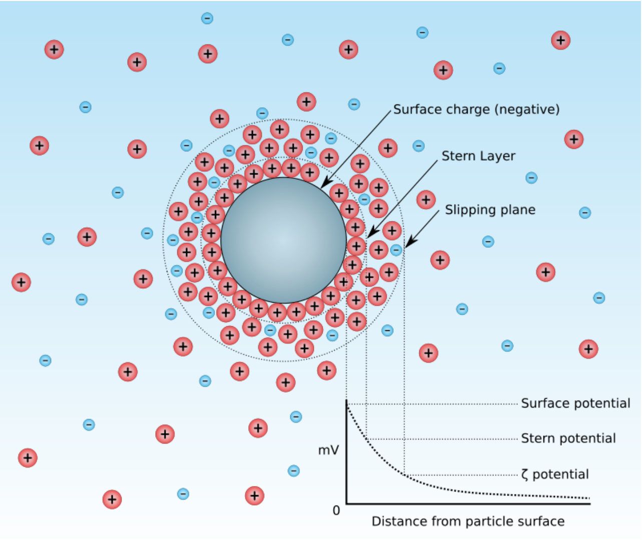

Figure 5: Ionic concentration and potential difference as a function of distance

Why is the need for this potential? Observing our particles in movement would be very difficult, and almost, even impossible to measure their entropies and temperatures. Therefore, we need long-term stability, for which ζ potential comes into scene.

The solvent that will be used, shall be put into external field, electric one. Since, this potential is not measured directly, we have models for that. Later, we will talk for some factors that affects this potential and changes it drastically. On this purpose, we find use of DVLO Theory.

11 DVLO Theory

The main purpose in this theory is to show that there are some sort of forces, later will be explained, that impact the stability of our system, colloidal. From ζ potential, we emphasized that we need long-term stability, and we must find a way to solve and explain this phenomena.

First, we have the external field, and we know that there will be attraction and repulsion depending of particles charge. And, from this we can infer that stability is dependent upon electro-potential energy V_{DVLO}:

$$V_{DVLO} = V_A + V_R + V_M \tag{23}$$

Where, V_A stands for attractive forces, in general van der Waals forces, V_R stands for repulsive forces, due to counterions, V_M stands for potential energy from solvent. The V_M potential is just a marginal contribution.

What we really care of are attractive and repulsive forces, for which they are responsible for balance of the system, and further, stability. We may find also use of virial theorem here, connecting kinetic energy with given potential.

Attractive and repulsive forces acts in distances. Further, we show:

$$V_A = -\frac{A}{12\pi d^2} \tag{24}$$

where **A** is the Hamaker constant for different solvents, **d** the distance, or particle separation from each other. Then comes:

$$V_R = 2\pi\epsilon a\zeta^2 e^{-\kappa d} \tag{25}$$

where **a** is the particle radius, ϵ is the solvent permeability, κ function of ionic composition, ζ is potential. The Hamaker constant helps us determining the interaction energy of Van der Waals forces. There are tables that shows this constant for different solvents, for which is not important to our task. If these two forces are in balance, we can have stability, and further determine ζ potential.

Particles will undergo Brownian motion, and therefore we will see these particles approaching to each other. We have to try to achieve colloidal stability, in order to get indirect measurements of ζ potential. This stability is maintaned from steric repulsion and electrostatic stabilization.

12 Virial Theorem and link with ζ Potential

Our system will be of a colloidal one, and we have to give attention to two layers of this system, inner or Stern layer, and outer or Diffuse layer, which keeps our system bound. We should strongly remind the use of virial theorem in a bound system and in stability.

For the whole system, with a given potential energy, we have:

$$2 < E_k >= n < U_{total} > \tag{25}$$

where n is the number of particles inside the system. From eq(18):

$$\hat{H}\psi_i = -\frac{\hbar^2}{2}\sum_i^n \frac{1}{m_i}(\psi_i \Delta s_i + s_i \Delta \psi_i + 2\boldsymbol{\nabla} s_i \boldsymbol{\nabla} \psi_i)$$

without potential energy of any particle inside, and saying that $\hat{H}$ is the kinetic energy of inside particles, we can relate the potential energy of DVLO Theory, which is our outer region of system, with the inner region.

From eq(23), we can get the potential energy from electro-potential energy, by multiplying with the charge:

$$U_{total} = QV_{DVLO} \quad <=> \quad U_{total} = nqV_{DVLO} \tag{26}$$

where Q is total charge which is dependent on the number of particles and the charge itself.

From eq(25) and eq(26), we will have:

$$2 < E_k >= n < nqV_{DVLO} > \quad <=> \quad 2 < E_k >= n^2 q < V_{DVLO} > \tag{27}$$

Now using the relations, between hamiltonian, in our case the kinetic energy with the inferred equation:

$$2\hat{H}\psi_i = n^2 q < V_{DVLO} > \psi_i \tag{28}$$

having more,

$$2\hat{H}\psi_i = n^2 q < V_A + V_R > \psi_i$$

deducing,

$$2\hat{H}\psi_i = n^2 q \left(< V_A > + < V_R >\right) \psi_i \tag{29}$$

and inferring the relation,

$$2\hat{H}\psi_i = n^2 q \left(-\frac{A}{12\pi} < \frac{1}{d^2} > +2\pi\epsilon a\zeta^2 < e^{-\kappa d} > \right) \psi_i \tag{30}$$

writing now the full equation,

$$\boxed{-\hbar^2 \sum_i^n \frac{1}{m_i}(\psi_i \Delta s_i + s_i \Delta \psi_i + 2\boldsymbol{\nabla} s_i \boldsymbol{\nabla} \psi_i) = n^2 q \left(-\frac{A}{12\pi} < \frac{1}{d^2} > +2\pi\epsilon a\zeta^2 < e^{-\kappa d} > \right) \psi_i} \tag{31}$$

giving us the exact measurement of local entropy from ζ potential and ζ potential from local entropy.

To further represent eq(31) in more compact way, we can write:

$$\boxed{\sum_i^n \frac{\Delta(s_i\psi_i)}{m_i} = \frac{qn^2}{\hbar^2} \left(\frac{A}{12\pi} < \frac{1}{d^2} > \quad - \quad 2\pi\epsilon a\zeta^2 < e^{-\kappa d} > \right) \psi_i} \tag{32}$$

Local entropy will be affected from the factors that ζ potential is affected, which are:

1. pH
2. Conductivity
3. Concetration

This task is a difficult one, even if the colloidal system is of two particles, since the equation will be very hard to compute.

We will try to do this computation as in N-body problem, taking approximations and then deducing the temperature of only one particle.

13 Electrokinetic effects due to applied field

In applied field our system will behave different, and will show interactions between particles. When having interaction, there will be charges and there will be formation of structures. These electric charges are present in the surface of particles.

The link between temperature, entropy, surface charge is found in mobility of particles. These effects are due to electrokinetic effects of the particles which consists of:

1. Electrophoresis
2. Electroosmosis
3. Streaming potential
4. Sedimentation potential

Electrophoresis, is the study of the movement of a charged particle relative to the system suspended under the influence of applied field.

Electroosmosis, is the study of the movement of a liquid to a stationary charged surface.

Streaming potential, is the study of the electric field generated when a liquid is forced to flow through a stationary charged surface.

Sedimentation potential, is the study of the electric field generated when charged particles sediment.

Our case consists in the first item, electrophoresis study. Supposingly, having a field applied toward electrolyte, charged particles will be attracted from electrode of opposite charge, and there will be viscous forces acting on the particles which tends to oppose this movement.

In the case of equilibrum, which is the case we are interested in, velocity shall be constant. We will try to link this velocity, to our object, local entropy, local temperature. The velocity in a unit field will be called as the particle mobility, or electrophoretic mobility.

The colloidal system will be of nanoparticles, which are affected from electric field. This mobility, also called as drift velocity:

$$\mu_E = \frac{v}{E}$$

Or in a moderated way and easy for us to study:

$$\mu_E = \frac{2\epsilon\zeta f(\kappa a)}{3\eta}$$

where ζ is potential, ϵ is dielectric constant, η is viscosity, and $f(\kappa a)$ is Henry's function, where κ is Debye screening length, more use find of, κ^{-1}.

This model is mostly used for aqueous media, and we would be able to moderate concetration. There are different approximations made for Henry's function.

14 Conclusions

In this work, we tried to find a framework for a more direct and local description of the temperature, with the aim of generalizing the concept at several scales. We extended the work to apply this framework for both introducing temperature effect on the description of the mobility of particle in a surface for example and to find a way to access to local temperature measurement through its mobility in more complex environment like polar liquid, water. Unfortunnately, due to confinement and moving of the lab, it was difficult to achieve all the goals, but a promising approach to link mobility (translational states) and temperature through a Lagrangian formalism was initiated. Finally, we gave a link with an experimental accessible measure and local temperature is proposed. My idea is now an open problem, with assistance of prof. Nouari Kebaili and the final goal is to solve eq(32) for nth particles and/or one particle system. Finding the local entropy, gives us access to calculate the local temperature.

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