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A FORMULATION FOR THE ACTIVITY OF SIMPLE MOLECULES

Part I

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ABSTRACT

While the use of continuum approach is useful to study fluids and fluid flows in order to understand, to forecast and to make quantitative estimations in many important problems from engineering point of view, some other problems are still very very far from a thorough understanding and of generalized tools of estimation. Suffice to mention the word "turbulence" and phenomenae leading to turbulence (transition, receptivity) as examples.

The humble thought of the author is that some attention must also be given to molecular behaviour of fluids if the macroscopy of the phenomenon is in a state where we think we are at a deadlock. Furthermore, it is interesting to investigate and to learn the microscopic behaviour even if the macroscopic state does not seem to pose a problem.

No doubt, the powerof numerical simulation gives the opportunity to see the activity of molecules. And it is hoped that this may be used to advantage to observe and study the fluid molecules at different flow regimes.

This paper is concerned essentially with the development of a formulation to simulate the molecular activity. The mechanical activity is restricted to spinless motion of molecules.

First the mathematical formulation of numerical simulation which is a simple algebraic model is exposed. The formulation is discussed in relation to simplifications and assumptions used in the derivation. Though the formulation may easily be used in three dimensions, presented results in Part II are obtained in two dimensions.

METHOD

Formulation

Consider a simple molecule (i) of mass "m" moving under the influence of the force F(r) generated by another molecule at a distance "r". According to Newton's 2. Law of motion:

1
$$m\frac{d^2r}{dt^2} = m\frac{dU}{dt} = F(r)$$

But:

2
$$\frac{dU}{dt} = U\frac{dU}{dr} = \frac{d}{dr}\left(\frac{U^2}{2}\right)$$

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Generally $$(U\bullet\nabla)U+\boxed{UX(\nabla XU)}=\nabla\frac{U^2}{2}$$

With the exception of the term in the dotted rectangle, this equality is the generalized form of the relation used in **(2)**. The term in the rectangle is zero if the particle does not have spin.

With respect to the definition of force potential:

3 $$F(r)=-\frac{d\Psi}{dr}$$

where Ψ(r) is the force potential. Therefore:

$$m\frac{d}{dr}\left(\frac{U^2}{2}\right)=-\frac{d\Psi}{dr}$$

Hence one arrives to:

4 $$\left|m\frac{U^2}{2}+\Psi\right|_{i(t)}^{i(t+\Delta t)}=0$$

or, $$m\frac{U^2}{2}+\psi=\textbf{constant.}$$

which says that the sum of potential and kinetic energy is constant.

The expansion in a time interval of Δt of **(4)** yields:

$$m\left[U^2(t+\Delta t)-U^2(t)\right]+2\Psi(t+\Delta t)-2\Psi(t)=0$$

The difference **"** $\Psi(t+\Delta t)-\Psi(t)$**"** represents the potential at "r(t + Δt)" with respect to "r(t)" and is responsible for the generation of the mutual force F(r) at time "t + Δt". These two molecules are labelled "i" and "j" and the distance between them as "(r_{ij}, t)".Then defining

$$\Psi(t+\Delta t)-\Psi(t)=\Phi(r_{ij},\Delta t)$$

(4) is written as:

4a $$m\left[U^2(t+\Delta t)-U^2(t)\right]+2\Phi(r_{ij},\Delta t)=0$$

For a system of "N" identical molecules (of the same mass) where molecule "i" is under the combined effect of remaining molecules, last relation becomes:

5 $$m\left[U^2(i,t+\Delta t)-U^2(i,t)\right]+2\sum_{\substack{j=1\\ j\neq i}}^{N}\Phi(r_{ij},\Delta t)=0$$

Therefore the speed at "t+Δt" of the molecule "i" is:

6 $$U(i,t+\Delta t)=\sqrt{U^2(i,t)-\frac{2}{m}\sum_{\substack{j=1\\ j\neq i}}^{N}\Phi(r_{ij},\Delta t)}$$

Equation **(5)** can further be developed. Let:

7
$$U(i,t+\Delta t) = U(i,t) + \sum_{\substack{j=1 \\ j\neq i}} \Delta U(i,j:\Delta t))$$

where $\Delta U(i,j;\Delta t)$ is the contribution of the molecule "j" to the velocity vector of the molecule "i" in the interval "t" to " t+Δt", therefore leading to the formation of $U(i,t+\Delta t)$.
Then **(5)** reduces to:

8
$$m\left[2U(i,t)\bullet\sum_{\substack{j=1 \\ j\neq i}}^{N}\Delta U(i,j:\Delta t)+\left(\sum_{\substack{j=1 \\ j\neq i}}^{N}\Delta U(i,j:\Delta t)\right)^2\right]+2\sum_{\substack{j=1 \\ j\neq i}}^{N}\Phi(r_{ij},\Delta t) = 0$$

The second term, (i.e. the square term) within the bracketed LHS can be expanded as:

9
$$\left(\sum_{\substack{j=1 \\ j\neq i}}^{N}\left(\Delta U_x(i,j;\Delta t)e_x+\Delta U_y(i,j;\Delta t)e_y\right)\right)^2 = \sum_{\substack{j=1 \\ j\neq i}}^{N}\left(\Delta U_x^2(i,j;\Delta t)+\Delta U_y^2(i,j;\Delta t)\right)+$$
$$+2\sum_{\substack{j=1 \\ j\neq i \\ k=j+1}}^{N}\left[\Delta U_x(i,j;\Delta t).\Delta U_x(i,k;\Delta t)+\Delta U_y(i,j;\Delta t).\Delta U_y(i,k;\Delta t)\right]$$

Where "e_x" and "e_y" are unit vectors along "x " and "y". The second term on the RHS of **(9)** may be omitted on the grounds that the influence of "j" and "k" molecules on "i" are uncorrelated. Taking only the first term on RHS of **(9),** the relation **(8)** can be reorganized as follows:

10
$$\sum_{\substack{j=1 \\ j\neq i}}^{N}\left(\Delta U_x^2(i,j;\Delta t)+\Delta U_y^2(i,j;\Delta t)+2U_x(i,t).\Delta U_x(i,j,\Delta t)+2U_y(i,t)\Delta U_y(i,j,\Delta t)+\frac{2}{m}\Phi(r_{ij},\Delta t)\right)=0$$

This equation is not sufficient to find $\Delta U_x(i,j;\Delta t)$ and $\Delta U_y(i,j;\Delta t)$. But, the vector composed by these elements is taken in the direction from x(i,t) to x(j,t). Therefore:

11
$$\frac{\Delta U_y(i,j;\Delta t)}{\Delta U_x(i,j;\Delta t)} = \frac{\Delta Y(i,j,t)}{\Delta X(i,j,t)}$$

where the elementary lengths on RHS are components of $r_{ij}(t)$.

With this premise and the condition that the influence of "j" particles on "i" are uncorrelated, the components of the velocity vector generated at time "t + Δt" by any "j" molecule", i.e. $\Delta U_x(i,j;\Delta t)$ can be found from:

12
$$\Delta U_x(i,j;\Delta t)\left[1+\frac{\Delta Y^2(i,j,t)}{\Delta X^2(i,j,t)}\right]=-\left[U_x(i,t)+U_y(i,t)\frac{\Delta Y(i,j,t)}{\Delta X(i,j,t)}\right]\pm$$
$$\sqrt{\left[U_x(i,t)+U_y(i,t)\frac{\Delta Y(i,j,t)}{\Delta X(i,j,t)}\right]^2-\frac{2}{m}\Phi(r_{ij},\Delta t)\left[1+\frac{\Delta Y^2(i,j,t)}{\Delta X^2(i,j,t)}\right]}$$

or:

13 $$\Delta U_x(i,j;\Delta t)\left[\Delta X^2(i,j,t)+\Delta Y^2(i,j,t)\right]=-\Delta X(i,j,t)\left[U_x(i,t)\Delta X(i,j,t,)+U_y(i,t)\Delta Y(i,j,t)\right]\pm$$

$$\pm\theta\sqrt{\Delta X^2\left\{\left[U_x(i,t)\Delta X(i,j,t)+U_y\Delta Y(i,j,t)\right]^2+\frac{2}{m}\left[\Delta X^2(i,j,t)+\Delta Y^2(i,j,t)\right]ABS\Phi(r_{ij},\Delta t)\right\}}$$

and $\Delta U_y(i,j;\Delta t)$ from **(11)**. (This incremental velocity is constant during "Δt", hence the label)

SOME CONSIDERATIONS ON THE FORMULATION

***Simulation Capability of the Formulation*:** The equation **(5)** (therefore **(6)**) is an exact solution of **(1)** under the **mechanical** restrictions:

A- The motion of particle is spinless.
B- The force exerted onto the particle has a potential.

The following step **(7)** and the consequential relation **(8)** are legitimate steps**.** So, relations **(7)** and **(8)** give exactly the magnitude of the velocity of a molecule under the influence of a given geographic state of remaining N–1 parent molecules.

Sole information of magnitude of velocity is surely not enough to locate its position at time t+Δt. Passage to equation **(9)** is achieved by expressing vector quantities in terms of their components.**(10)** requires the acceptance of another condition;

C- The influence of cousin molecules are uncorrelated.

This amounts to say that any parent molecule ignores the effect of others while it is affecting the target molecule. This is another physical constrain similar to A and perhaps B.
In order to find out incremental velocity components $\Delta U_x(i,j;\Delta t)$ and $\Delta U_y(i,j;\Delta t)$ this paper uses the complementary condition **(11)**:

D- The condition **(11)** means simply that the incremental velocity vector is directed to the affecting molecule. This is the direction along which the force generated by the potential is acting. It is a consequence of **(1)**.

The formulation explained so far is valid for any force potential and molecular activity within the premises A, B, C, and D.

Force Potential: The force potential adopted for simple molecules of this study is Lennard-Jones function. This is a model of force potential that ignores the interaction of molecules of more than two; or that it considers the interaction of only two molecules, i.e. the affecting one and the affected one.

14 $$\Phi(r_{ij}) = 4\varepsilon\left(\frac{\sigma^{12}}{r_{ij}^{12}}-\frac{\sigma^{6}}{r_{ij}^{6}}\right)$$

"ε" has the dimension of energy and related ambient temperature through Boltzmann constant. "σ" is the equilibrium distance where the force potential $\Phi(r_{ij})$ becomes zero. "r_{ij}" is the distance between the two molecules "i" and "j". We consider the "i" molecule as the one affected by "j" (or affecting) molecule.

A: If $r_{ij}>\sigma$, the dominating term in **(14)** is the second term. It yields an attraction force and "j" pulls "i" to itself. The sign of $\Phi(r_{ij})$ in **(12)** (the last term in square root) turns to be positive.
If $r_{ij}<\sigma$, the dominating term in **(14)** is the first term. It gives a repulsion force and "i" is repulsed from "j". The last term containing $\Phi(r_{ij})$ in **(12)** becomes **negative**. On the other hand if repulsive force is

considered starting from **(1)**, $\Phi(r_{ij})$ turns out to be negative, therefore with a positive sign in **(12)**. Therefore the contribution of the term containing $\Phi(r_{ij})$ is always positive no matter the numerical value comes out positive or negative. This is also logical from the poınt of view that $\Phi(r_{ij})$ must always contribute positively to the energy of the "i" molecule whether it is attracted to or repulsed from the "j" molecule. Similar argument is valid for the other term within the square root.
So the square root term is always positive definite. Hence, to simplify the calculations the last term of **(12)** is written as an absolute value as can be seen in **(13).** The direction of the effect of the square root is taken into consideration with a factor "θ" in front of the square root which is ± 1 depending whether the effect is attractive or repulsive.

B: If r_{ij} is smaller than equilibrium distance, this means that the affected molecule is within the repulsion zone of the affecting molecule. In such a case the ''j'' molecule applies in general an extremely large repulsion velocity to molecule ''i'' because of the first term of **(14)**. The ultimate consequence is a dispersion of molecules. This is a fact and has been observed when many molecule simulation is performed. The velocities thus generated are not realistic.
In order to remedy, the authors adopted the following scheme: if ''i'' molecule is within the repulsion zone of the ''j'' molecule, the ''i'' molecule is placed in the ''i-j'' direction to approximately 0.984 of equilibrium distance from the center of ''j'' molecule and the process is left to its natural development. According to this scheme, the velocity generated is repulsive and is of the order of the average velocity within the molecular activity under consideration.

Non-Dimensionalization: The last point is non-dimensionalization. Given **(13)** and **(14),** one can use the transformations**:**

15 $X, Y, r_{ij} \rightarrow \sigma(X, Y, r_{ij})$ and $(U_x, U_y, \Delta U_x, \Delta U_y) \rightarrow U_{ref}(U_x, U_y, \Delta U_x, \Delta U_y)$

where $U_{ref} = \sqrt{\frac{8\varepsilon}{m}}$

and arrives to:

16 $$\Delta U_x(i,j;\Delta t)\left[\Delta X^2(i,j,t)+\Delta Y^2(i,j,t)\right] = -\Delta X(i,j,t)\left[U_x(i,t)\Delta X(i,j,t,)+U_y(i,t)\Delta Y(i,j,t)\right]\pm$$

$$\pm\theta\sqrt{\Delta X^2(i,j,t)\left\{\left[U_x(i,t)\Delta X(i,j,t)+U_y\Delta Y(i,j,t)\right]^2+\left[\Delta X^2(i,j,t)+\Delta Y^2(i,j,t)\right]ABS\Phi(r_{ij},\Delta t)\right\}}$$

together with:

$$\Phi(r_{ij}) = \left(\frac{1}{r_{ij}^{12}}-\frac{1}{r_{ij}^{6}}\right)$$

Velocity Scaling and Velocity Distribution Controls: The overall kinetic energy of a system of molecules increases during the course of numerical simulation of the activity if left alone. This will be in contradiction with the equation **(4)**. Therefore velocity scaling is needed to be applied at every time step of the calculation of velocities to control and preserve the level of overall kinetic energy of the system. Also the distribution of velocity spectrum must be in conformity with the pertinent conventional distributions**.**

SECOND FORMULATION

The first term on RHS of **(9)** is not considered in the second formulation on the grounds that it is composed of second order terms. Hence one arrives to:

18 $$m\left[2U(i,t)\bullet\sum_{\substack{j=1\\ j\neq i}}^{N}\Delta U(i,j,\Delta t)\right] = -2\sum_{\substack{j=1\\ j\neq i}}^{N}\Phi(r_{ij},\Delta t)$$

or better

$$\sum_{\substack{j=1\\ j\neq i}}^{N}\left[U_x(i,t).\Delta U_x(i,j,\Delta t)+U_y(i,t).\Delta U_y(i,j,\Delta t)\right]=-\frac{1}{m}\sum_{\substack{j=1\\ j\neq i}}^{N}\Phi\left(r_{ij},\Delta t\right)$$

and

19
$$U_x(i,t).\Delta U_x(i,j;\Delta t)+U_y(i,t).\Delta U_y(i,j;\Delta t)=-\frac{1}{m}\Phi\left(r_{ij},\Delta t\right)$$

This equation is combined with **(11)** and yields:

20
$$\Delta U_x(i,j,\Delta t)=-\frac{\Phi\left(r_{ij},\Delta t\right).}{m}\left[U_x(i,t)+U_y(i,t)\frac{\Delta Y(i,j,t)}{\Delta X(i,j,t)}\right]^{-1}$$

To find $\Delta U_y(i,j;\Delta t)$, either **(11)** or

21
$$\Delta U_y(i,j,\Delta t)=-\frac{\Phi\left(r_{ij},\Delta t\right).}{m}\left[U_x(i,t)\frac{\Delta X(i,j,t)}{\Delta Y(i,j,t)}+U_y(i,t)\right]^{-1}$$

can be used. With **(7)** or **(8),** one arrives to:

22
$$U_x(i,t+\Delta t)=U_x(i,t)-\frac{1}{m}\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{\Phi\left(r_{ij},\Delta t\right)\Delta X(i,j,t)}{U_x(i,t)\Delta X(i,j,t)+U_y(i,t)\Delta Y(i,j,t)}$$

23
$$U_y(i,t+\Delta t)=U_y(i,t)-\frac{1}{m}\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{\Phi\left(r_{ij},\Delta t\right)\Delta Y(i,j,t)}{U_x(i,t)\Delta X(i,j,t)+U_y(i,t)\Delta Y(i,j,t)}$$

These relations are dimensionalized in terms of Leonard - Jones relation. “σ” is used as the reference for distances and “ $\sqrt{\frac{4\varepsilon}{m}}$ “ as the reference for velocities. Then **(22)** and **(23)** become:

24
$$U_x(i,t+\Delta t)=U_x(i,t)-\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{\theta\Phi\left(r_{ij},\Delta t\right)\Delta X(i,j,t)}{U_x(i,t)\Delta X(i,j,t)+U_y(i,t)\Delta Y(i,j,t)}$$

25
$$U_y(i,t+\Delta t)=U_y(i,t)-\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{\theta\Theta\Phi\left(r_{ij},\Delta t\right)\Delta Y(i,j,t)}{U_x(i,t)\Delta X(i,j,t)+U_y(i,t)\Delta Y(i,j,t)}$$

The meaning of “θ” is explained in the previous formulation.

Consideration on the Second Formulation

The second formulation gives almost the results when “r_{ij}“ is larger than “σ”. If they are close, the difference becomes larger.

EXTENSION TO THREE DIMENSIONS

The relation **(16)** can be extended to three dimensions. Since the incremental velocity vector is accepted to be in the direction of "r" vector:

26
$$\frac{\Delta Ux}{\Delta X} = \frac{\Delta Uy}{\Delta Y} = \frac{\Delta Uz}{\Delta Z}$$

where $r^2 = \Delta X^2 + \Delta Y^2 + \Delta Z^2$

Then, one arrives to:

27
$$\Delta U_x \left[\Delta X^2 + \Delta Y^2 + \Delta Z^2\right] = -\Delta X\left[U_x\Delta X + U_y\Delta Y + U_z\Delta Z\right] \pm$$
$$\pm\theta\sqrt{\Delta X^2\left\{\left[U_x\Delta X + U_y\Delta Y + U_z\Delta Z\right]^2 + \left[\Delta X^2 + \Delta Y^2 + \Delta Z^2\right]ABS\Phi\left(r_{ij}\right)\right\}}$$

with respect to all premises of the formulation. Similarly the other incremental components can be obtained from **(26)**.
The second formulation gives:

28
$$U_x(i,t+\Delta t) = U_x(i,t) - \sum_{\substack{j=1\\ j\neq i}}^{N} \frac{\Theta\Phi'\left(r_{ij},\Delta t\right)\Delta X(i,j;t)}{U_x(i,t)\Delta X(i,j;t) + U_y(i,t)\Delta Y(i,j;t) + U_z(i,t)\Delta Z(i,j,t)}$$

which can be repeated for "y" and "z" components.

EFFECTIVE ZONE OF INFLUENCE

An interesting and practical question is to determine the physical dimension of the zone occupied by other molecules influencing a particular molecule at a given level of approximation. 2D or 3D problem can be approached in the same manner as explained in the sequel for the case of 2D problem.
The idea is to determine the combined effect (on velocity) of molecules situated beyond the circle of radius "Rσ" on a given particle placed at the center of the circle. "σ" is defined in the text and "R" used here is dimensionless radius of influence.
It is assumed that the number-density of molecules per unit area "s" is constant. The constancy is assumed to avoid extensive formulation which can hide the simplicity of the calculation.
The contribution to the square of the magnitude of velocity at any instant of a molecule (i) from the region $R < r < \infty$ can be expressed using **(4)** or **(5).** Omitting the initial velocity, one obtains in non-dimensional form:

29
$$U_i^2 = \int_R^\infty -2\pi r s\Phi(r)dr$$

Let us take Lennard-Jones model used throughout this study.

$$\Phi(r) = \left[\frac{1}{r^{12}} - \frac{1}{r^6}\right]$$

Since the effect of molecules away from the molecule (i) are those of interest, the first term can be dropped from the potential function. Then:

$$U_i^2 = 2\pi s\int_R^\infty r\frac{1}{r^6}dr = \frac{\pi s}{2}R^{-4} \qquad \text{and}$$

30
$$U_i(R) = \sqrt{\frac{\pi s}{2}}\,R^{-2}$$

This formula approximates the effect of the molecules outside of the circle of radius "R" centered at the affected molecule (i).
Though **(30)** is valid for the region where r > R, we define: $U_i(1)$ to eliminate the term in the square root One arrives to:

31
$$I = \frac{U_i(R)}{U_i(1)} = R^{-2}$$

"I" is the "influence number" representing the relative effect of the molecules located outside of the zone of radius R (i.e. R< r < ∞) as compared to the effect of **all** molecules surrounding the molecule (i).

Table 1: Influence number corresponding to selected radius

R	10	20	30	50
I	10^{-2}	$2.5\ 10^{-3}$	$1.1\ 10^{-3}$	$4\ 10^{-4}$

For example, if R = 30, the effect of molecules outside of R = 30 will correspond to an effect of 1.1 ‰ on U_i. If the zone containing all molecule has a radius of R_0, the number of effective molecules in the zone1< r < R to be considered in calculations is reduced by factor of:

32
$$NEMF = \left(\frac{R}{R_0}\right)^2$$

where NEMF stands for "number of effective molecules factor".
With R = 30 and R_0 = 100, the number of molecules in the "effective zone of influence" is only 10 % of all molecules.
In the case of a 3D problem, the equivalent relations for **(30)** and **(31)** are:

33
$$I = \frac{U_i(R)}{U_i(1)} = R^{-3}$$

34
$$NEMF = \left(\frac{R}{R_0}\right)^3$$

On the other hand, the precaution is taken to choose "R" such that NEMF ≥ 10 %, an arbitrary number.

SOME APPLICATIONS (revised)*

Three Aligned but Quarantined Molecules

Kinetics: Consider three molecules aligned on a common axis as depicted in Figure1 and somehow isolated from the influence of other molecules. In view of Lennard-Jones potential:

35
$$\frac{U(x)}{U_o} = \pm\left[\frac{1}{x^6} - \frac{1}{x^{12}} - \frac{1}{(\lambda_o - x)^6} + \frac{1}{(\lambda_o - x)^{12}}\right]^{\frac{1}{2}}$$

expresses the velocity of the molecule between two other molecules "λ" apart. The meaning of symbols are as follow:

* This part of the text is revised in order to account for a sign error in the previous publication.

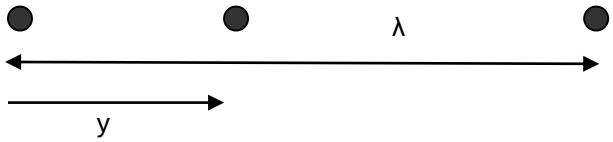

Figure 1: Three Aligned but Quarantined Molecules

$Y = x\sigma$; $\lambda = \lambda_o\sigma$; $U_o = 2\sqrt{\frac{2\varepsilon}{m}}$ where "σ" and "ε" appear in the Lennard-Jones model of force potential $\Phi(y) = 4\varepsilon\left[\frac{\sigma^{12}}{y^{12}} - \frac{\sigma^{6}}{y^{6}}\right]$. "m" is the common mass of molecules and "σ" is the distance from the molecule where the potential becomes zero. "ε" and "σ" are common constants of molecules making the substance.
Numbers are given below to illustrate the effect of "λ_o" on velocity of mid molecule.

Table 2: Some calculations for the effect of "λ_o" on mid molecule velocity

λ_o	20	10	5	3	2.50	2.2
X_{Utop}	1.097	1.12	1.12	1.12	1.09	1.09
$\frac{U_{TOP}}{U_o}$	0.485	0.50	0.50	0.48	0.361	--
X_K	2.15	2.13	2.10	1.482	--	--

These velocities have to be considered for static conditions; this means that the velocity shown in the table is the mid molecule when it occupies the position "x" whereas the two other molecules occupy fixed positions at x=0 and x=λ_o, hence "λ_o" apart. The numbers in the Table are values for the LHS of the symmetry point at $\lambda_o/2$ and the velocities are negative in sign, meaning that they are directed to the molecule at x = 0.
Top velocity occurs almost invariable at x =1.12 for larger "λ_o" and also with an almost fixed value of $\frac{U_{TOP}}{U_o}$ = 0.50. This is to be expected because of the dominance of the molecule at x = 0 (or at x = λ_o) as compared to the effect of the other molecule at a distance of λ_o. The velocity at $\lambda_o/2$, i.e. $\frac{U_{MID}}{U_o}$, is zero as it should be.

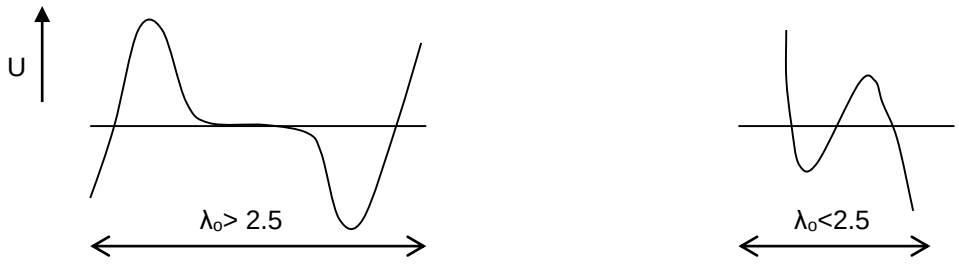

Figure 2: Mid molecule velocity variation

The character of velocity variation in terms of "x" changes if λ_o is bigger or smaller than 2.5 as depicted schematically in the Figure 2.

Under the influence of combined potentials of two molecules, zero velocity of mid molecule is reached not at x = 1 (i.e. y = σ), but at x* = 0.98 (i.e. y = σ* = 0.98σ)

As an example, the velocity U_{TOP} of the gas Ar is calculated. For this gas the following data is available: σ = 3.418Å, ε =124K and m = $6.63x10^{-23}$gr. Therefore:

$$U_0 = 4.5x10^4 \text{cm/s and } U_{TOP} = 0.5x4.5x10^4 = 2.25x10^4 \text{ cm/s if } \lambda_0 > 2.5$$

This speed is smaller than "the most probable speed" in Maxwell-Boltzmann spectrum which is around $3.50x10^4$ cm/s for Ar. Surely this average velocity is the joint effect of many molecules surrounding any particular molecule under consideration, whereas in Figure 2 the three molecules are quarantined from the effect of other molecules. Simulation of many molecules will give the average velocity.

Vibrations: One can try a frequency estimation assuming that either the middle molecule or the side molecules perform a vibrational motion. If the middle molecule perform a periodic motion between the side molecules the distance left free for the molecule to go from one to the other molecule is 05σ if $\lambda_o = 2.5\sigma$ .Top velocity under these circumstances is $0.36U_o$. The average velocity for this motion can be half of the top velocity. Then the period of vibration becomes:

$$T_{LIN} = \frac{2x0.5x3{,}418.10^{-8}}{0.5x0.36x450.10^4} = 0.042 \text{ ps}$$

and a frequency of $f_{LIN} = 24$ Tc/s*

This period (or frequency) may perhaps be considered to correspond to "average periods of molecular rotations" which is of the order of "ps"* [Feynman, 1967]. It looks strange that the associated speed corresponds almost to most probable speed. If it is true, it means that Ar molecules are mostly in vibrational state. Yet, it may be noted that the MB (Maxwell-Boltzmann) spectrum of Ar is highly peaky and "most probable speed", "average speed" and "rms" of speeds" are highly close to each other. The vibrational collision described above is not expected to have a long life, the **overall** behavior hints the short lived vibrational motion of "wavelet"s.

The effective zone of influence is selected with a radius of influence of 100LU. This means I = $10^{-4}$and NEMF = 0.168 whereas the radius of the zone containing all molecules is ≈ 244σ. To make it clear, instead of dealing with 4900 molecules at each time step, 16.8% of it, i.e. only 820 molecules are used in the calculations and this will suffice to see the effect of all parent molecules on the selected molecule. Though a radius of influence of 50LU gives an acceptable I (i.e.4 10^{-4}), the corresponding NEMF = 0.04 is less than 10%. This number (10%) is taken arbitrarily as the lower limit for NEMF throughout the applications.

CONCLUSION

The author is not aware of the existence of the formulation developed in this paper as related to the numerical simulation of the molecular activity. Therefore the title reflects the notion that the method is a new or different one.
The method is mathematically exact to calculate instantaneous velocities. It is highly efficient for computer usage as will be illustrated in the following paper.

* Feynman mentions period of 1 ps.
Feynman Lectures of Physics vol. I. Addison-Wesley Pub. Co. 1967. p: 4-5.

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Bibliography

Donald, G. (2005) *Molecular and Particle Modelling of Laminar and Turbulent Flow.* River Edge NJ. USA World Scientific Publishing Co.

Erkoç, Ş. (2004) *Lecture Notes on Simulations of Many-Particle Systems*. Department of Physics, METU

Feynman, R. (1967) *The Feynman Lectures on Physics*. Addison-Wesley Pub. Co.