Dynamical Equations Of Periodic Systems Under Constant External Stress

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PURPOSE

To derive the concrete mathematical form of dynamical equations for the period vectors of a periodic system under constant external stress, from Newton's Second Law.

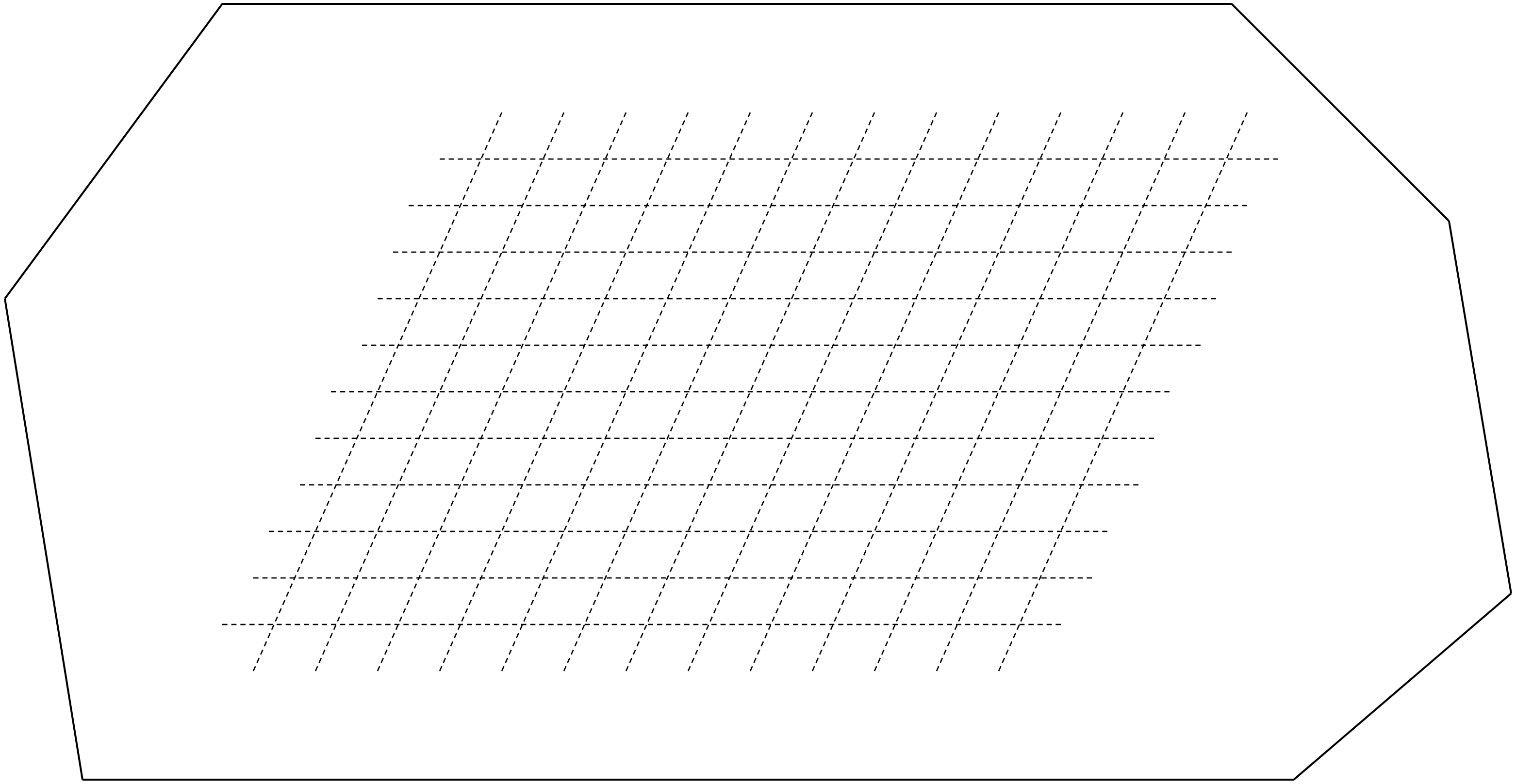
http://arxiv.org/pdf/cond-mat/0209372.pdf

Classical Molecular Dynamics (MD)

widely used in many fields.

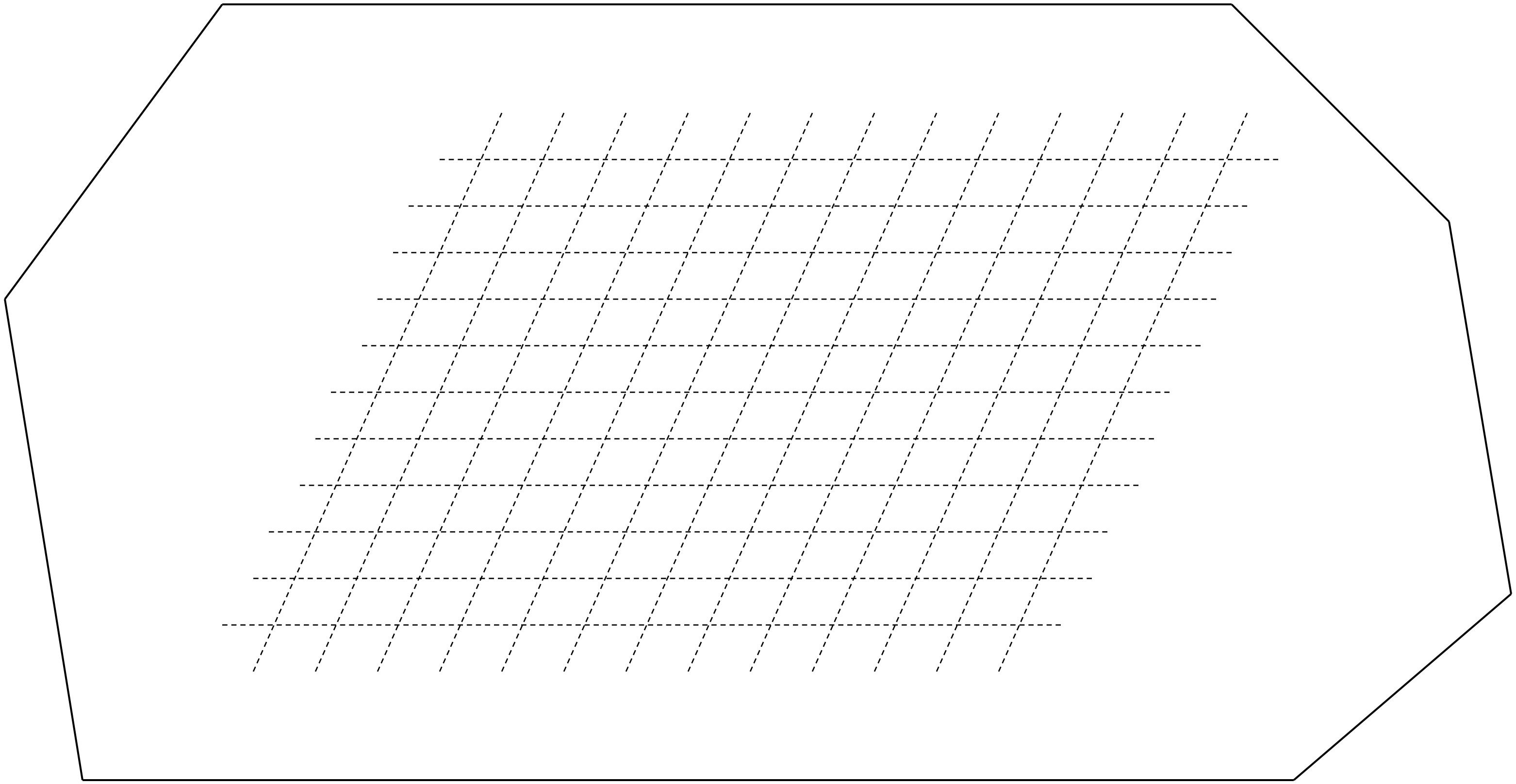
Periodic boundary conditions are often employed, then the system becomes a dynamical crystal filled with repeating cells.

In this work, the whole system is modeled as a limited macroscopic bulk, composed of unlimited number of repeated microscopic cells in three dimensions, with surface effect ignored.

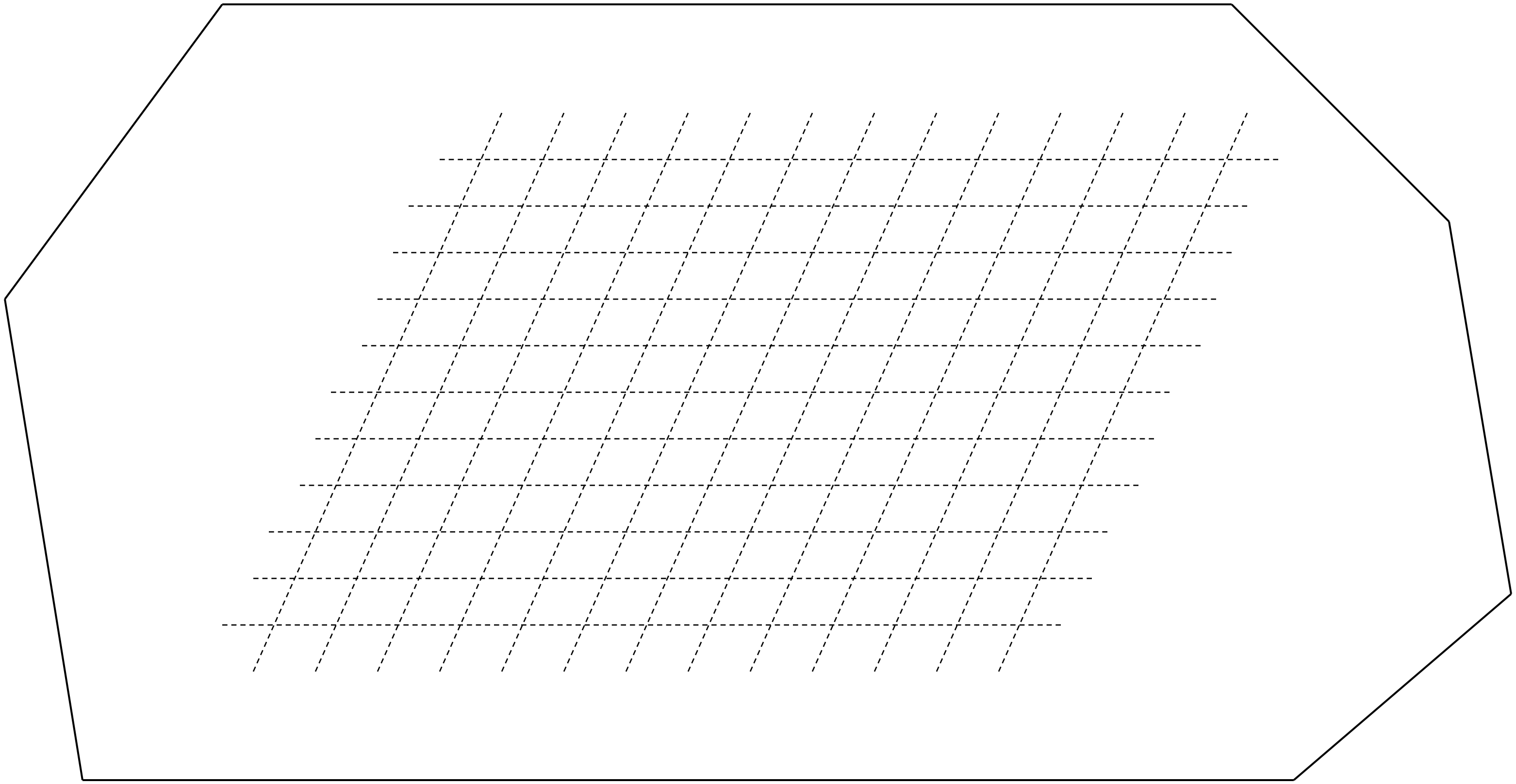


As usual, the cell in the center

is called MD cell. Particles in it called MD particles with position vectors $\mathbf{r}_i$, $i = 1, 2, \cdots, n$.



For each cell, the three edge vectors $\mathbf{a}, \ \mathbf{b}, \ \mathbf{c}$ (forming a right-handed triad) are the period vectors of the system.



Degrees of freedom of the system.

Then the MD particle position vectors and the period vectors are the full degrees of freedom of the system.

What about the periods?

The dynamics of the particles is just Newton's Second Law on them.

Another respect: external forces

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External forces will definitely cause its internal structure to change.

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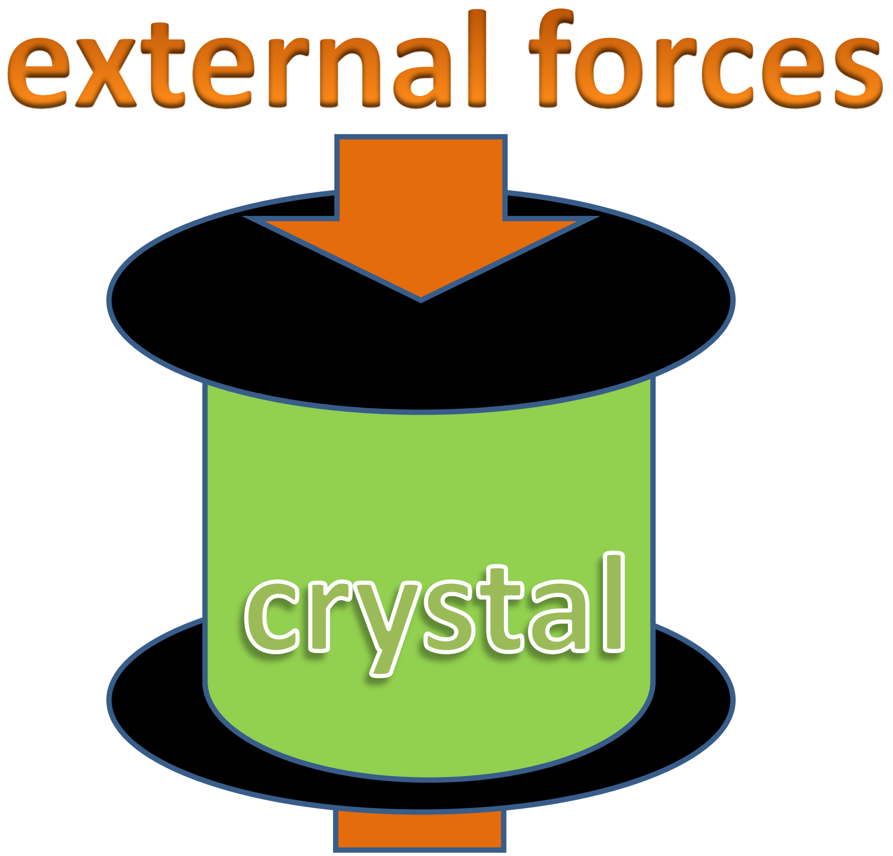


In 1980, Parrinello and Rahman

proposed their theory of the period dynamics (PRMD), where they introduced a Lagrangian and brought it into the Lagrangian Dynamical Equation to produce dynamics for both the MD particles and the periods.

Phys. Rev. Lett. **45**, 1196 (1980)

and

J. Appl. Phys. **52**, 7182 (1981)

Equations of PRMD (constant external pressure)

$$L = \tfrac{1}{2}\sum m_i \dot{\vec{s}}_i{}' \underline{G}\, \dot{\vec{s}}_i - \sum_i \sum_{j>i} \varphi(r_{ij}) + \tfrac{1}{2} W\, \mathrm{Tr}(\dot{\underline{h}}' \dot{\underline{h}}) - p_{\mathrm{ext}} \Omega. \qquad (1)$$

$$\ddot{\vec{s}}_i = m_i^{-1} \sum_{j \neq i} \chi(r_{ij})(\vec{s}_i - \vec{s}_j) - \underline{G}^{-1} \dot{\underline{G}}\, \dot{\vec{s}}_i, \qquad (2)$$

$$\ddot{\underline{h}} = W^{-1}(\underline{\pi} - p_{\mathrm{ext}})\underline{\sigma}. \qquad (3)$$

$$\Omega \overleftrightarrow{\pi} = \sum_i m_i \vec{v}_i \vec{v}_i + \sum_i \sum_{j>i} \chi(r_{ij})(\vec{r}_i - \vec{r}_j)(\vec{r}_i - \vec{r}_j), \qquad (4)$$

with $\underline{h}$ be the matrix formed by $\{\vec{a}, \vec{b}, \vec{c}\}$

$\vec{r}_i = \xi_i \vec{a} + \eta_i \vec{b} + \zeta_i \vec{c} = \underline{h}\, \vec{s}_i,$ $\qquad (\xi_i, \eta_i, \zeta_i)$

$\chi(r)$ to denote $-d\varphi / r dr$, the vector $\vec{v}_i$ being $\underline{h}\, \dot{\vec{s}}_i$.

Phys. Rev. Lett. **45**, 1196 (1980)

PRMD

combined with the well-known Car-Parrinello MD later, has been used extensively in many kinds of simulations.

In 1983, Nosé and Klein pointed out

The result is the usual Newton's second law equation with a correction term arising from the change in shape of the MD cell.

$$m_i \ddot{\mathbf{s}}_i = \mathbf{h}^{-1} \mathbf{f}_i - m_i \mathbf{G}^{-1} \dot{\mathbf{G}} \dot{\mathbf{s}}_i. \qquad (2.5)$$

in the paper

MOLECULAR PHYSICS, 1983, VOL. 50, NO. 5, 1055–1076

This implies that the generated dynamical equations for the MD particles in PRMD are not that of Newton's Second Law.

Another drawback in PRMD

The generated dynamical equation for the periods under constant external stress $\mathbf{S}$

$$W\ddot{\mathbf{h}} = (\boldsymbol{\pi} - p)\boldsymbol{\sigma} - \mathbf{h}\boldsymbol{\Sigma}. \qquad (2.25)$$

$$\boldsymbol{\Sigma} = \mathbf{h}_0^{-1}(\mathbf{S} - p)\mathbf{h}_0'^{-1}\Omega_0. \qquad (2.24)$$

in their paper J. Appl. Phys. **52**, 7182 (1981) .

It is not in a form where the periods are driven by the imbalance between the internal and external stresses. Then when the system reaches an equilibrium state, the internal and external stresses may not balance each other.

In any case, PRMD

can find the true equilibrium states under constant external pressure and zero temperature, when all velocities and accelerations are zero.

Not using Lagrangian Dynamics, we will

Keep Newton's Second Law for the MD particle as its original

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \quad (i = 1, 2, \cdots, n)$$

Apply Newton's Second Law on halves of the system and statistics over system translation and particle moving directions to derive dynamical equations of the periods.

As a result, our

dynamical equations are in the form where the periods are driven by the imbalance between internal and external stresses.

The internal stress has both a full interaction term and a kinetic-energy term.

Some notations

By using the periods $\mathbf{a},\ \mathbf{b},\ \mathbf{c}$, any cell can be represented with $\mathbf{T} = T_{\mathbf{a}}\mathbf{a} + T_{\mathbf{b}}\mathbf{b} + T_{\mathbf{c}}\mathbf{c}$, where $T_{\mathbf{a}},\ T_{\mathbf{b}},\ T_{\mathbf{c}}$ are any integers.

For the MD cell $\mathbf{T} = 0$.

Cell volume $\Omega = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$

Cell surface vectors:

$$\sigma_{\mathbf{a}} = \mathbf{b} \times \mathbf{c},\ \sigma_{\mathbf{b}} = \mathbf{c} \times \mathbf{a},\ \sigma_{\mathbf{c}} = \mathbf{a} \times \mathbf{b}$$

$$\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \text{or}\ \mathbf{c}$$

More notations

Only pair potential is considered

$$\varphi^{(2)}(r_{i,j}) = \varphi^{(2)}(|\mathbf{r}_i - \mathbf{r}_j|)$$

Force acting on particle j in cell $\mathbf{T}'$ by particle i in cell $\mathbf{T}$ is denoted with

$$\mathbf{f}_{i,\mathbf{T}\to j,\mathbf{T}'}$$

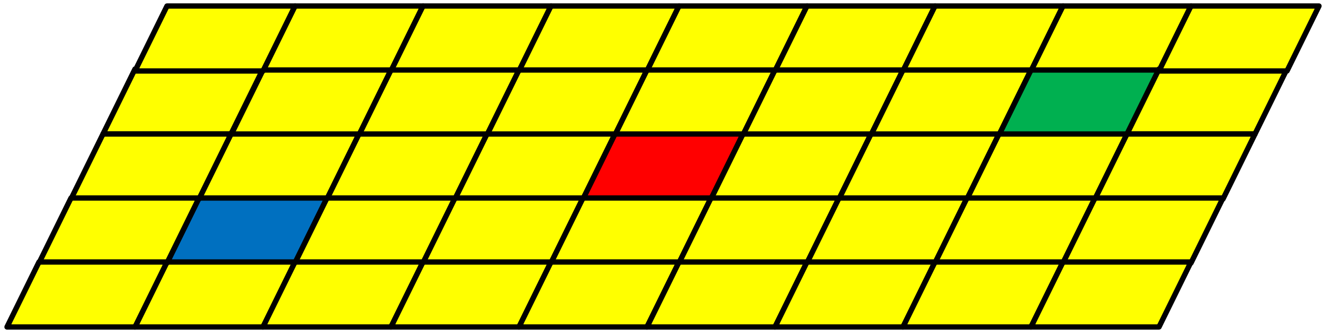
External stress $\overleftrightarrow{\Upsilon}$

with external pressure p as a special case

$$\overleftrightarrow{\Upsilon} = p \overleftrightarrow{I}$$

where $\overleftrightarrow{I}$ is a unit matrix.

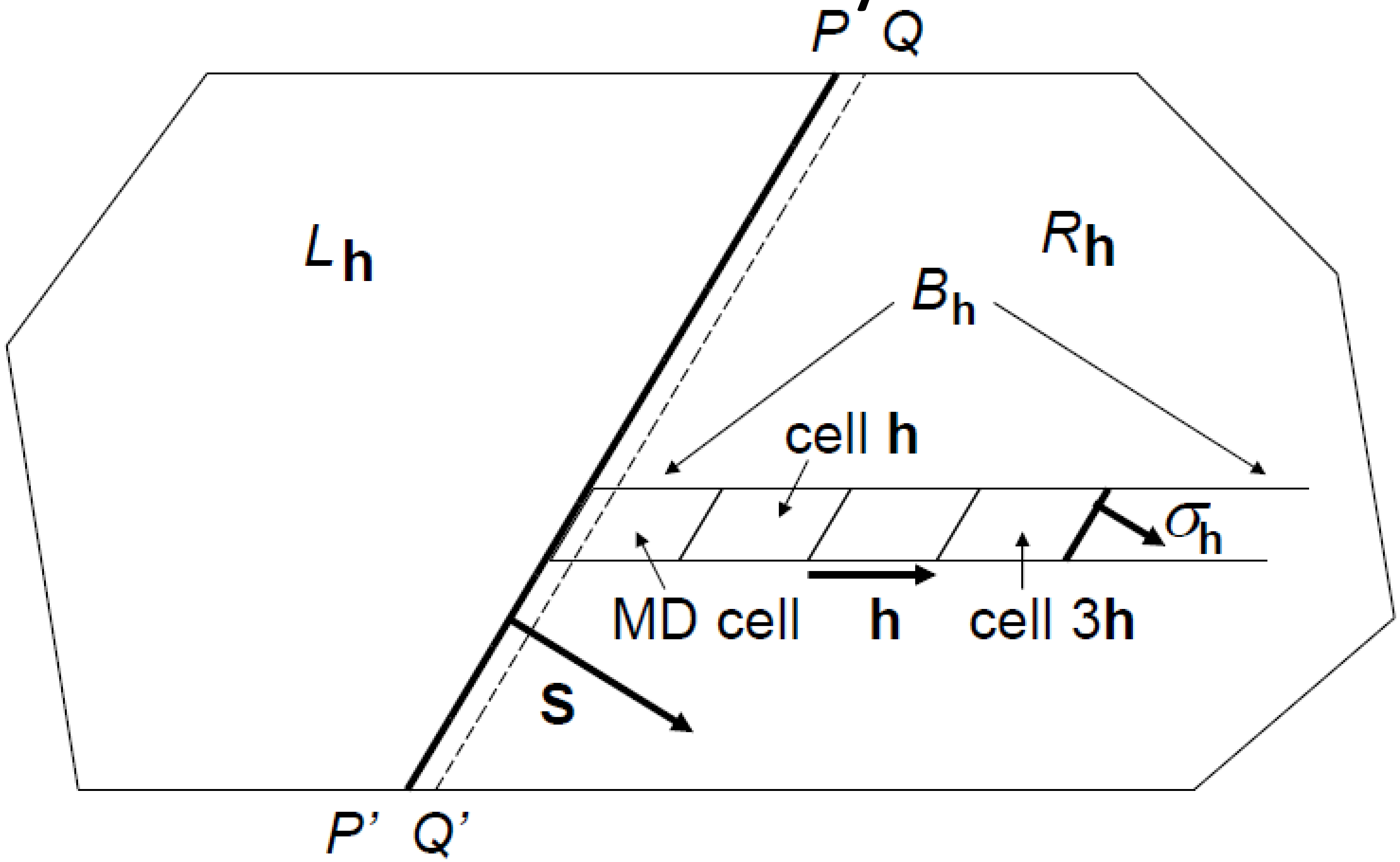
Net force on the MD cell



Since for any action from the green cell on the red MD cell, the reaction is equal to the action from the blue on the red, we have

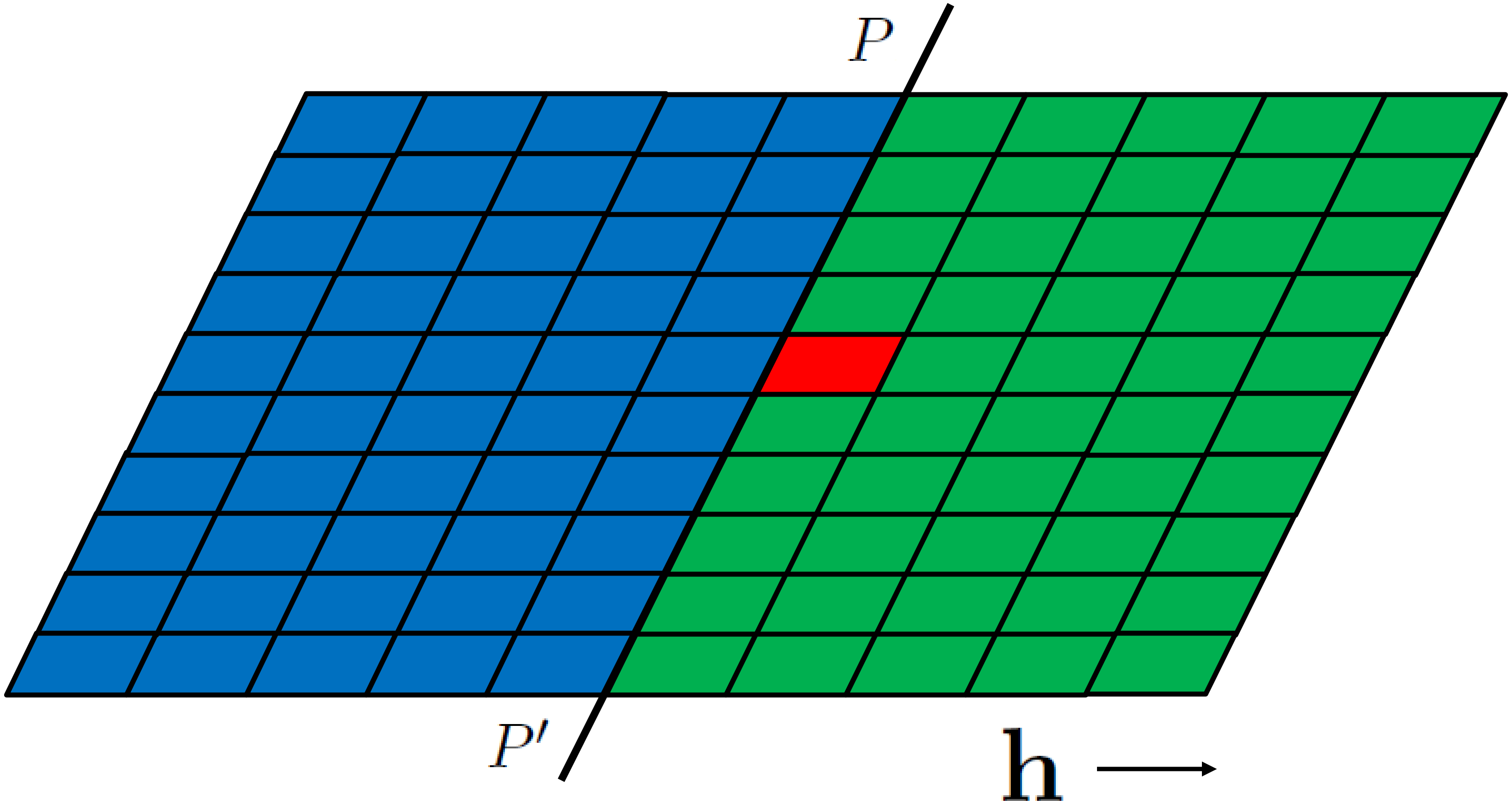
$$\sum_{i=1}^{n} m_i \ddot{\mathbf{r}}_i = \sum_{i=1}^{n} \mathbf{F}_i = 0.$$

Now let us first cut the system into two parts



with plane PP', so that for a given period $\mathbf{h}$, the right (R_h) part contains $\mathbf{T} = T_\mathrm{a}\mathbf{a} + T_\mathrm{b}\mathbf{b} + T_\mathrm{c}\mathbf{c}$ cells of $T_\mathrm{h} \geq 0$, the rest in the left (L_h) part.

A better illustration

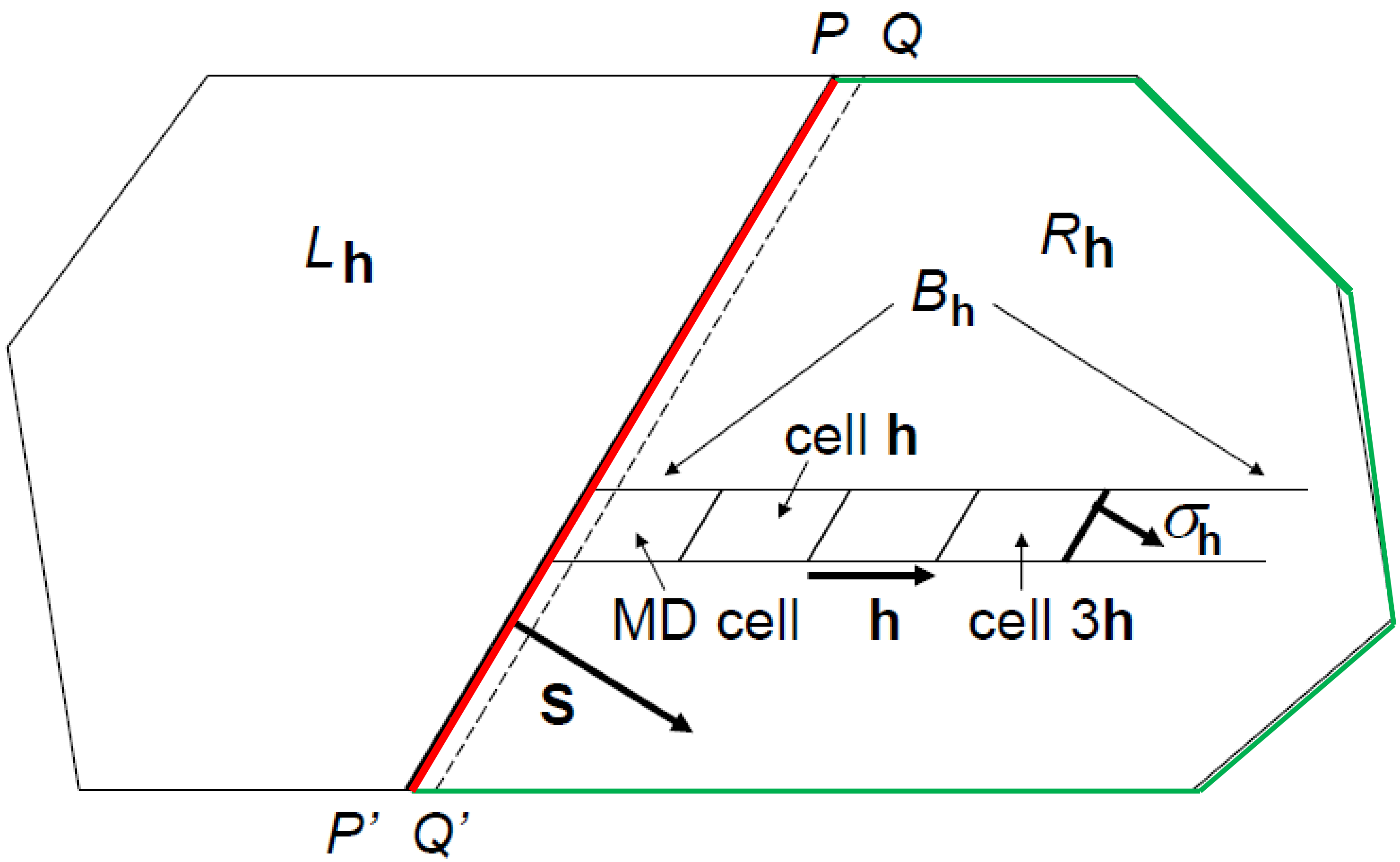


The red is the MD cell.

The net external force on $R_{\mathbf{h}}$

$$\mathbf{F}_{E,R} = \int_{R_{\mathbf{h}},sf} \overrightarrow{\overrightarrow{\Upsilon}} \cdot d\mathbf{s} = \overrightarrow{\overrightarrow{\Upsilon}} \cdot \int_{R_{\mathbf{h}},sf} d\mathbf{s} = \overrightarrow{\overrightarrow{\Upsilon}} \cdot \mathbf{S},$$

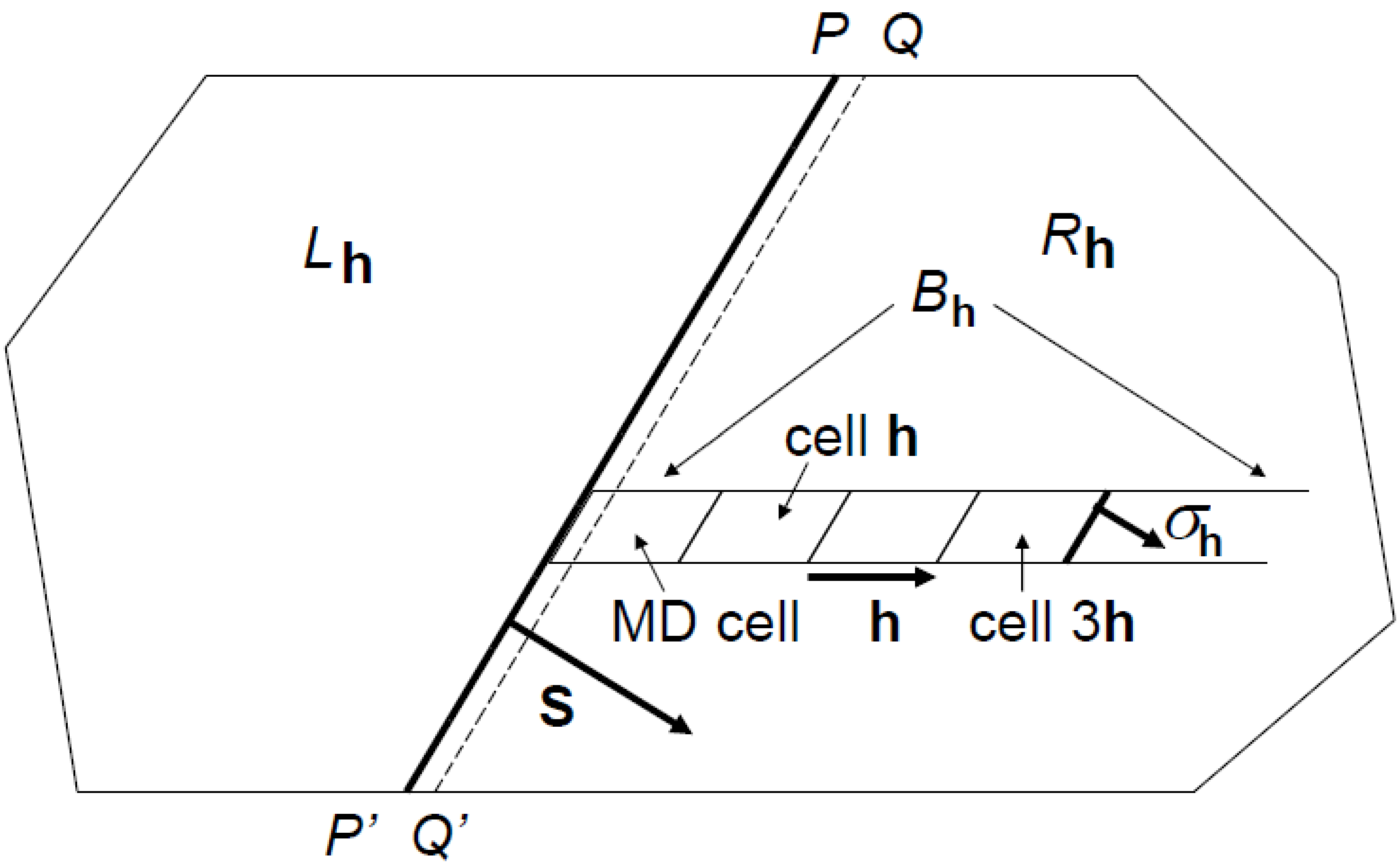
$\mathbf{S}$ is the cross section vector in plane PP'



Newton's Second Law on $R_{\mathbf{h}}$

$$M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{L \to R} + \overrightarrow{\overrightarrow{\Upsilon}} \cdot \mathbf{S}.$$

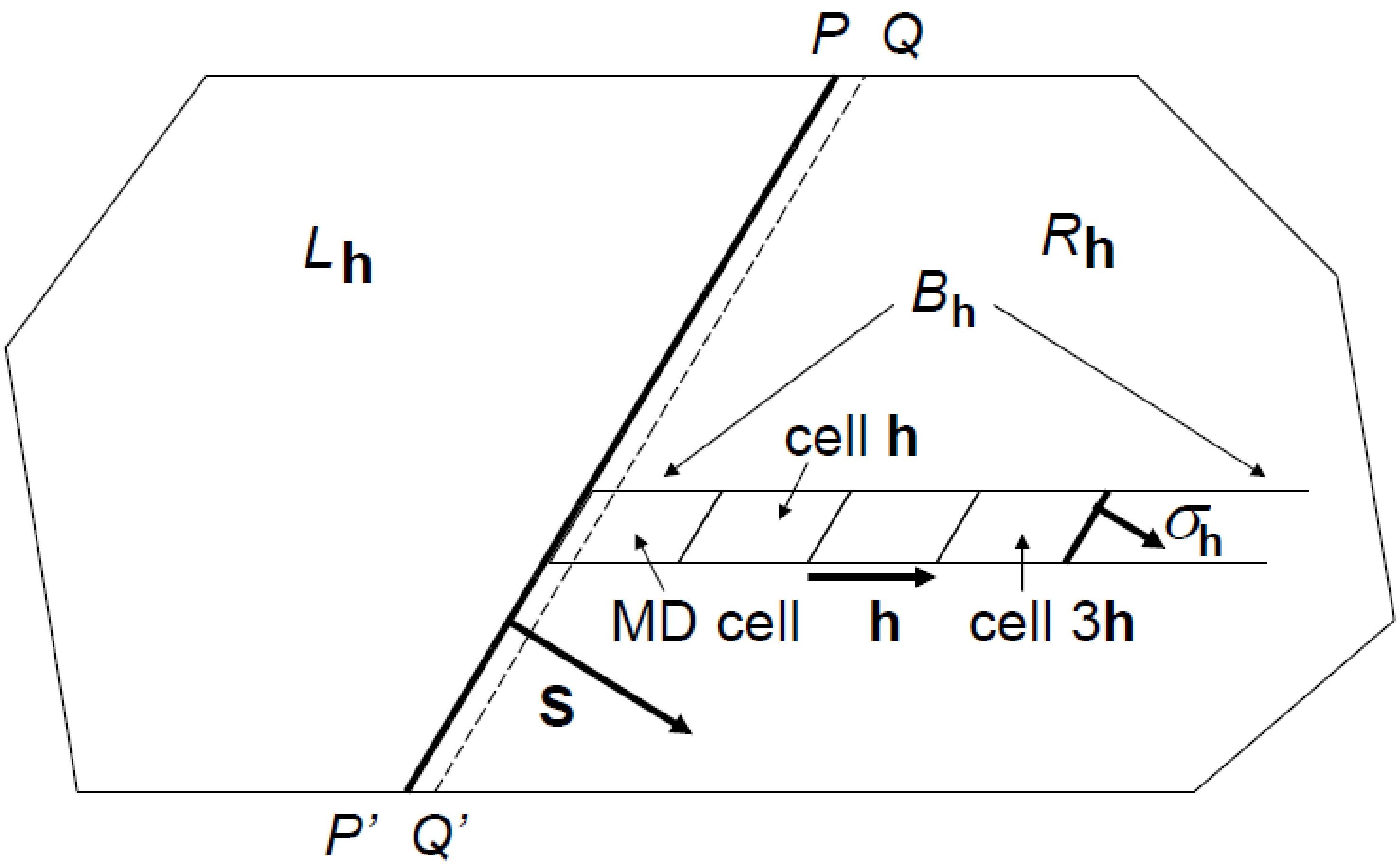
$\mathbf{F}_{L \to R}$ is the net force on $R_{\mathbf{h}}$ by $L_{\mathbf{h}}$



Newton's Second Law on $R_{\mathbf{h}}$

$$M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{L \to R} + \overset{\rightrightarrows}{\Upsilon} \cdot \mathbf{S}, \qquad N_{\mathbf{h}} = |\mathbf{S}| \, / \, |\sigma_{\mathbf{h}}|$$

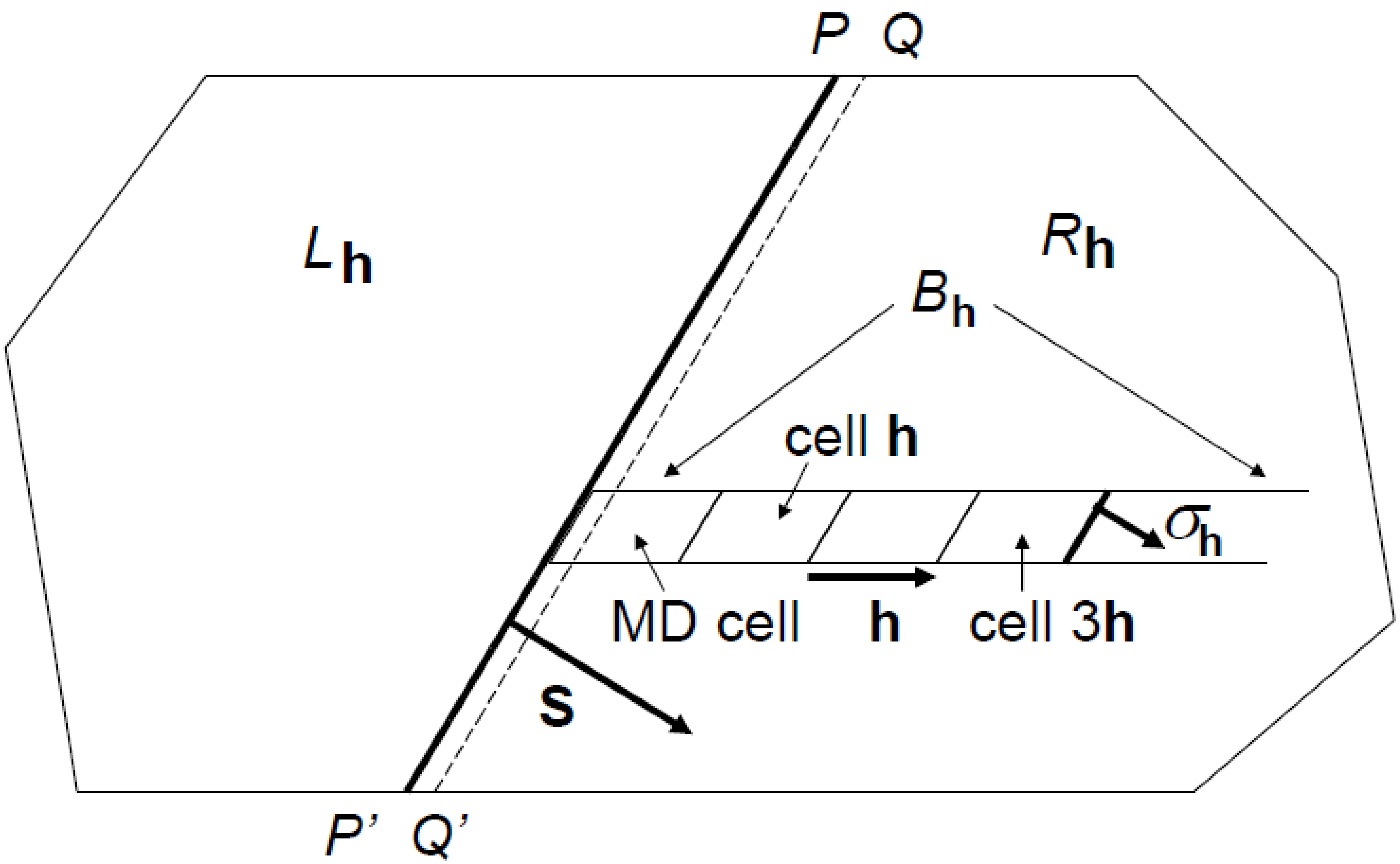
$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overset{\rightrightarrows}{\Upsilon} \cdot \sigma_{\mathbf{h}}$$



Newton's Second Law on $R_{\mathbf{h}}$

$$M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{L\to R} + \overset{\Rightarrow}{\Upsilon} \cdot \mathbf{S}.$$

$\mathbf{F}_{L\to R}$ is evenly distributed cell by cell in PP'



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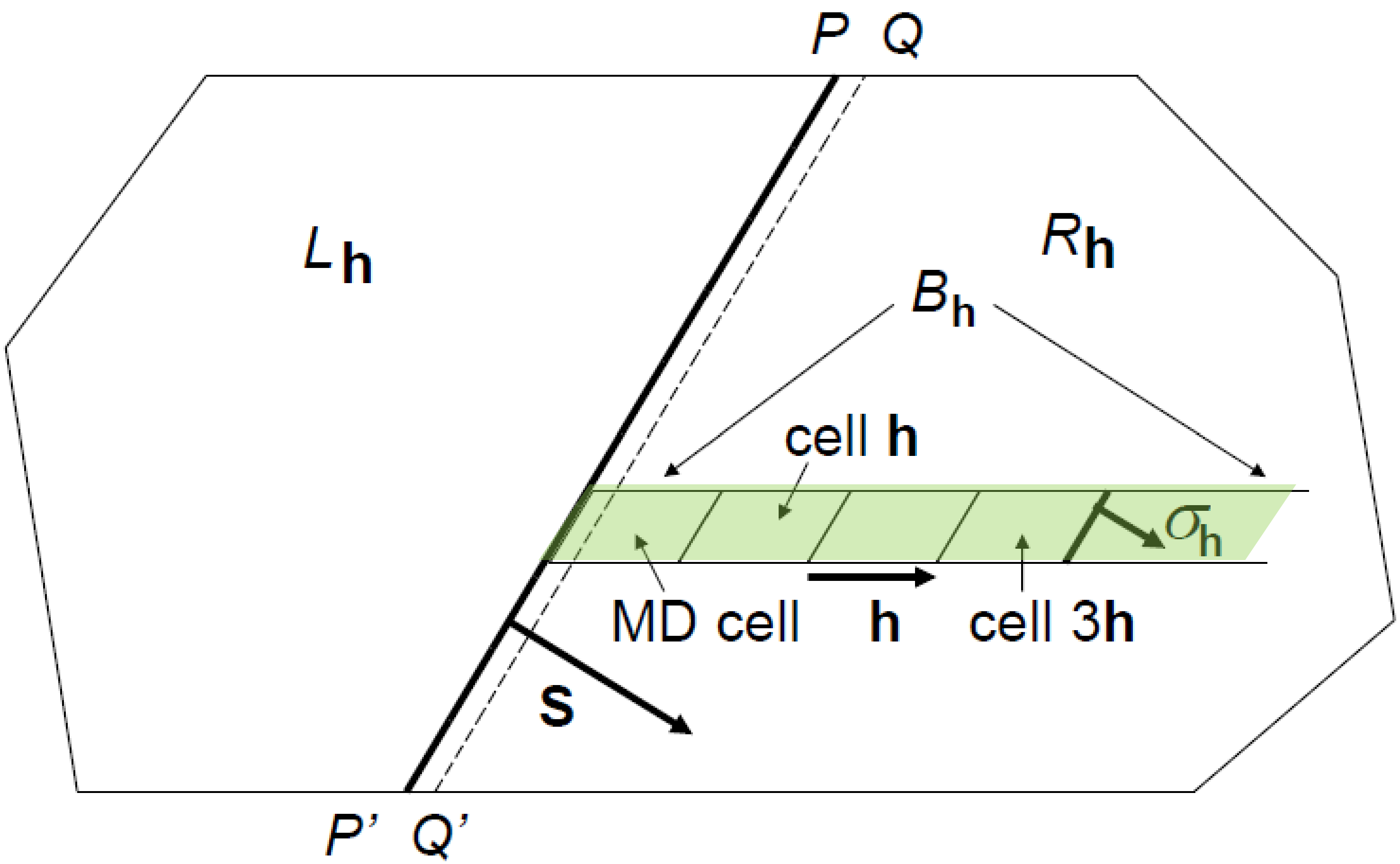
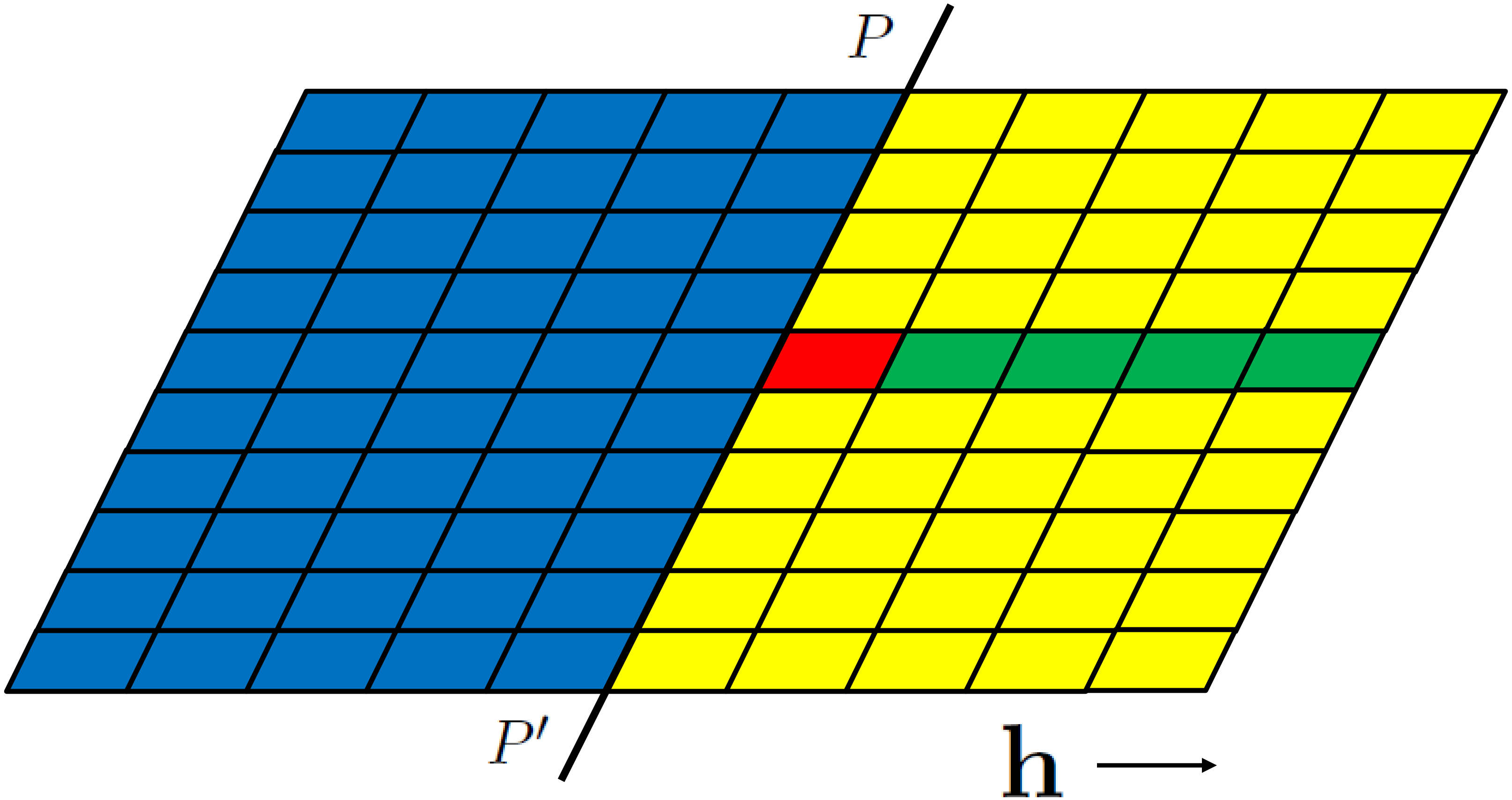
$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overset{\rightrightarrows}{\Upsilon} \cdot \sigma_{\mathbf{h}}$$

$B_{\mathbf{h}}$ "half cell bar"

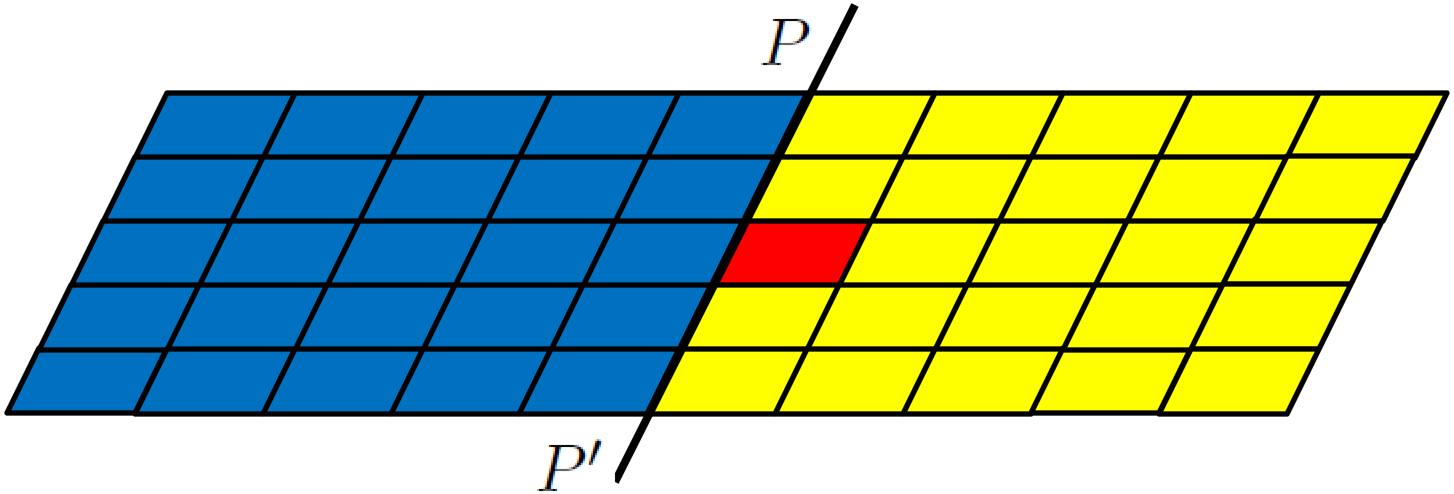


$\mathbf{F_h}$ is the net force of blues on red and greens

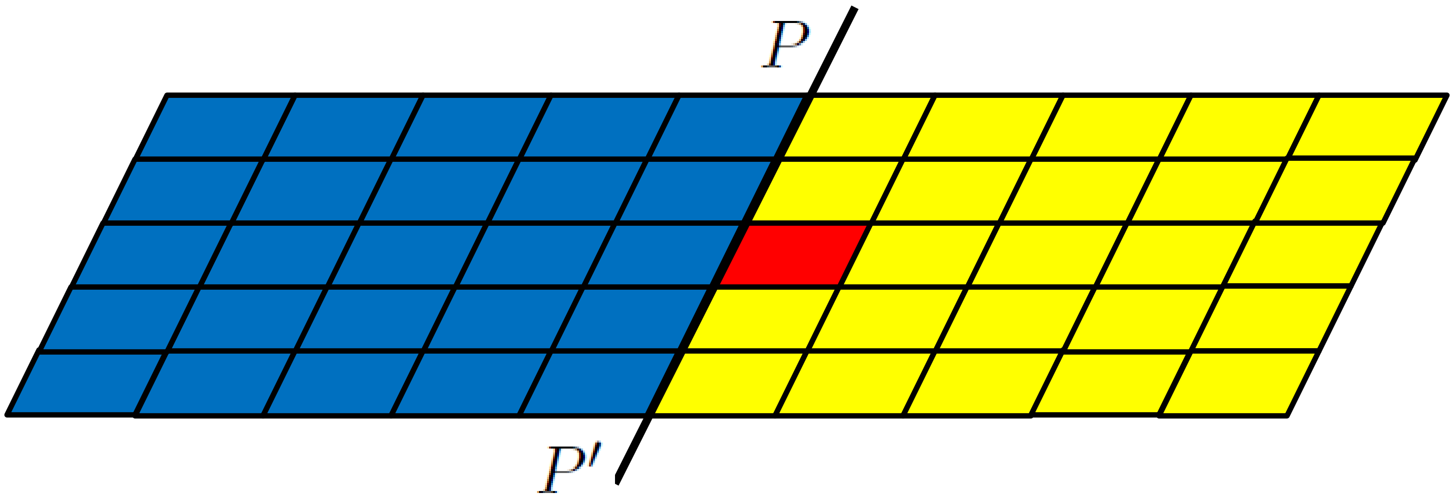


The red is the MD cell.

The net force of blues on red



is the negative of that of red on blues.



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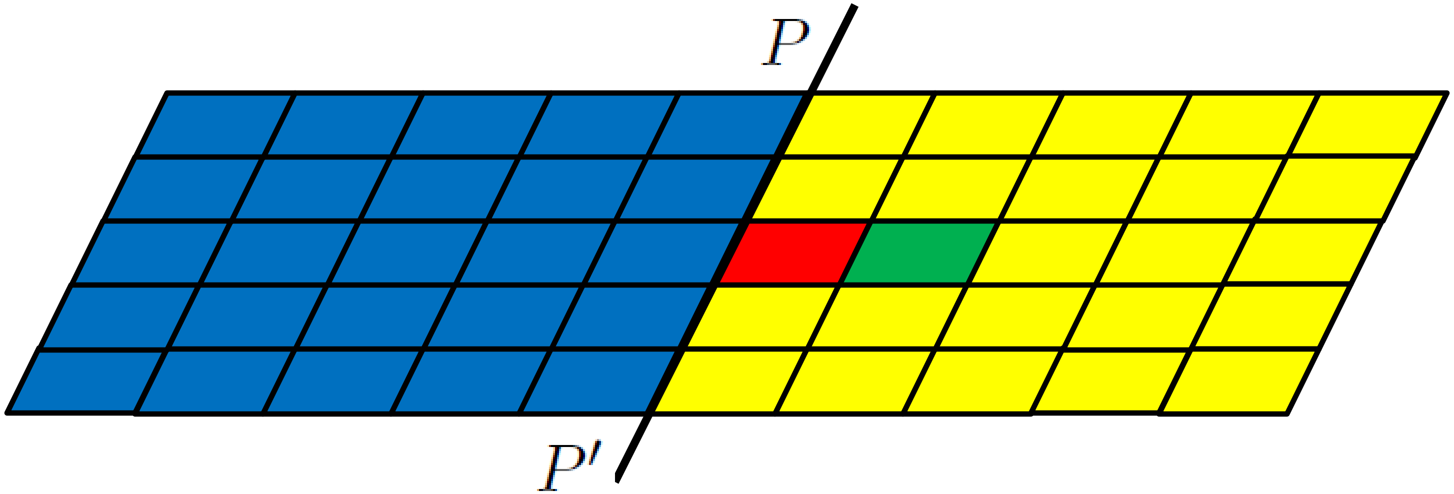

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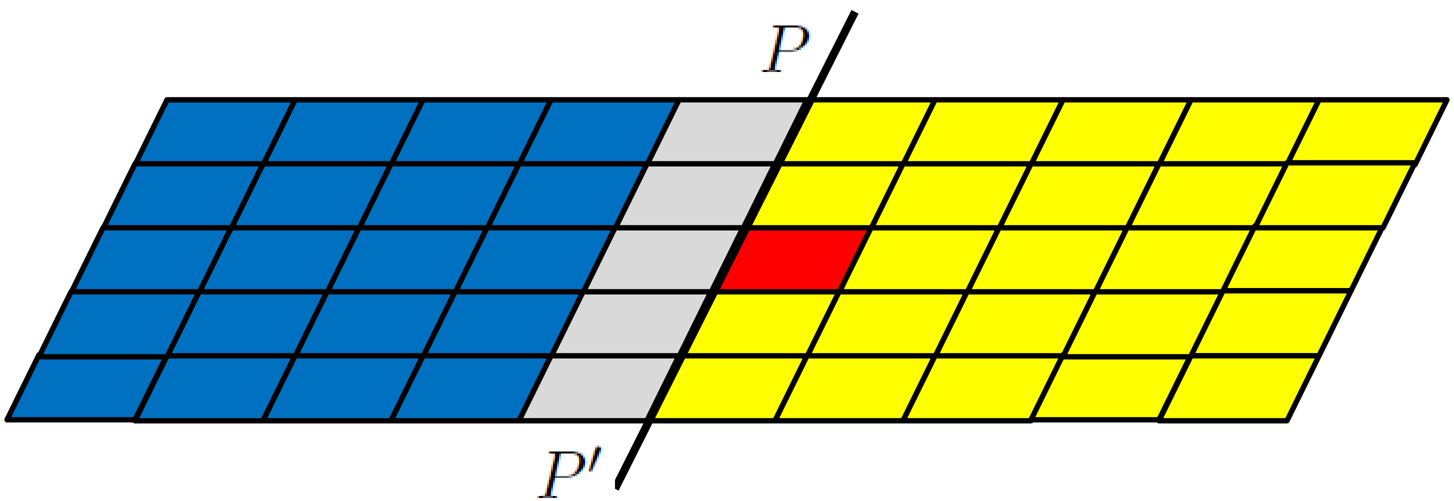

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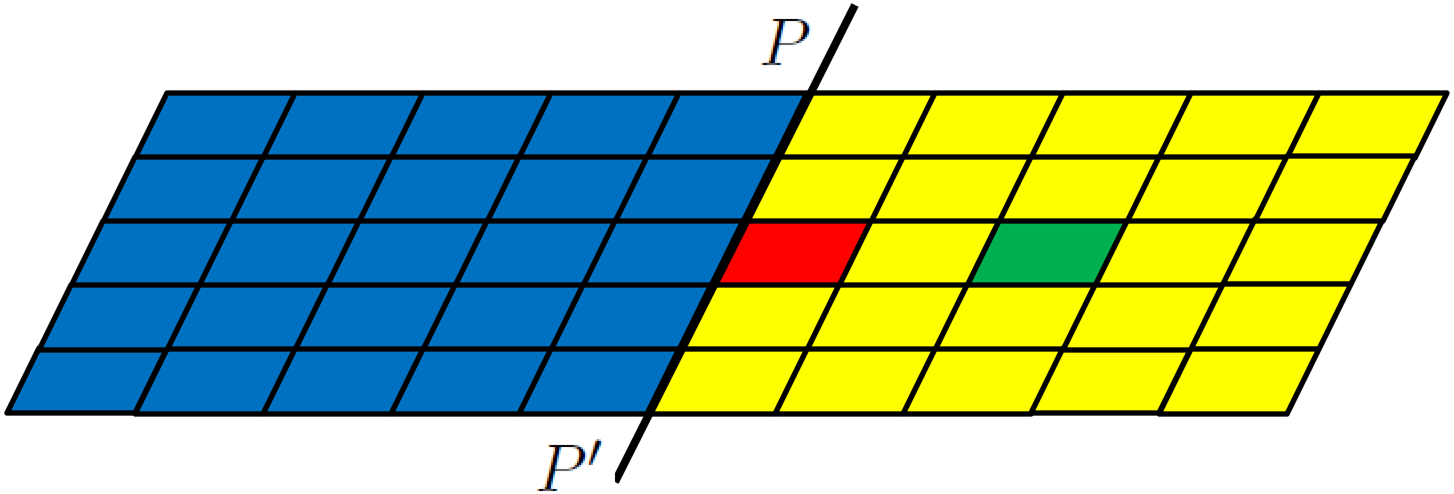

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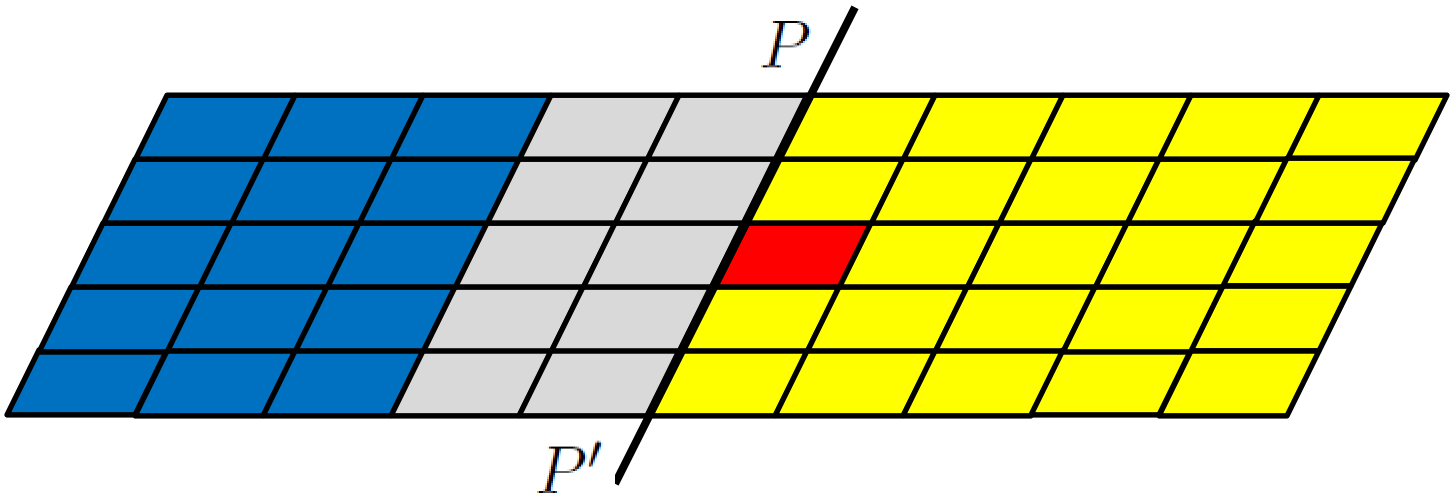

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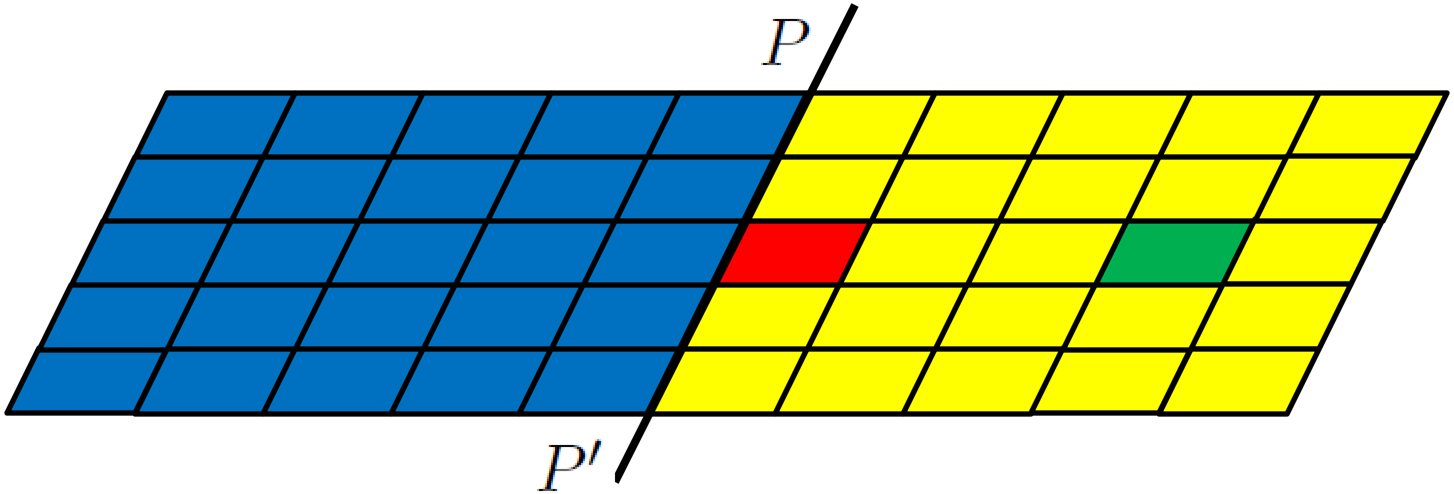

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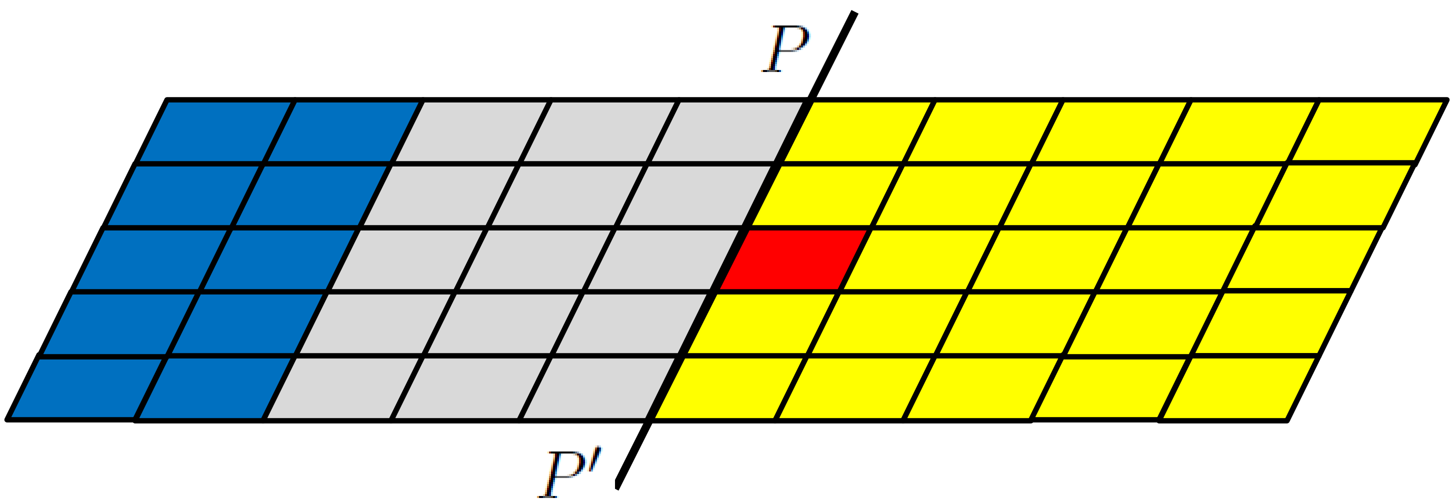

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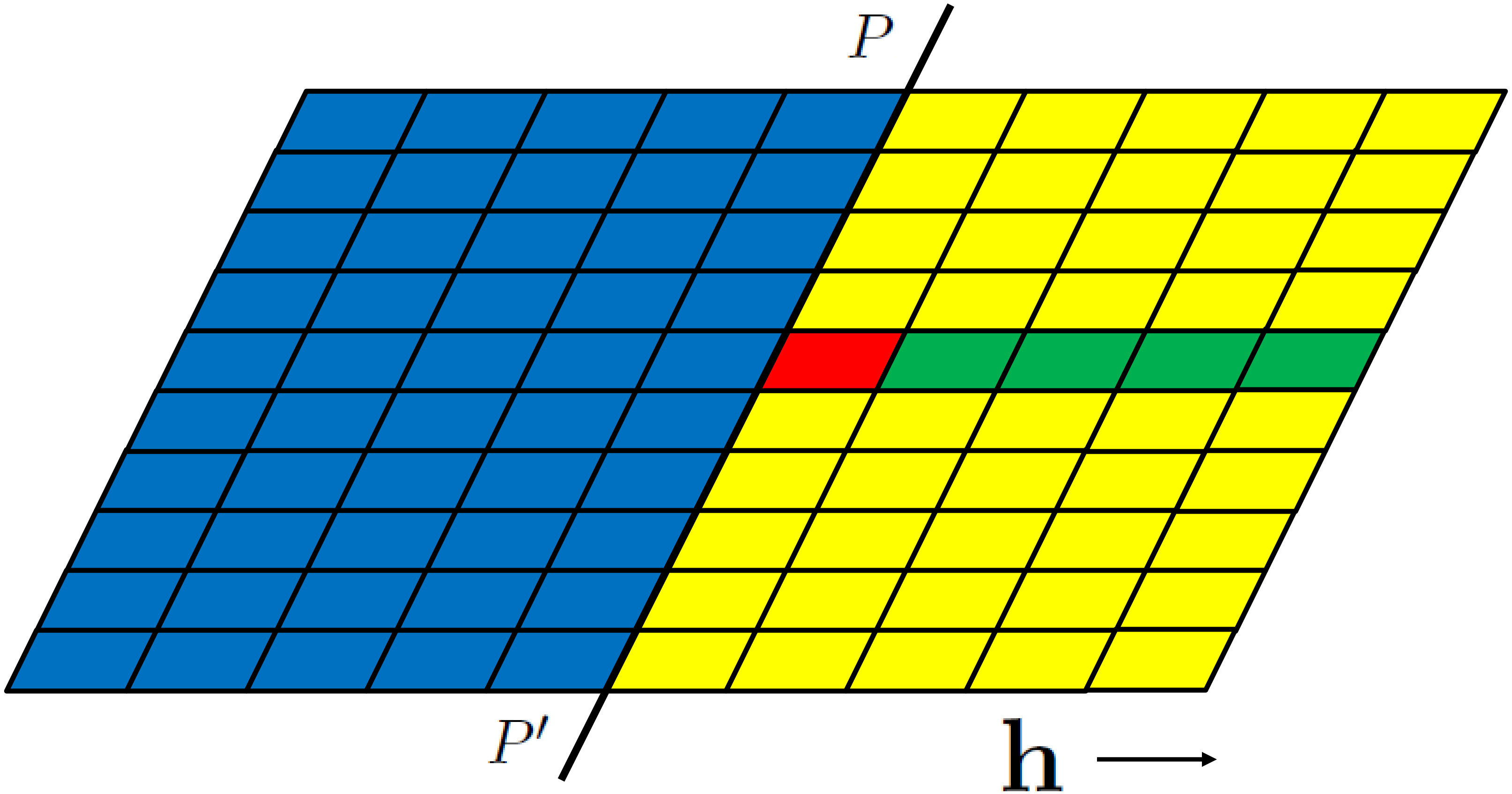
Newton's Second Law on $R_{\mathbf{h}}$

$$M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{L\to R} + \overset{\rightharpoonup\rightharpoonup}{\Upsilon} \cdot \mathbf{S},$$

$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overset{\rightharpoonup\rightharpoonup}{\Upsilon} \cdot \sigma_{\mathbf{h}}$$

$$\mathbf{F}_{\mathbf{h}} = \sum_{\mathbf{T}}^{(T_{\mathbf{h}}<0)} \sum_{i,j=1}^{n} T_{\mathbf{h}} \mathbf{f}_{i,\mathbf{0}\to j,\mathbf{T}}$$

$\mathbf{F_h}$ is the net force of blues on red and greens



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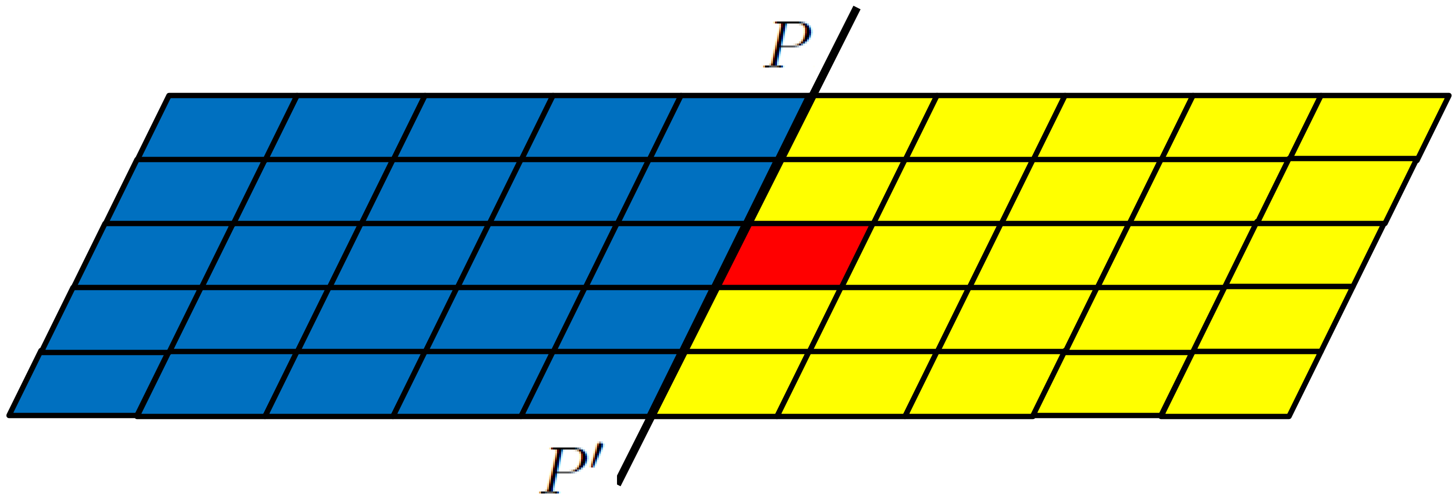
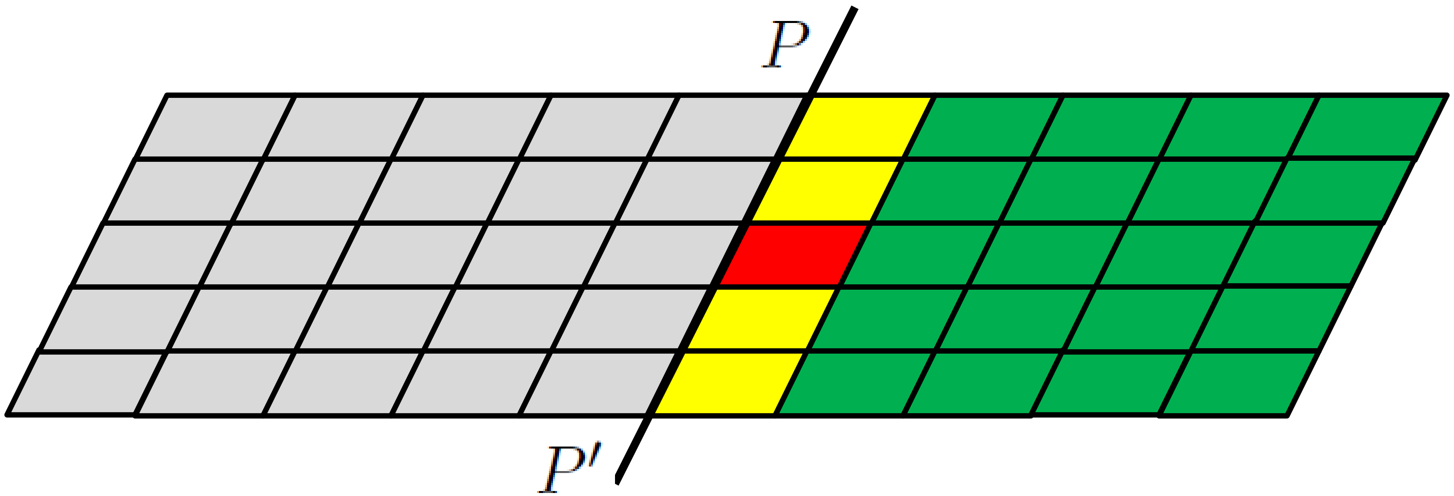
The net force of blues on red



is equal to that of red on greens.



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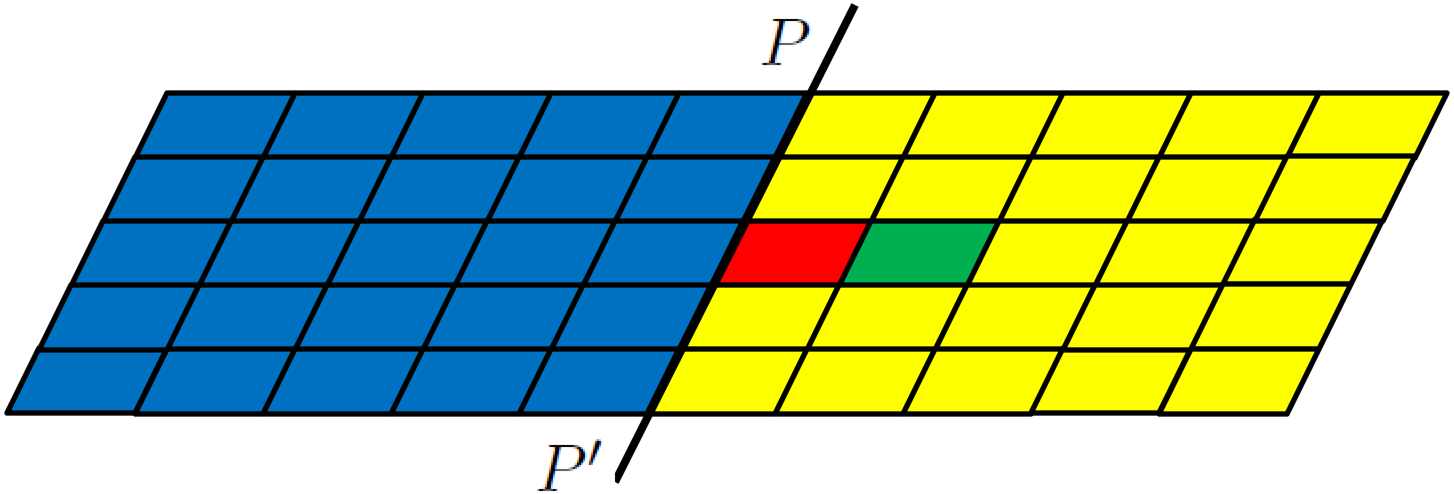
The net force of blues on green



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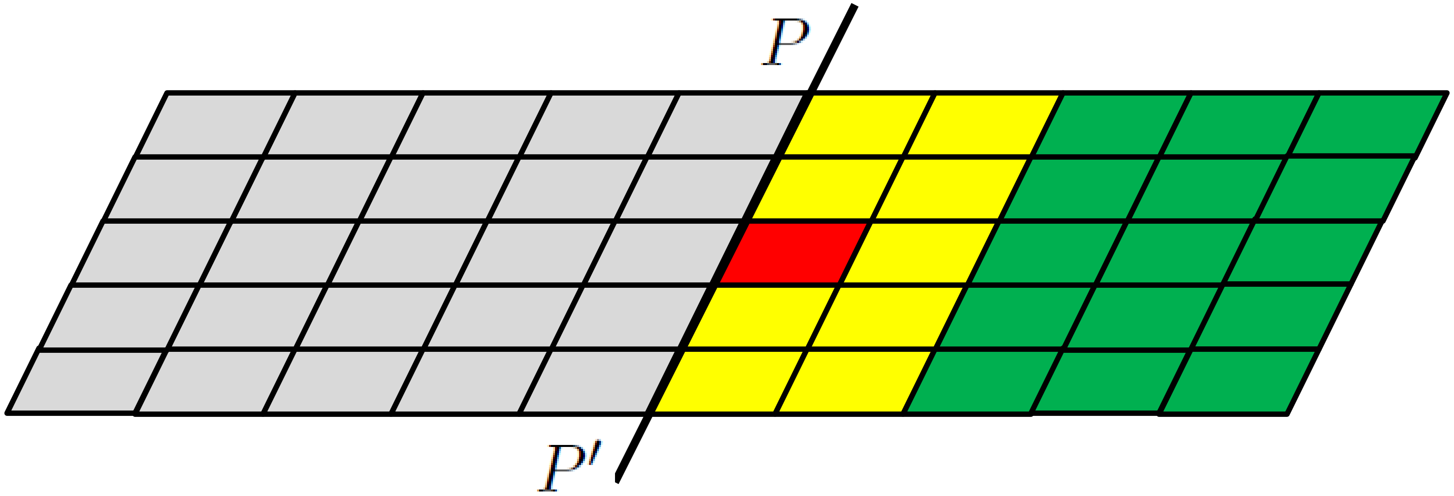

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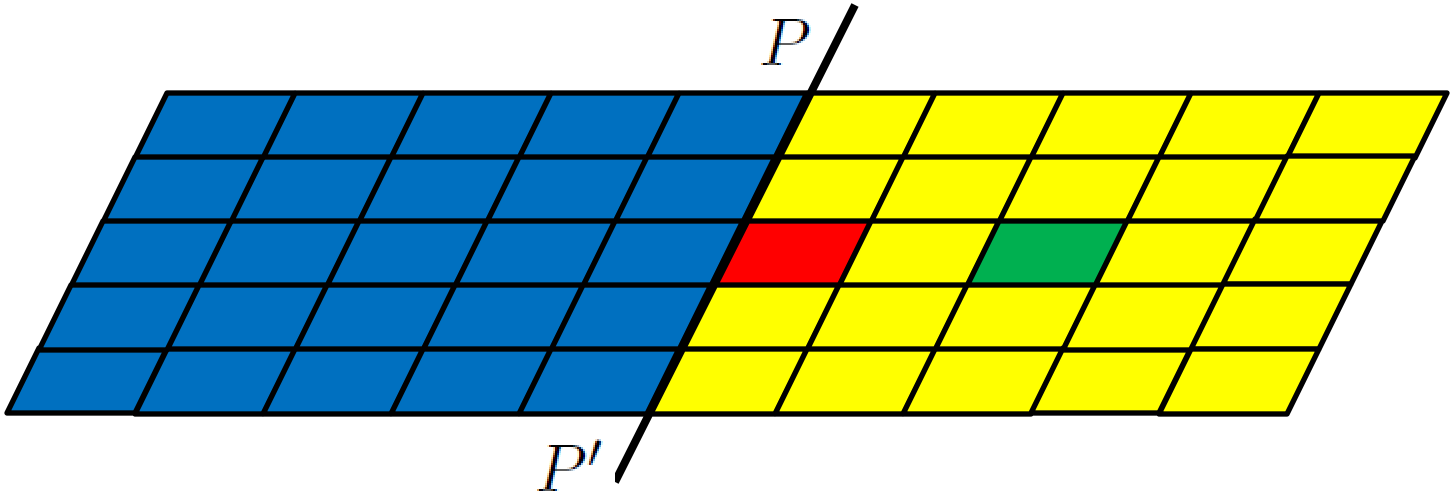

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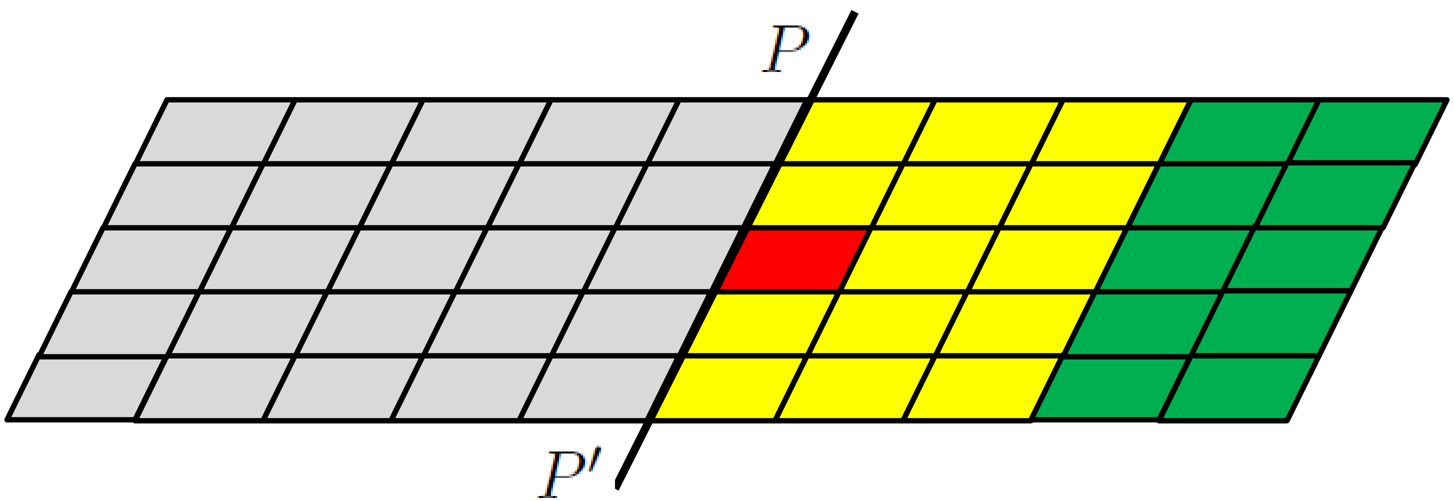

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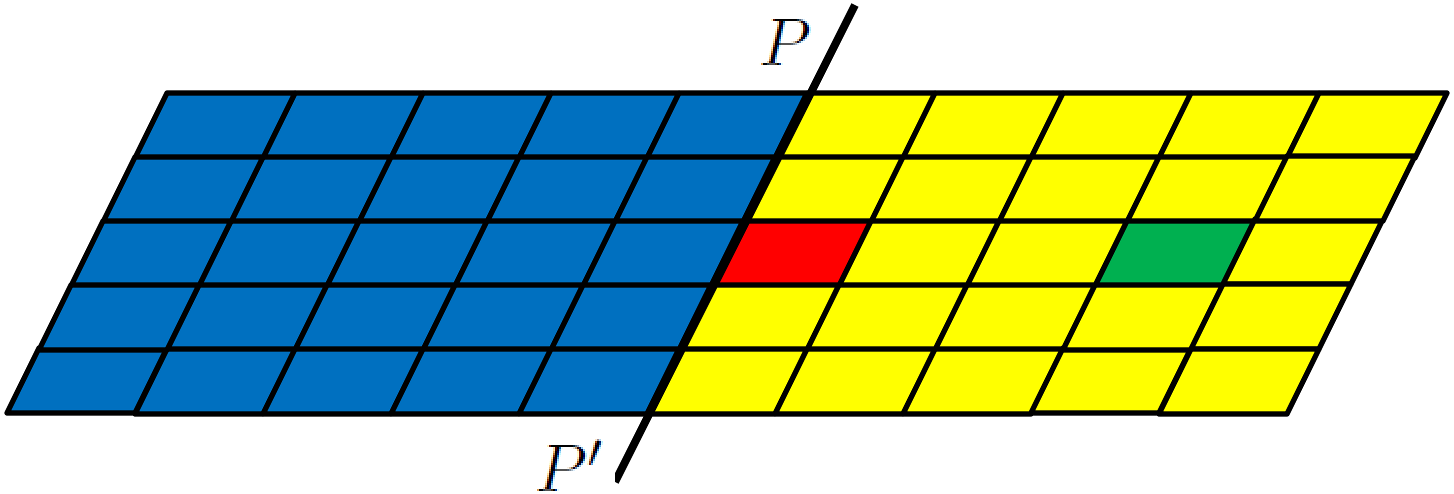

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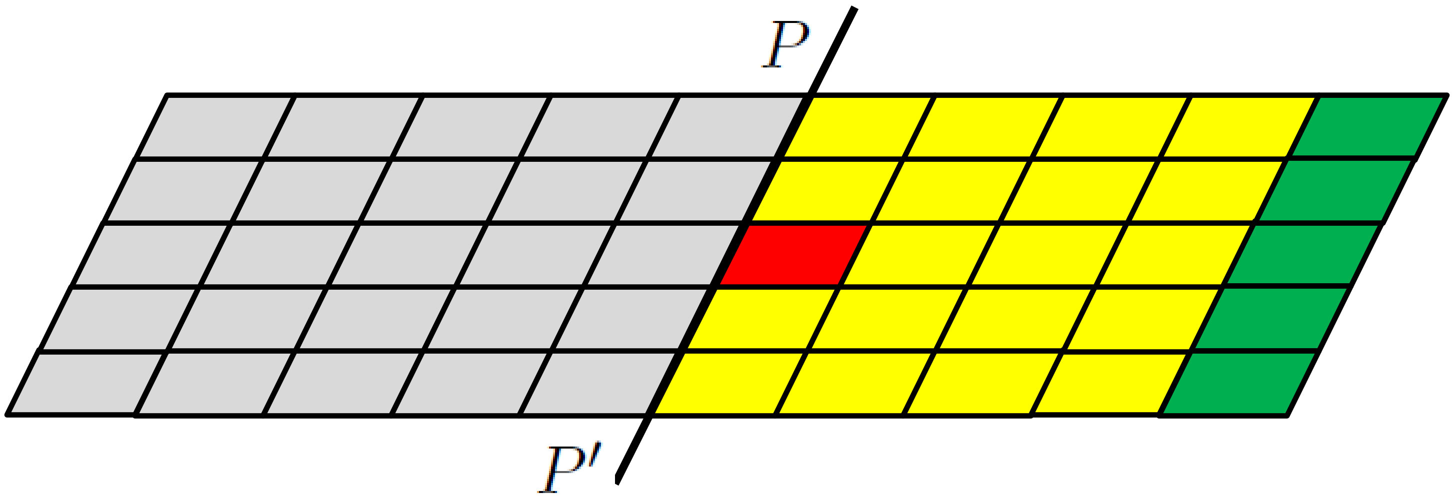

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Newton's Second Law on $R_{\mathbf{h}}$

$$M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{L\to R} + \overset{\rightrightarrows}{\Upsilon} \cdot \mathbf{S},$$

$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overset{\rightrightarrows}{\Upsilon} \cdot \sigma_{\mathbf{h}}$$

$$\mathbf{F}_{\mathbf{h}} = \sum_{\mathbf{T}}^{(T_{\mathbf{h}}<0)} \sum_{i,j=1}^{n} T_{\mathbf{h}} \mathbf{f}_{i,\mathbf{0}\to j,\mathbf{T}} = \sum_{\mathbf{T}}^{(T_{\mathbf{h}}>0)} \sum_{i,j=1}^{n} T_{\mathbf{h}} \mathbf{f}_{i,\mathbf{0}\to j,\mathbf{T}}$$

$$= \frac{1}{2} \sum_{\mathbf{T}\neq 0} \sum_{i,j=1}^{n} T_{\mathbf{h}} \mathbf{f}_{i,\mathbf{0}\to j,\mathbf{T}}.$$

Recalling potential energy of the MD cell

$$E_{p,MD} = \sum_{i>j=1}^{n} \varphi^{(2)}(|\mathbf{r}_i - \mathbf{r}_j|) +$$

$$+ \frac{1}{2} \sum_{\mathbf{T} \neq 0} \sum_{i,j=1}^{n} \varphi^{(2)}(|\mathbf{r}_i - \mathbf{r}_j - \mathbf{T}|)$$

Introducing main interaction tensor/dyad

$$\overset{\rightrightarrows}{\varepsilon}_{main} = -\frac{1}{\Omega}\left[\left(\frac{\partial E_{p,MD}}{\partial \mathbf{a}}\right)\mathbf{a} + \left(\frac{\partial E_{p,MD}}{\partial \mathbf{b}}\right)\mathbf{b} + \left(\frac{\partial E_{p,MD}}{\partial \mathbf{c}}\right)\mathbf{c}\right]$$

$$\overset{\rightrightarrows}{\varepsilon}_{main} = \frac{1}{2\Omega}\sum_{\mathbf{T}\neq 0}\sum_{i,j=1}^{n} \mathbf{f}_{i,\mathbf{0}\rightarrow j,\mathbf{T}}\mathbf{T}$$

Remembering $\mathbf{h} \cdot \sigma_{\mathbf{h}'} = \Omega \delta_{\mathbf{h},\mathbf{h}'}$

$$\mathbf{F}_{\mathbf{h}} = \overset{\leftrightarrow}{\varepsilon}_{main} \cdot \sigma_{\mathbf{h}}$$

in

$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overset{\leftrightarrow}{\Upsilon} \cdot \sigma_{\mathbf{h}}$$

The left side of $\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overrightarrow{\overrightarrow{\Upsilon}} \cdot \sigma_{\mathbf{h}}$

$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \frac{1}{N_{\mathbf{h}}} \sum_{\mathbf{T} \in R_{\mathbf{h}}} \sum_{i=1}^{n} m_i \left(\ddot{\mathbf{r}}_i + \ddot{\mathbf{T}} \right) = \frac{M_{cell}}{N_{\mathbf{h}}} \sum_{\mathbf{T} \in R_{\mathbf{h}}} \ddot{\mathbf{T}}$$

where $M_{cell} = \sum_{i=1}^{n} m_i$ and $\ddot{\mathbf{T}} = T_{\mathbf{a}} \ddot{\mathbf{a}} + T_{\mathbf{b}} \ddot{\mathbf{b}} + T_{\mathbf{c}} \ddot{\mathbf{c}}$

and $\sum_{i=1}^{n} m_i \ddot{\mathbf{r}}_i = \sum_{i=1}^{n} \mathbf{F}_i = 0.$ is used.

The left side of $\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overrightarrow{\overrightarrow{\Upsilon}} \cdot \sigma_{\mathbf{h}}$

$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \alpha_{\mathbf{h},\mathbf{a}} \ddot{\mathbf{a}} + \alpha_{\mathbf{h},\mathbf{b}} \ddot{\mathbf{b}} + \alpha_{\mathbf{h},\mathbf{c}} \ddot{\mathbf{c}},$$

where $\alpha_{\mathbf{h},\mathbf{h}'} = \frac{M_{cell}}{N_{\mathbf{h}}} \sum_{\mathbf{T} \in R_{\mathbf{h}}} T_{\mathbf{h}'} \quad (\mathbf{h}' = \mathbf{a},\ \mathbf{b},\ \mathbf{c}).$

Since in $R_{\mathbf{h}}$, any $T_{\mathbf{h}}$ is non-negative, and for any $T_{\mathbf{h}' \neq \mathbf{h}}$, there exists $-T_{\mathbf{h}'}$ to cancel it, then $\alpha_{\mathbf{h},\mathbf{h}' \neq \mathbf{h}}$ is zero.

$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \alpha_{\mathbf{h},\mathbf{h}} \ddot{\mathbf{h}}$$

First form of the period dynamics

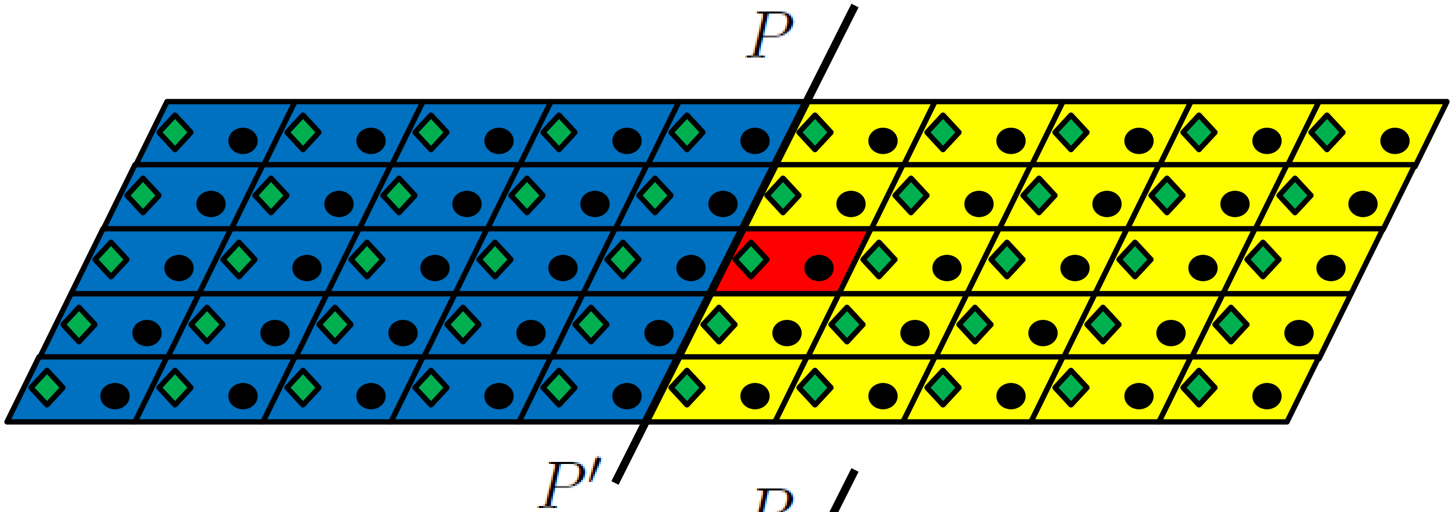
$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overrightarrow{\overrightarrow{\varepsilon}}_{main} + \overrightarrow{\overrightarrow{\Upsilon}}\right) \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c}).$$

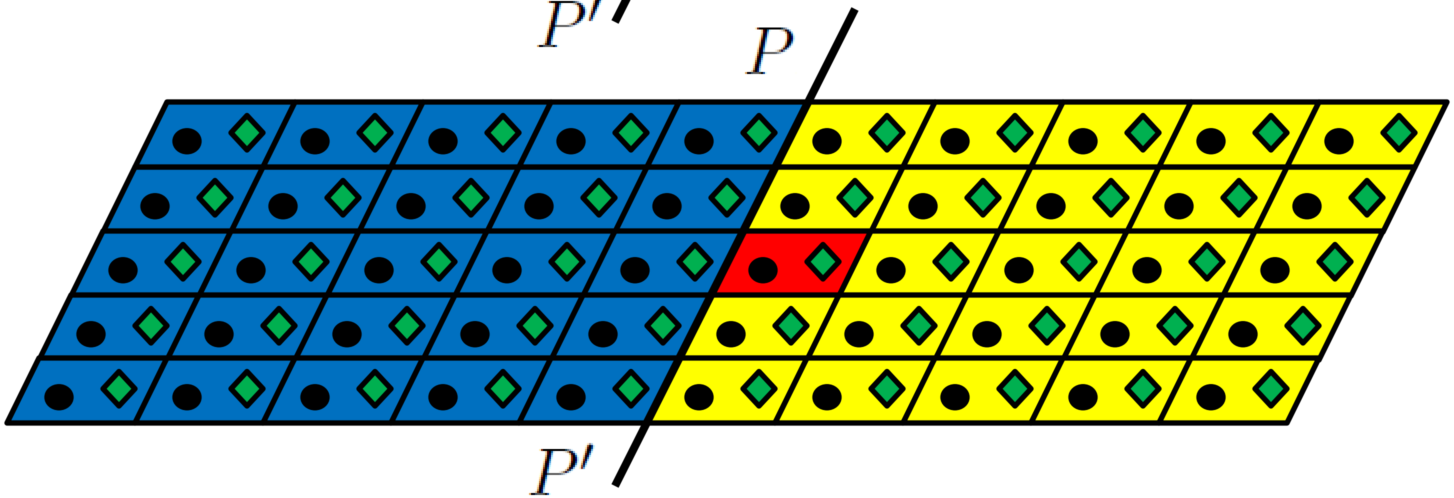
directly from simplifying Newton's Second Law

$$M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{L\to R} + \overrightarrow{\overrightarrow{\Upsilon}} \cdot \mathbf{S},$$

$$\frac{1}{N_{\mathbf{h}}} M_R \ddot{\mathbf{r}}_{RC} = \mathbf{F}_{\mathbf{h}} + \overrightarrow{\overrightarrow{\Upsilon}} \cdot \sigma_{\mathbf{h}}$$

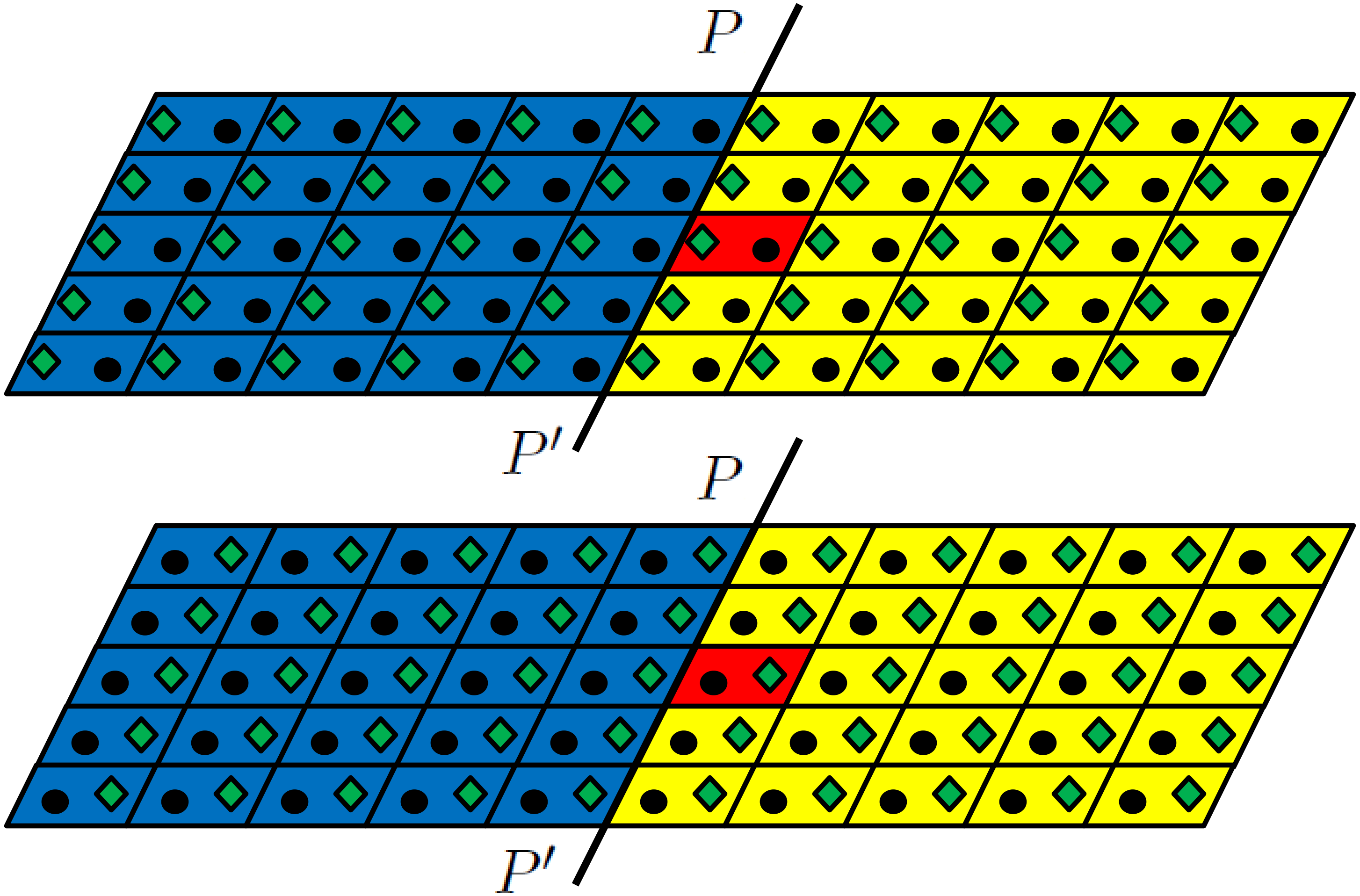
Now let us consider two states





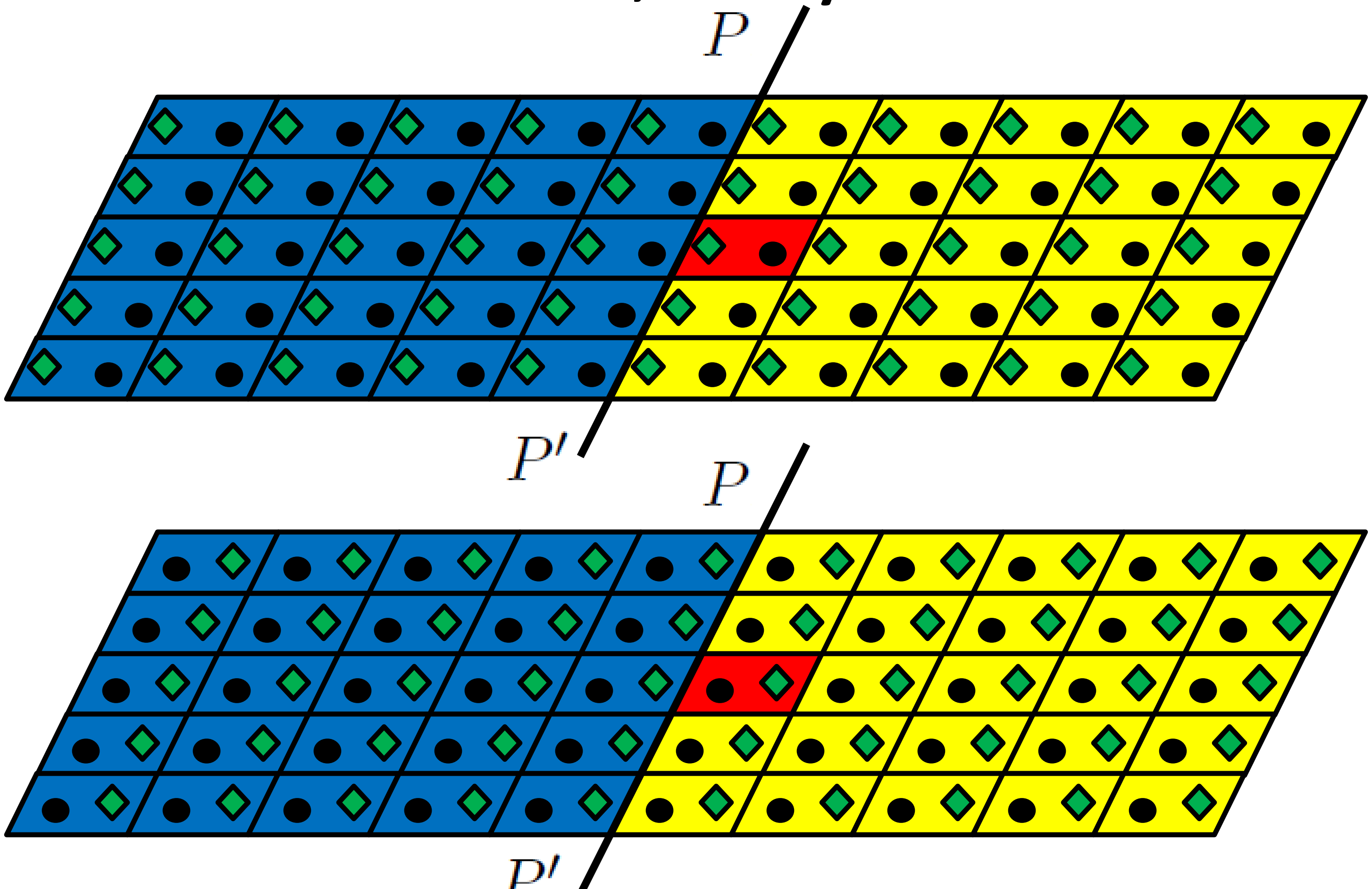
Only difference is translation between them.

Since they are indistinguishable



We should take an unweighted average of the dynamical equations over all such states.

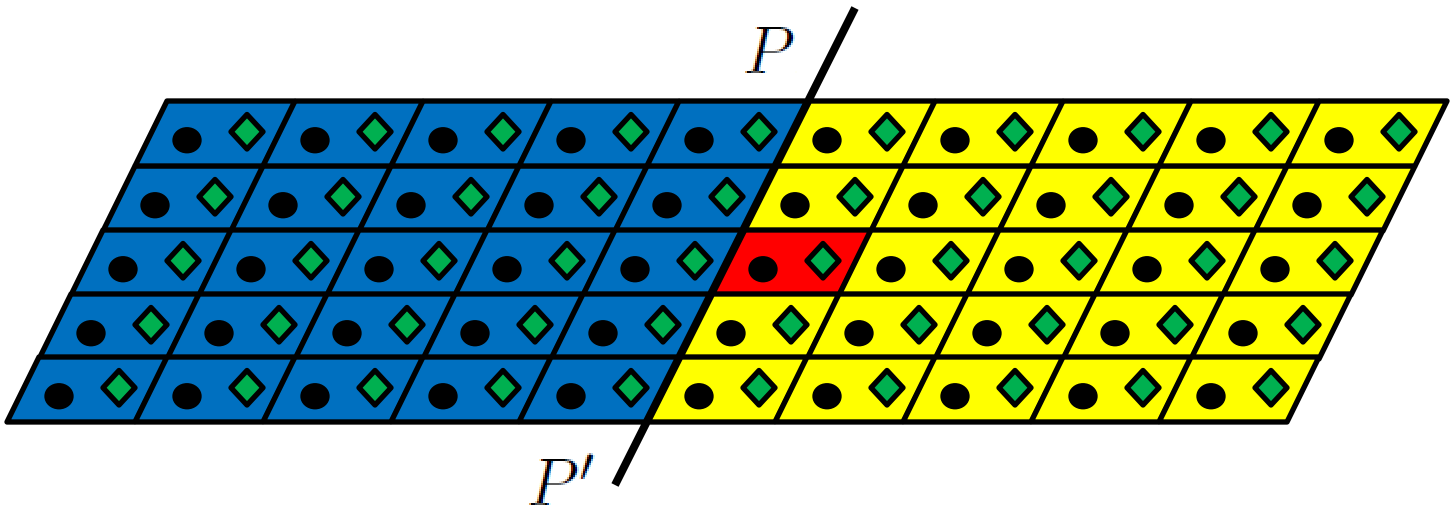
In all such states, only $\overrightarrow{\overrightarrow{\varepsilon}}_{main}$ different



$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overrightarrow{\overrightarrow{\varepsilon}}_{main} + \overrightarrow{\overrightarrow{\Upsilon}}\right) \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c}).$$

What we really need is the unweighted average of

$$\overrightarrow{\varepsilon}_{main}$$



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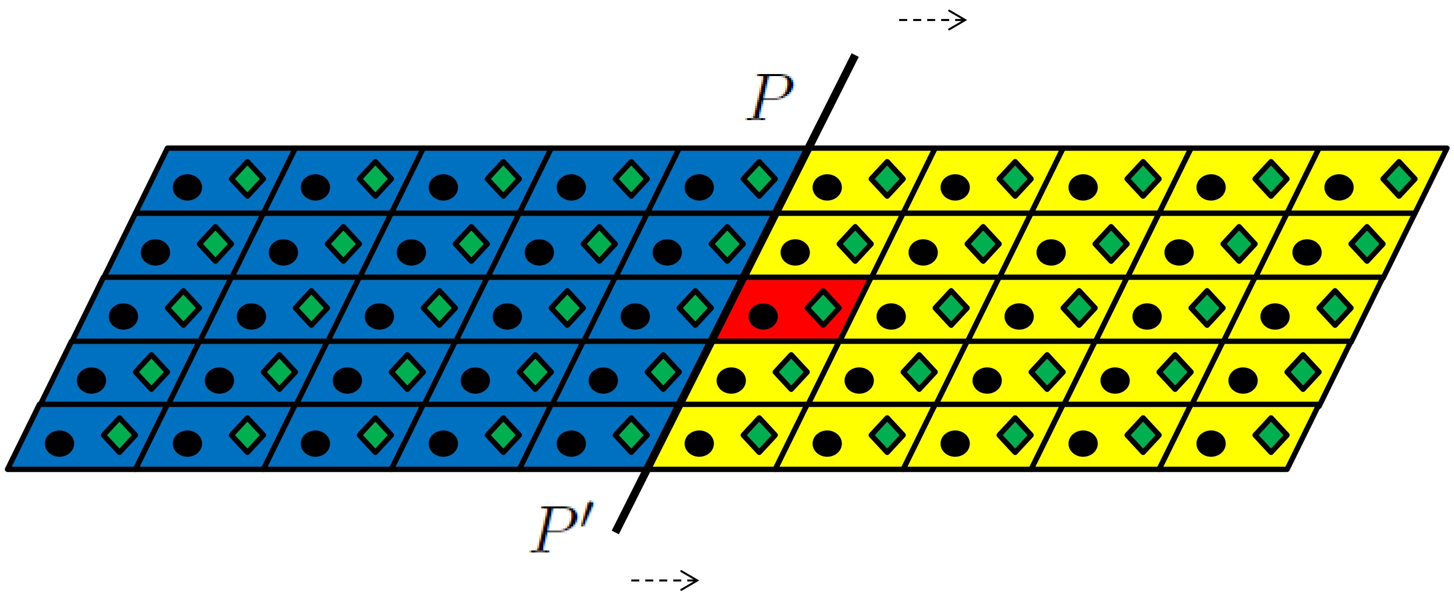
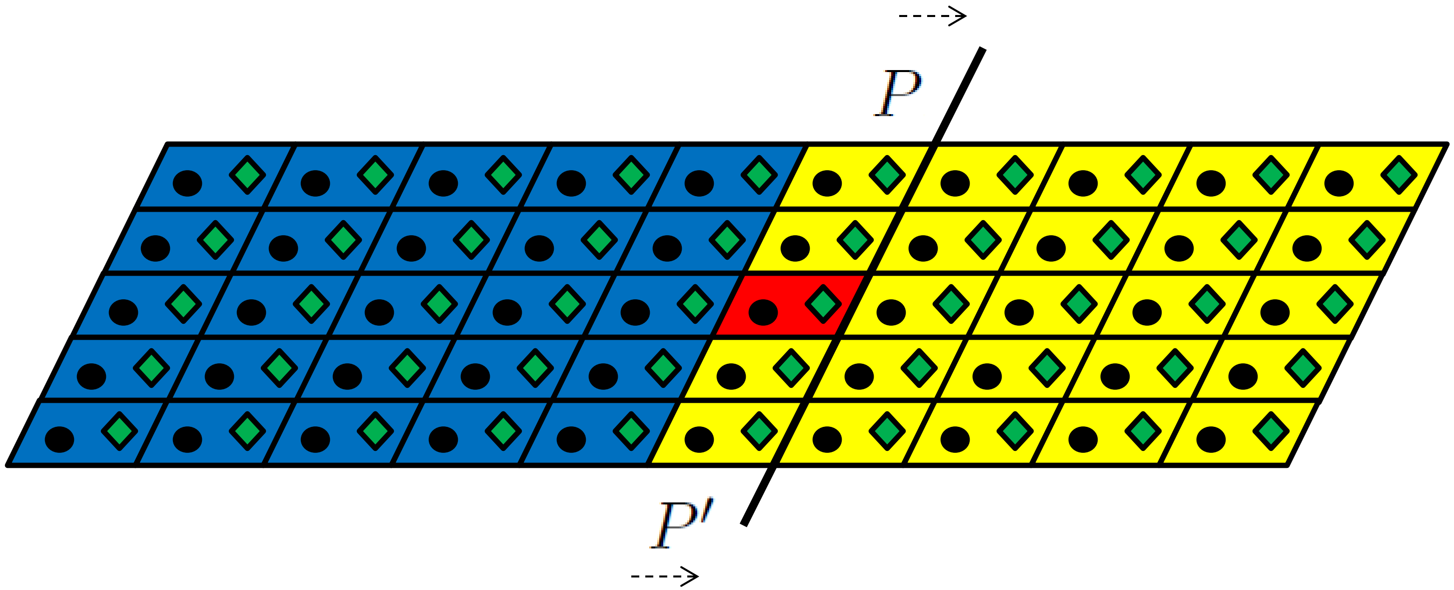


The total amount of such states can be represented by the volume of the MD cell Ω .

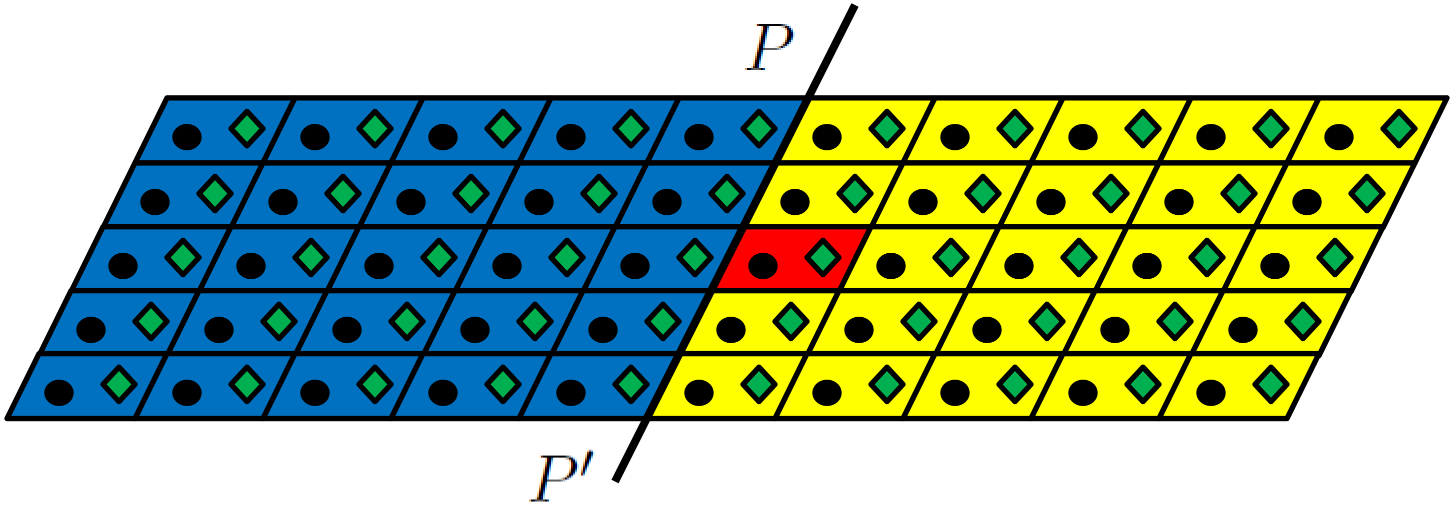
What we really need is the unweighted average of

$$\overrightarrow{\overrightarrow{\varepsilon}}_{main}$$

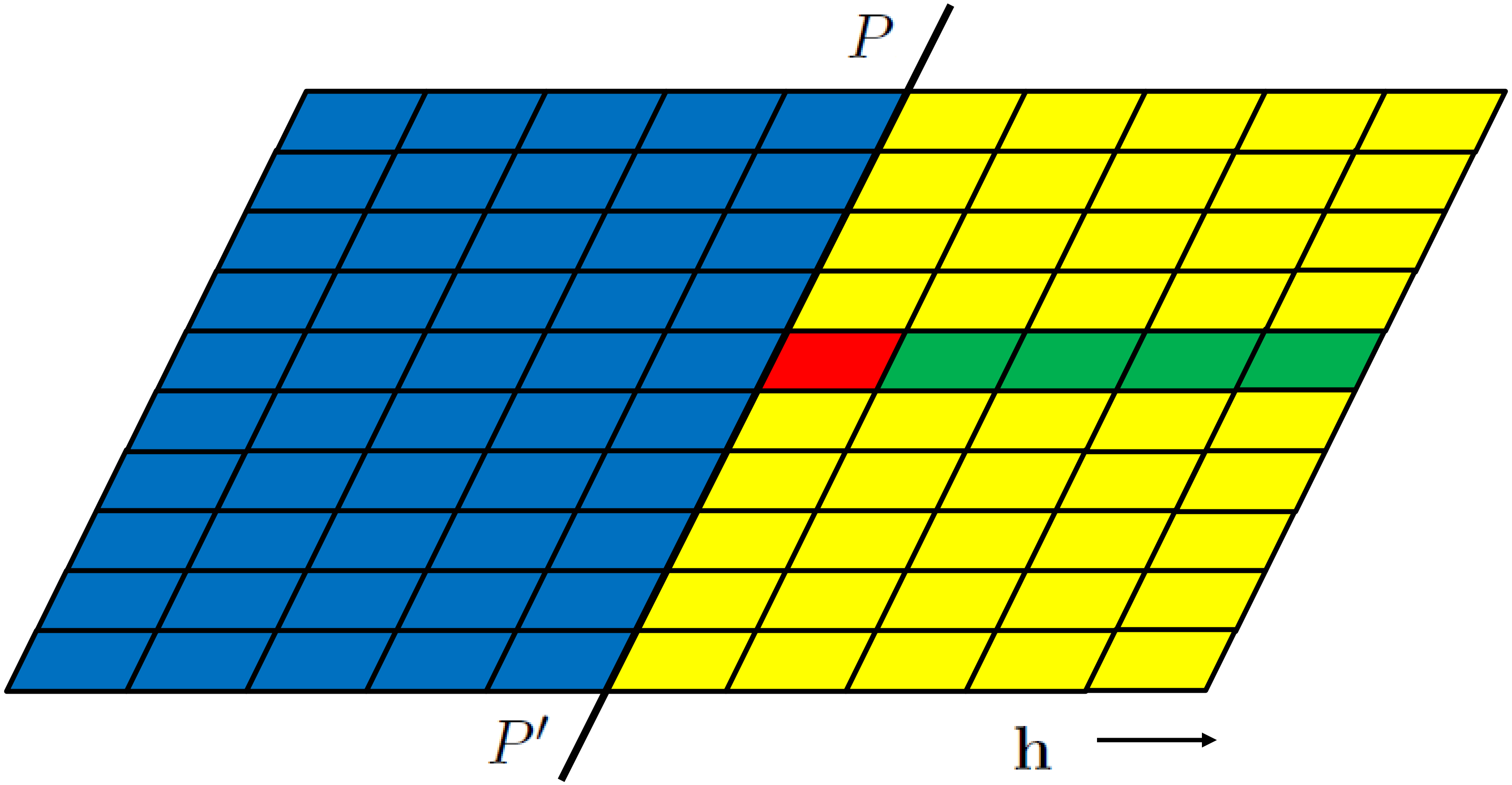


The total amount of such states can be represented by the volume of the MD cell Ω .

Relative to $\overrightarrow{\varepsilon}_{main}$ in the following situation, four cases should be considered for additional interactions.

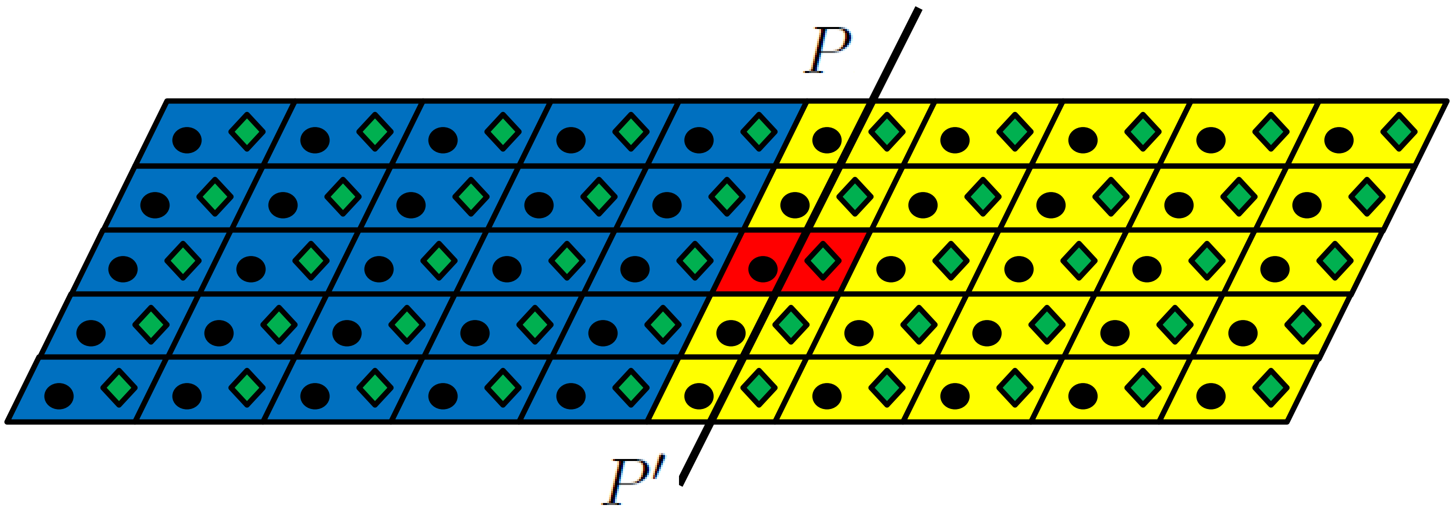


$\overrightarrow{\varepsilon}_{main}$ represents the net force of blues on red and greens



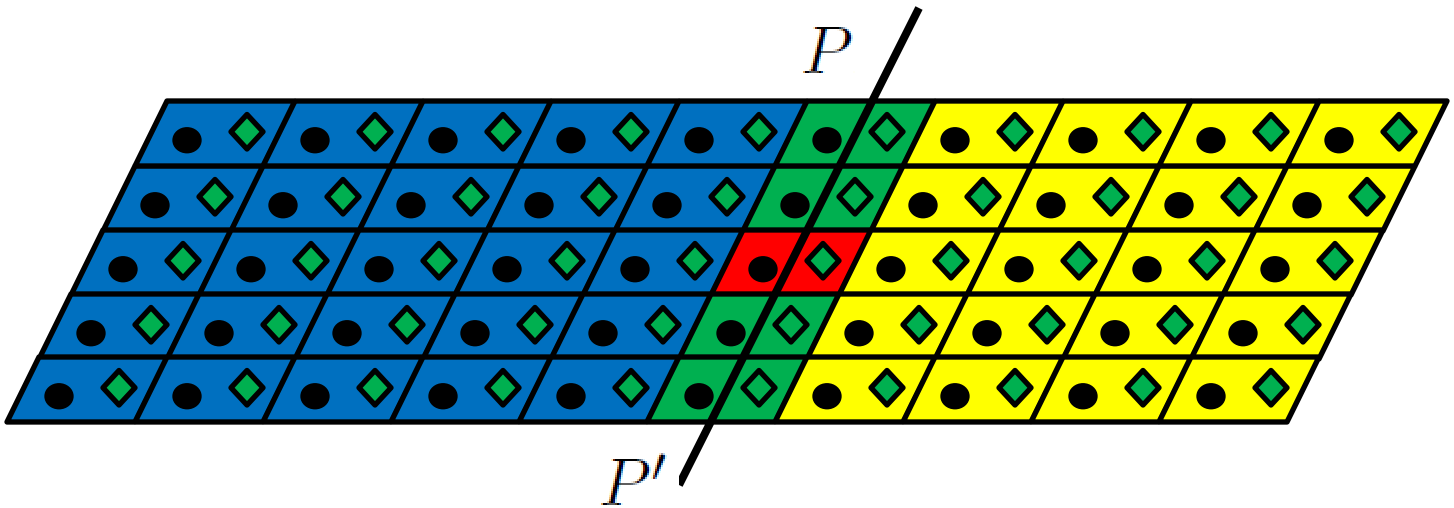
The red is the MD cell.

Case 1, whenever PP' passes through an MD particle, the old forces from blues on it should be deleted.



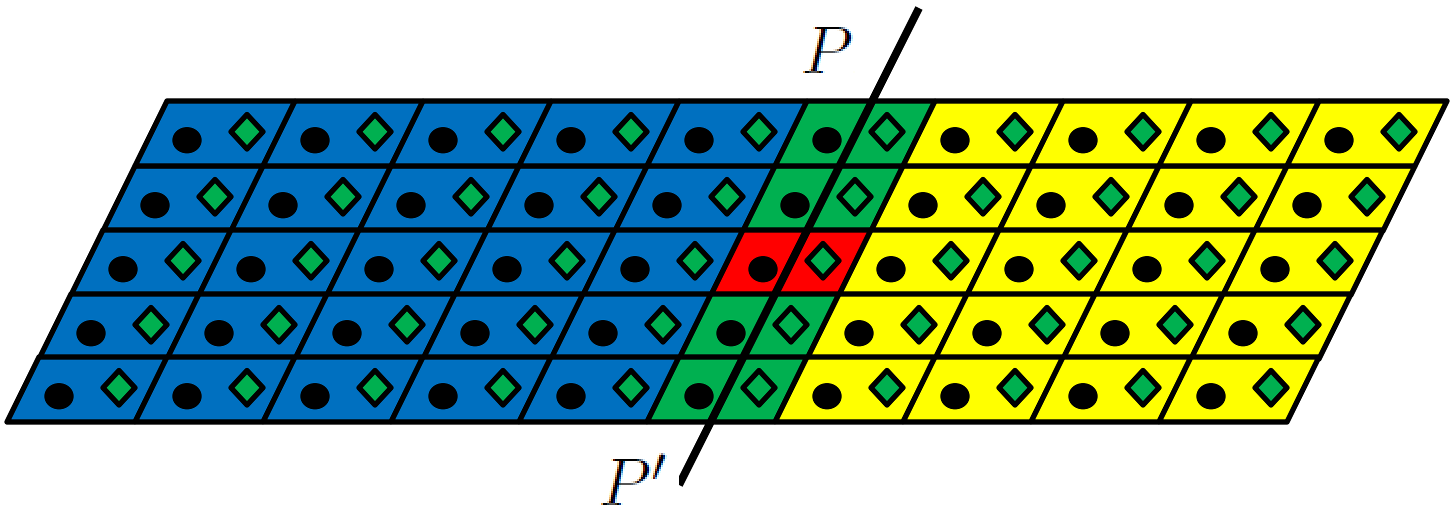
The amount of such states is $(\mathbf{h} - \mathbf{r}_i) \cdot \sigma_{\mathbf{h}}$

Case 2, whenever PP' passes through an MD particle, the forces from it on yellows should be added.



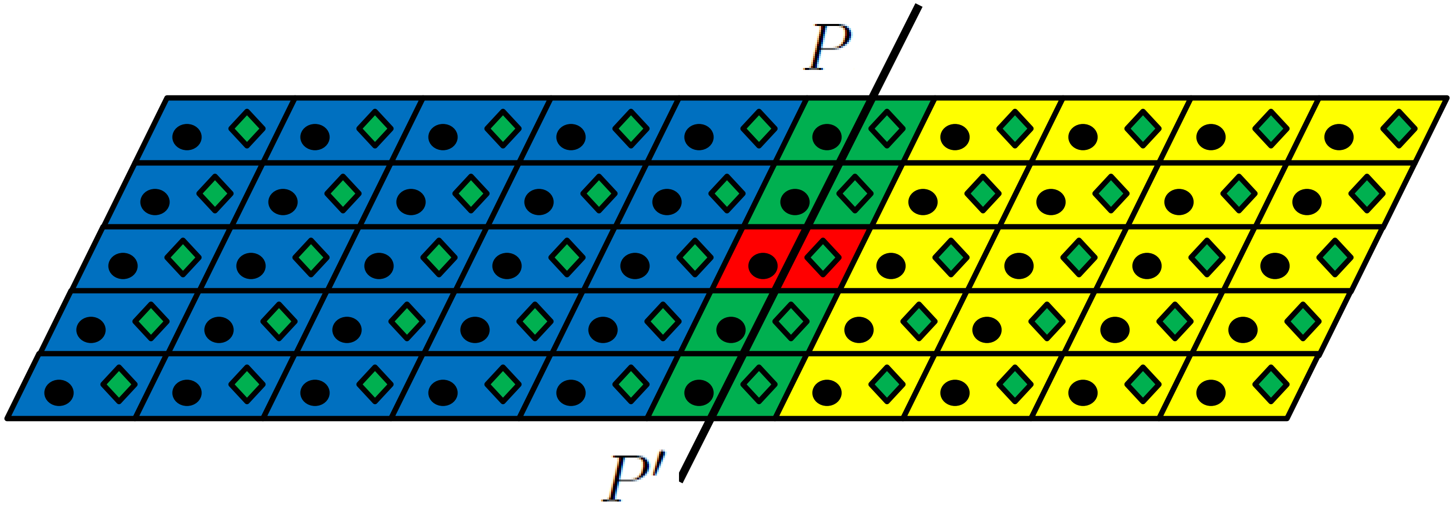
The amount of such states is $(\mathbf{h} - \mathbf{r}_i) \cdot \sigma_{\mathbf{h}}$

Case 3, whenever PP' is between two MD particles, the forces from left on right should be added.



The amount of such states is $|(\mathbf{r}_i - \mathbf{r}_j) \cdot \sigma_\mathbf{h}|$

Case 4, whenever PP' is between two MD particles, the forces from left in the greens on right MD particles should be added.



The amount of such states is $|(\mathbf{r}_i - \mathbf{r}_j) \cdot \sigma_{\mathbf{h}}|$

Period Dynamics $(\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c})$

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\varepsilon}_{main} + \overleftrightarrow{\Upsilon}\right) \cdot \sigma_{\mathbf{h}}$$ (first form)

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\varepsilon} + \overleftrightarrow{\Upsilon}\right) \cdot \sigma_{\mathbf{h}}$$ (improved)

where the full interaction tensor

$$\overleftrightarrow{\varepsilon} = \overleftrightarrow{\varepsilon}_{main} + \overleftrightarrow{\varepsilon}_{p} \qquad \overleftrightarrow{\varepsilon}_{p} = \frac{1}{\Omega}\sum_{i=1}^{n}\mathbf{F}_i\mathbf{r}_i$$

Now let us consider

forces associated with transport of momentum across geometrical planes,

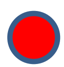
even without collision or any other interactions

Forces only due to momentum transportation

But what is it?

Considering a single particle $m \neq 0$

without being acted by any regular force,
but running with a constant velocity $\mathbf{v} \neq 0$



Considering a single particle $m \neq 0$

without being acted by any regular force,
but running with a constant velocity $\mathbf{v} \neq 0$

Since it passes through many planes, is
there any additional force acting on it?

Considering a single particle $m \neq 0$

without being acted by any regular force,
but running with a constant velocity $\mathbf{v} \neq 0$

Since it passes through many planes, is there any additional force acting on it?

As a matter of fact,

systems can be defined in two ways.

The first way,

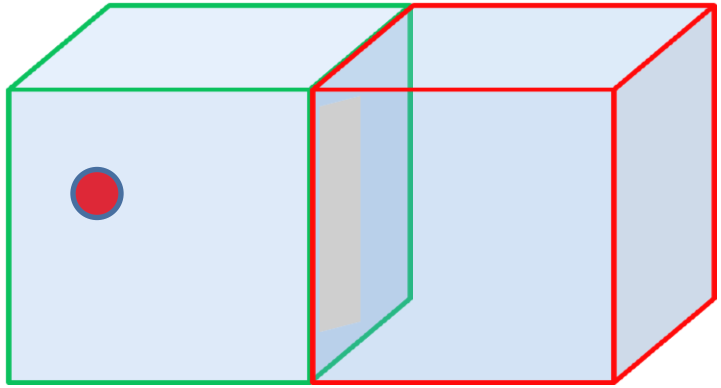
systems are defined based on materials or particles.

For example, the above single particle, then no additional force should be considered, in order to satisfy Newton's Laws.

The other way,

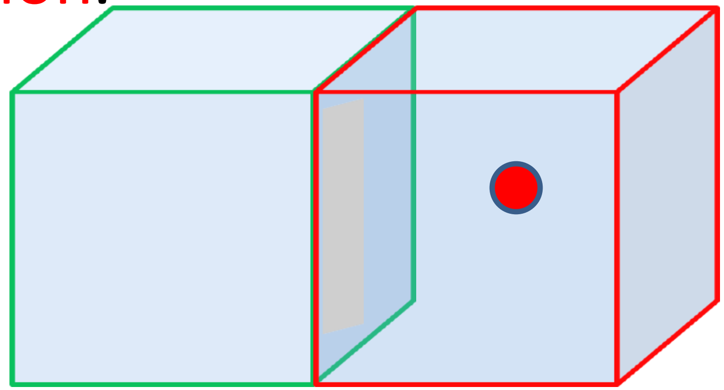
systems are defined based on space.

For example, still for the same single particle running process, we can define systems like red and green boxes, only based on space.

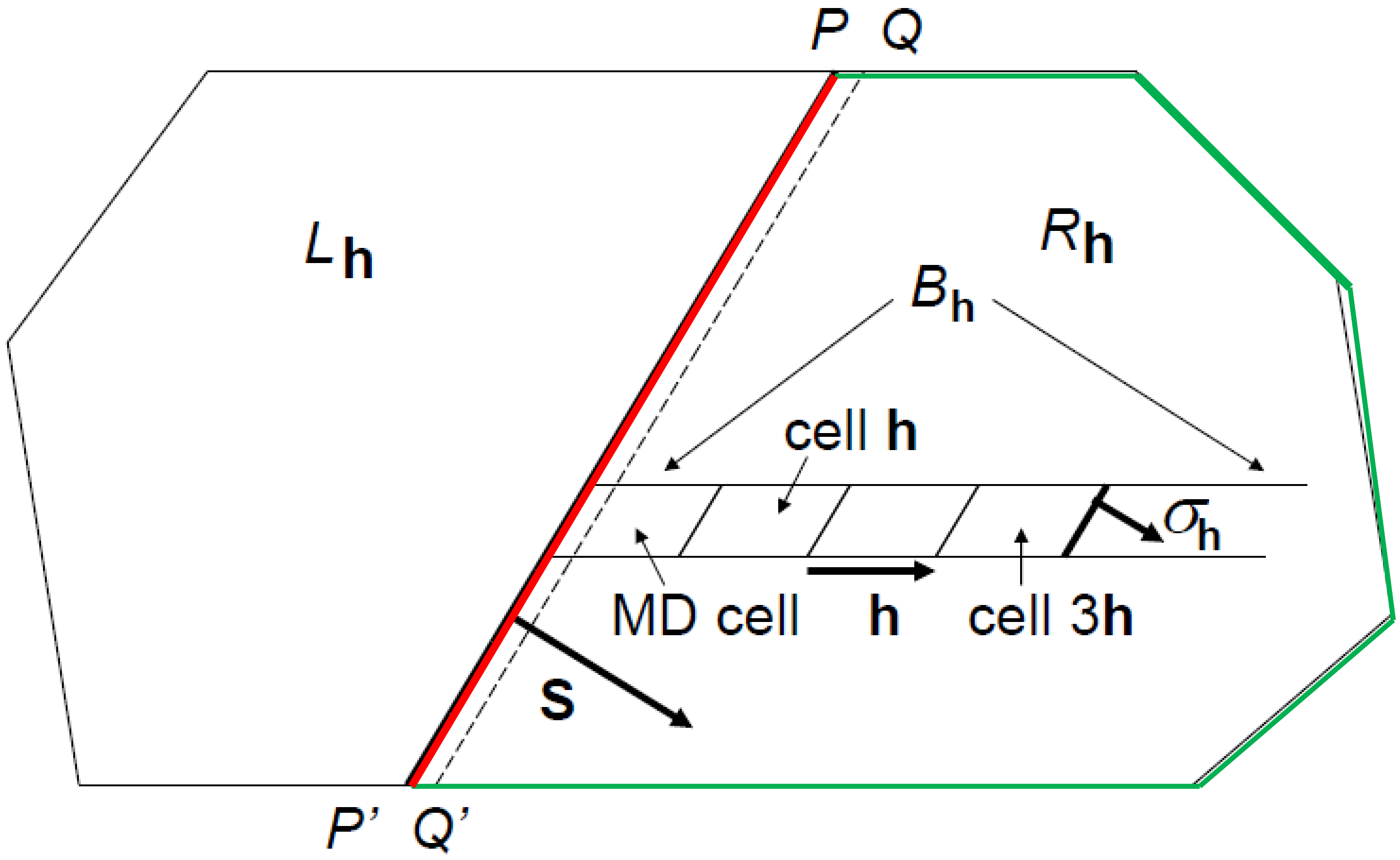


When the particle passes through

the plane between the red and green systems in $\triangle t$ the momentum of the systems are changed. In order to satisfy Newton's Laws, we can say there are forces between the two systems $\pm m\mathbf{v}/\triangle t$ This is the force purely associated with momentum transportation.



Our half systems are indeed defined based on space. Then such forces should be considered.

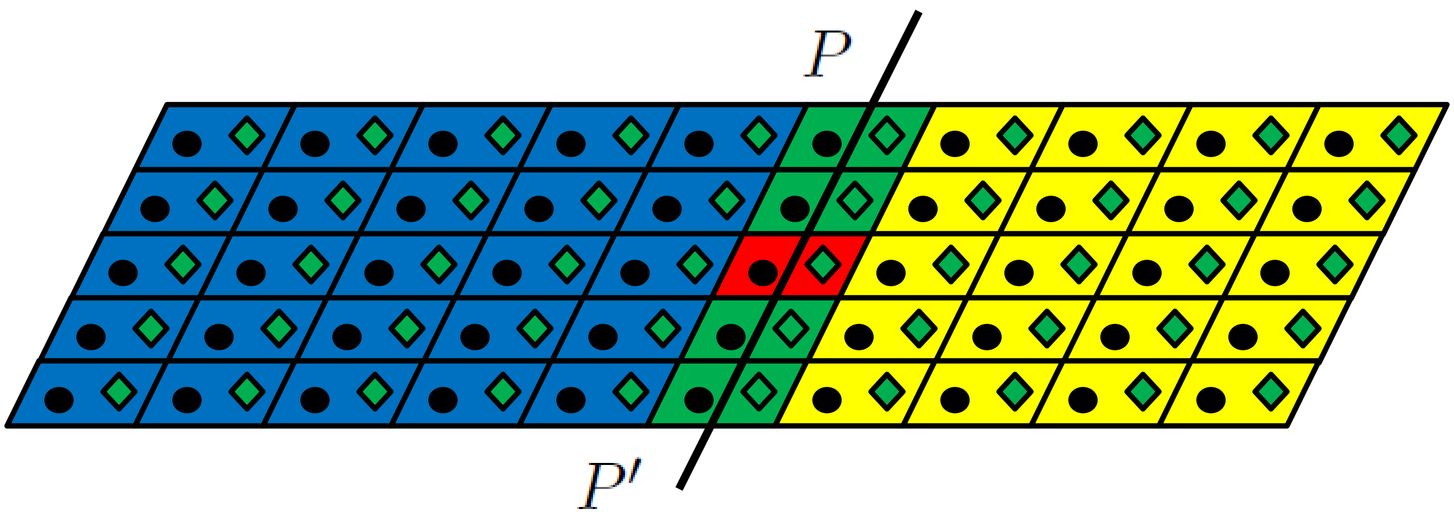


In all the previous translated-only states

During a unit time, particles passes $|\dot{\mathbf{r}}_i \cdot \sigma_{\mathbf{h}}|$ amount of states. Then the total

$$\frac{1}{\Omega}\sum_{i=1}^{n} m_i \dot{\mathbf{r}}_i \dot{\mathbf{r}}_i \cdot \sigma_{\mathbf{h}}$$

should be added into the dynamical equation.



Period Dynamics $(\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c})$

$$\alpha_{\mathbf{h},\mathbf{h}} \ddot{\mathbf{h}} = \left(\overset{\rightrightarrows}{\varepsilon}_{main} + \overset{\rightrightarrows}{\Upsilon} \right) \cdot \sigma_{\mathbf{h}}$$

(first form)

$$\alpha_{\mathbf{h},\mathbf{h}} \ddot{\mathbf{h}} = \left(\overset{\rightrightarrows}{\varepsilon} + \overset{\rightrightarrows}{\Upsilon} \right) \cdot \sigma_{\mathbf{h}}$$

(improved)

$$\overset{\rightrightarrows}{\varepsilon} = \overset{\rightrightarrows}{\varepsilon}_{main} + \overset{\rightrightarrows}{\varepsilon}_{p} \qquad \overset{\rightrightarrows}{\varepsilon}_{p} = \frac{1}{\Omega} \sum_{i=1}^{n} \mathbf{F}_i \mathbf{r}_i$$

$$\alpha_{\mathbf{h},\mathbf{h}} \ddot{\mathbf{h}} = \left(\overset{\rightrightarrows}{\pi}' + \overset{\rightrightarrows}{\Upsilon} \right) \cdot \sigma_{\mathbf{h}}$$

(further improved)

where the instantaneous internal stress

$$\overset{\rightrightarrows}{\pi}' = \overset{\rightrightarrows}{\varepsilon} + \overset{\rightrightarrows}{\tau}' \qquad \overset{\rightrightarrows}{\tau}' = \frac{1}{\Omega} \sum_{i=1}^{n} m_i \dot{\mathbf{r}}_i \dot{\mathbf{r}}_i$$

The last consideration

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\pi}' + \overleftrightarrow{\Upsilon}\right)\cdot\sigma_{\mathbf{h}}$$

(further improved)

where the instantaneous internal stress

$$\overleftrightarrow{\pi}' = \overleftrightarrow{\varepsilon} + \overleftrightarrow{\tau}' \qquad \overleftrightarrow{\tau}' = \frac{1}{\Omega}\sum_{i=1}^{n} m_i \dot{\mathbf{r}}_i \dot{\mathbf{r}}_i$$

The periods should not depend on the instantaneous directions of particles microscopic motion, as they can be measured under constant external pressure and temperature.

The last unweighted average of the

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overrightarrow{\overrightarrow{\pi}}' + \overrightarrow{\overrightarrow{\Upsilon}}\right) \cdot \sigma_{\mathbf{h}}$$ (further improved)

where the instantaneous internal stress

$$\overrightarrow{\overrightarrow{\pi}}' = \overrightarrow{\overrightarrow{\varepsilon}} + \overrightarrow{\overrightarrow{\tau}}' \qquad \overrightarrow{\overrightarrow{\tau}}' = \frac{1}{\Omega}\sum_{i=1}^{n} m_i \dot{\mathbf{r}}_i \dot{\mathbf{r}}_i$$

over all particles' moving directions.

Period Dynamics $(\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c})$

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\pi}' + \overleftrightarrow{\Upsilon}\right)\cdot\sigma_{\mathbf{h}}$$

(further improved)

$$\overleftrightarrow{\pi}' = \overleftrightarrow{\varepsilon} + \overleftrightarrow{\tau}' \qquad \overleftrightarrow{\tau}' = \frac{1}{\Omega}\sum_{i=1}^{n} m_i \dot{\mathbf{r}}_i \dot{\mathbf{r}}_i$$

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\pi} + \overleftrightarrow{\Upsilon}\right)\cdot\sigma_{\mathbf{h}}$$

(last)

where the internal stress $\overleftrightarrow{\pi} = \overleftrightarrow{\varepsilon} + \overleftrightarrow{\tau}$

$$\overleftrightarrow{\tau} = \frac{1}{3\Omega}\sum_{i=1}^{n} m_i \left|\dot{\mathbf{r}}_i\right|^2 \overleftrightarrow{I} = \frac{2}{3\Omega}E_{k,MD}\ \overleftrightarrow{I}$$

Period Dynamics $(\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c})$

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\varepsilon}_{main} + \overleftrightarrow{\Upsilon}\right) \cdot \sigma_{\mathbf{h}}$$

(first form)

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\varepsilon} + \overleftrightarrow{\Upsilon}\right) \cdot \sigma_{\mathbf{h}}$$

(improved)

$$\overleftrightarrow{\varepsilon} = \overleftrightarrow{\varepsilon}_{main} + \overleftrightarrow{\varepsilon}_{p} \qquad \overleftrightarrow{\varepsilon}_{p} = \frac{1}{\Omega}\sum_{i=1}^{n}\mathbf{F}_i\mathbf{r}_i$$

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\pi}' + \overleftrightarrow{\Upsilon}\right) \cdot \sigma_{\mathbf{h}}$$

(further improved)

$$\overleftrightarrow{\pi}' = \overleftrightarrow{\varepsilon} + \overleftrightarrow{\tau}' \qquad \overleftrightarrow{\tau}' = \frac{1}{\Omega}\sum_{i=1}^{n} m_i\dot{\mathbf{r}}_i\dot{\mathbf{r}}_i$$

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\pi} + \overleftrightarrow{\Upsilon}\right) \cdot \sigma_{\mathbf{h}} \qquad \overleftrightarrow{\tau} = \frac{2}{3\Omega}E_{k,MD}\overleftrightarrow{I}$$

(last)

$$\overleftrightarrow{\pi} = \overleftrightarrow{\varepsilon} + \overleftrightarrow{\tau}$$

Summary

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \quad (i = 1, 2, \cdots, n),$$

$$\alpha_{\mathbf{h},\mathbf{h}} \ddot{\mathbf{h}} = \left(\overleftrightarrow{\pi} + \overleftrightarrow{\Upsilon} \right) \cdot \sigma_{\mathbf{h}} \qquad (\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c})$$

$$\overleftrightarrow{\pi} = \overleftrightarrow{\varepsilon} + \overleftrightarrow{\tau} \qquad \overleftrightarrow{\varepsilon} = \overleftrightarrow{\varepsilon}_{main} + \overleftrightarrow{\varepsilon}_{p}$$

$$\overleftrightarrow{\tau} = \frac{2}{3\Omega} E_{k,MD} \overleftrightarrow{I} \qquad \overleftrightarrow{\varepsilon}_{p} = \frac{1}{\Omega} \sum_{i=1}^{n} \mathbf{F}_i \mathbf{r}_i$$

$$\overleftrightarrow{\varepsilon} = -\frac{1}{\Omega} \sum_{\mathbf{z} \in \mathrm{DOF}} \left(\frac{\partial E_{p,MD}}{\partial \mathbf{z}} \right) \mathbf{z}$$

Applications

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overleftrightarrow{\pi} + \overleftrightarrow{\Upsilon}\right) \cdot \sigma_{\mathbf{h}} \qquad (\mathbf{h} = \mathbf{a},\ \mathbf{b},\ \mathbf{c})$$

$$\overleftrightarrow{\pi} = -\frac{1}{\Omega} \sum_{\mathbf{z} \in \mathrm{DOF}} \left(\frac{\partial E_{p,MD}}{\partial \mathbf{z}}\right) \mathbf{z} + \frac{2}{3\Omega} E_{k,MD}\ \overleftrightarrow{I}$$

Applicable in any periodic system, especially in piezoelectric and piezomagnetic simulations.

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Questions?

Thank you much very for your attention!

More details:
http://arxiv.org/pdf/cond-mat/0209372.pdf
and some printed copies available for picking up.

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