Density dependent UCG code: theory and implementation

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Note: In this document, the definition of the state probability $p_{s_i,\alpha/\beta}$ is quite complicated, so we will use following reduced notation of the probability to implement it into the force field formula henceforth. A short-hand notation will be marked as blue line.

1 Probability function setting

1.1 Definition of density-dependent state probability

1.1.1 Number function

Now, consider the probability function is totally dependent on the local geometry of the molecule. Define the number function w_i as below.

$$w_i = \sum_j \frac{1}{2}\left(1 - \tanh(\frac{r_{ij} - r_{cut}}{0.001 \cdot r_{cut}})\right)$$

By using a short-hand notation

$$\begin{aligned} w_i &= \sum_j \frac{1}{2}\left(1 - \tanh(\frac{r_{ij} - r_{cut}}{0.001 \cdot r_{cut}})\right) \\ &= \sum_j \frac{1}{2}(1 - t(r_{ij})) \\ &:= \sum_j w_{ij} \end{aligned}$$

1.1.2 Choice of r_{cut}

We can set r_{cut} value arbitrarily less than r_{ljcut} to ensure that for $r_{ij} \leqslant r_{lj}$ $w_{ij} \simeq 1$ which can add one particle in the number function. The behavior of w_{ij} function is highly dependent on the cut-off value, see the figure below. Figure 1 denotes the behavior of w_{ij} function in terms of different r value. In this case, r_{cut} is chosen as 3.5 Å.

Therefore, number function w_{ij} shows following behavior: $w_{ij} \simeq 1$ (when $r < r_{cut}$), $w_{ij} \simeq 0$ (when $r > r_{cut}$).

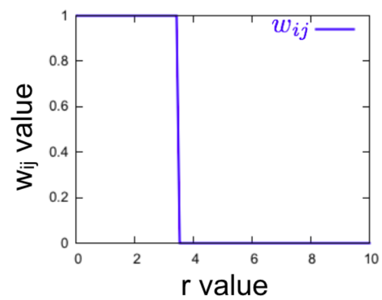

Figure 1: A behavior of w_i function by differing r value: $r_{cut} = 3.5$Å

Also, let's set the corresponding "normalized" probability for two states as

$$P_{i,a} = +\frac{1}{2} \cdot \tanh(\frac{w_i - c}{0.1c}) + \frac{1}{2}$$
$$P_{i,b} = -\frac{1}{2} \cdot \tanh(\frac{w_i - c}{0.1c}) + \frac{1}{2}$$

which gives $P_{i,a} + P_{i,b} = 1$, the normalized probability. For the sake of brevity, we use the short-hand notation henceforth as:

$$P_{i,a} = +\frac{1}{2}(\tanh(\frac{w_i - c}{0.1c}) + 1)$$
$$P_{i,b} = -\frac{1}{2}(\tanh(\frac{w_i - c}{0.1c}) - 1)$$

However, it is worth mentioning that the shape of these probabilities also determined by the c value.

1.1.3 Choice of c value

Since the state probability is a function of c value, it is needed to select an appropriate c value to assign the right state probability. To show the effect of c value over the state probability, let's examine the c value dependency on the $P_{i,a}$ probability. From definition,

$$P_{i,a} = +\frac{1}{2} \cdot \tanh(\frac{w_i - c}{0.1c}) + \frac{1}{2}$$

Thus, changing the c value will effect the shape of slope of tanh function and the reflection point of the $P_{i,a}$ value due to $\frac{\partial P_{i,a}}{\partial w_i} = 0 \leftrightarrow w_i = c$, see Figure 2.

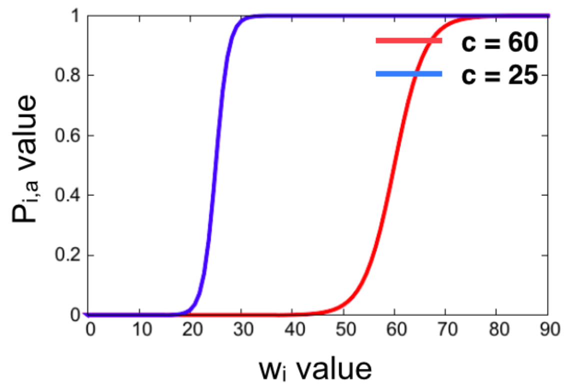

Figure 2: A dependence of state probability function $P_{i,a}$ on the coefficient c value

1.1.4 Final probability definition

Thus, plugging the expression of w_i into $P_{i,a}$ and $P_{i,b}$ gives

$$
\begin{aligned}
P_{i,a} &= +\frac{1}{2} \cdot \tanh\left(\frac{\frac{1}{2}\sum_j (1 - \tanh(\frac{r_{ij} - r_{cut}}{0.001 \cdot r_{cut}})) - c}{0.1c}\right) + \frac{1}{2} \\
&= +\frac{1}{2} \cdot \tanh\left(\frac{\frac{1}{2}\sum_j (1 - \tanh(\frac{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} - r_{cut}}{0.001 \cdot r_{cut}})) - c}{0.1c}\right) + \frac{1}{2} \\
&= +\frac{1}{2} \cdot \tanh\left(\frac{j}{0.2c} - \frac{1}{0.2c}\sum_j \tanh(\frac{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} - r_{cut}}{0.001 \cdot r_{cut}}) - 10\right) + \frac{1}{2}
\end{aligned}
$$

Thus the partial derivative of the system is

$$
\nabla_i P_{i,a} = \left(\frac{\partial}{\partial x_i} P_{i,a}, \frac{\partial}{\partial y_i} P_{i,a}, \frac{\partial}{\partial z_i} P_{i,a}\right)
$$

Each component is followed as

$$
\begin{aligned}
\frac{\partial}{\partial x_i} P_{i,a} =& \frac{1}{2} \cdot \mathrm{sech}^2\left(\frac{\frac{1}{2}\sum_j (1 - \tanh(\frac{r_{ij} - r_{cut}}{0.001 \cdot r_{cut}})) - c}{0.1c}\right) \times \frac{\partial}{\partial x}\left(\frac{\frac{1}{2}\sum_j (1 - \tanh(\frac{r_{ij} - r_{cut}}{0.001 \cdot r_{cut}})) - c}{0.1c}\right) \\
&= \frac{1}{2} \cdot S(r_{ij}) \times T(r_{ij})
\end{aligned}
$$

Let's say the first and the second part of the RHS as $S(r_{ij})$, $T(r_{ij})$, then by above equation

$$S(r_{ij}) = \operatorname{sech}^2\left(\frac{w_i - c}{0.1c}\right)$$

Also for $T(r_{ij})$,

$$\begin{aligned}
T(r_{ij}) :&= \frac{\partial}{\partial x}\Big(\frac{\frac{1}{2}\sum_j(1-\tanh(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}))-c}{0.1c}\Big) \\
&= -\frac{1}{0.2c}\frac{\partial}{\partial x}\left(\sum_j \tanh\Big(\frac{\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}-r_{cut}}{0.001\cdot r_{cut}}\Big)\right) \\
&= -\frac{1}{0.2c}\sum_j \operatorname{sech}^2\Big(\frac{\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}-r_{cut}}{0.001\cdot r_{cut}}\Big) \\
&\quad \times \frac{(x_i-x_j)}{0.001\cdot r_{cut}\cdot\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}} \\
&= -\frac{1}{0.2c}\sum_j \operatorname{sech}^2\Big(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}\Big)\times\frac{\Delta x}{0.001\cdot r_{cut}\cdot r_{ij}} \\
&= -\frac{1}{0.2c}\sum_j \frac{\partial}{\partial x}t(r_{ij})
\end{aligned}$$

which is

$$t(r_{ij}) = \tanh\Big(\frac{r_{ij}-r_{cut}}{0.001 r_{cut}}\Big)$$

The notation used in LAMMPS is $\Delta x = x_i - x_j$, $\Delta y = y_i - y_j$, $\Delta z = z_i - z_j$. Thus,

$$\begin{aligned}
\frac{\partial}{\partial x_i}P_{i,a} &= \frac{1}{2}\cdot S(r_{ij})\times T(r_{ij}) \\
&= \frac{1}{2}\cdot\operatorname{sech}^2\left(\frac{w_i-c}{0.1c}\right)\cdot T(r_{ij}) \\
&= \frac{1}{2}\cdot\operatorname{sech}^2\left(\frac{\frac{1}{2}\sum_j(1-\tanh(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}))-c}{0.1c}\right)\times\left(-\frac{1}{0.2c}\sum_j\operatorname{sech}^2\Big(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}\Big)\times\frac{\Delta x}{0.001\cdot r_{cut}\cdot r_{ij}}\right) \\
&= -\frac{1}{0.4c}\cdot\operatorname{sech}^2\left(\frac{\frac{1}{2}\sum_j(1-\tanh(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}))-c}{0.1c}\right)\times\left(\sum_j\operatorname{sech}^2\Big(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}\Big)\times\frac{\Delta x}{0.001\cdot r_{cut}\cdot r_{ij}}\right) \\
&= -\frac{1}{0.4c}\cdot\operatorname{sech}^2\left(\frac{w_i-c}{0.1c}\right)\times\left(\sum_j\frac{\partial}{\partial x}t(r_{ij})\right) \\
&= -\frac{\operatorname{sech}^2(\frac{w_i-c}{0.1c})}{0.004c\cdot r_{cut}}\times\left(\sum_j\operatorname{sech}^2\Big(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}\Big)\right)\times\left[\frac{\Delta x}{r_{ij}},\frac{\Delta y}{r_{ij}},\frac{\Delta z}{r_{ij}}\right]
\end{aligned}$$

Similarly,

$$\frac{\partial}{\partial y_i}P_{i,a} = -\frac{1}{0.2c}\cdot \text{sech}^2\left(\frac{\sum_j(1-\tanh(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}))-c}{0.1c}\right)\times\left(\sum_j \text{sech}^2(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}})\times\frac{\Delta y}{0.001\cdot r_{ij}}\right)$$
$$= -\frac{1}{0.2c}\cdot \text{sech}^2\left(\frac{w_i-c}{0.1c}\right)\times\left(\sum_j \frac{\partial}{\partial y}t(r_{ij})\right)$$
$$\frac{\partial}{\partial z_i}P_{i,a} = -\frac{1}{0.2c}\cdot \text{sech}^2\left(\frac{\sum_j(1-\tanh(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}}))-c}{0.1c}\right)\times\left(\sum_j \text{sech}^2(\frac{r_{ij}-r_{cut}}{0.001\cdot r_{cut}})\times\frac{\Delta z}{0.001\cdot r_{ij}}\right)$$
$$= -\frac{1}{0.2c}\cdot \text{sech}^2\left(\frac{w_i-c}{0.1c}\right)\times\left(\sum_j \frac{\partial}{\partial z}t(r_{ij})\right)$$

Therefore, the $\nabla_i P_{i,a}$ is followed as

$$\begin{aligned}\nabla_i P_{i,a} &= (\frac{\partial}{\partial x_i}P_{i,a}, \frac{\partial}{\partial y_i}P_{i,a}, \frac{\partial}{\partial z_i}P_{i,a})\\ &= -\frac{\text{sech}^2(\frac{w_i-c}{0.1c})}{0.004c\cdot r_{cut}}\times\left(\sum_j \text{sech}^2(\frac{r_{ij}-r_{cut}}{0.001 r_{cut}})\right)\times\left[\frac{\Delta x}{r_{ij}},\frac{\Delta y}{r_{ij}},\frac{\Delta x}{r_{ij}}\right]\end{aligned} \tag{1}$$

1.2 Neighbor hypothesis

However, for this probability, the dependence of r_i is not strictly followed by p_{s_i} term. For example, p_{s_j} can have a dependency on the r_i value.

Lemma: if the particle j is in a neighbor of the particle i, then also particle i is in a neighbor of the particle j.
Proof:

$$\begin{aligned}p_{s_j} = p_{s_j}(r_i) &\to i \in \mathcal{N}(r_j, r_{lj\ cut})\\ &\leftrightarrow |r_i - r_j| \leqslant r_{lj\ cut}\\ &\leftrightarrow |r_j - r_i| \leqslant r_{lj\ cut}\\ &\leftrightarrow j \in \mathcal{N}(r_i, r_{lj\ cut})\end{aligned}$$

□

This Lemma is easily explained by the following diagram.

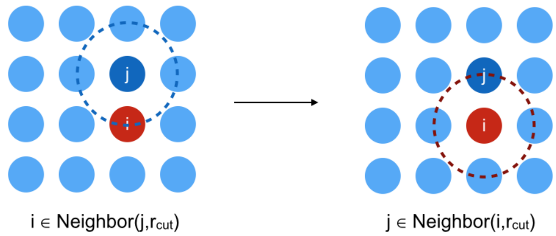

Figure 3: A relation about neighboring particles

1.3 Summation scheme

Therefore, to consider the summation over particles i, j, k,

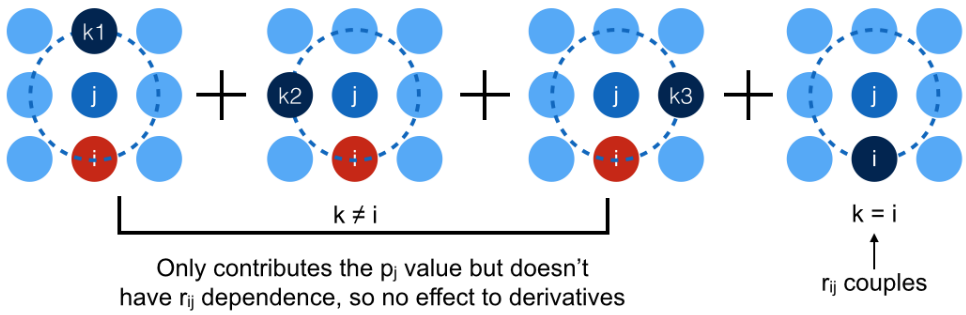

Figure 4: Summation among three particles i, j, k

2 Force Field expression

2.1 Mixed UCG FF LJ parameters

From the past note that I've implemented in the mixed UCG ansatz, the force acting on particle i can be expressed from the free energy expression $w^{mix}(\mathbf{r}^n)$.

$$w^{mix}(\mathbf{r}^n) = \sum_{\text{particles } i} \sum_{\text{states } \alpha} p_{s_i,\alpha}(\mu_\alpha - kT\ln(p_{s_i,\alpha})) + \sum_{\text{neighs } ij} \sum_{\text{state pairs } \alpha,\beta} p_{s_i,\alpha} p_{s_j,\beta} u_{\alpha\beta}(r_{ij}) \tag{2}$$

Thus, the force expression is

$$\mathbf{f}_i \equiv -\nabla_i w^{mix}(\mathbf{r}^n) \tag{3}$$

$$\mathbf{f}_i = -\nabla_i \left(\sum_j \sum_\alpha p_{s_j,\alpha}(\mu_\alpha - kT\ln(p_{s_j,\alpha})) + \sum_{jk}\sum_{\alpha\beta} p_{s_j,\alpha}p_{s_k,\beta}u_{\alpha,\beta}(r_{jk}) \right) \tag{4}$$

$$\begin{aligned} \mathbf{f}_i = &-\sum_j \sum_\alpha (\nabla_i p_{s_j,\alpha})(\mu_\alpha - kT\ln(p_{s_j,\alpha}) - kT) + \dots \\ &\dots - \sum_{jk}\sum_{\alpha\beta} p_{s_j,\alpha}p_{s_k,\beta}\nabla_i u_{\alpha\beta}(r_{jk}) - \sum_{jk}\sum_{\alpha\beta}(\nabla_i(p_{s_j,\alpha}p_{s_k,\beta}))u_{\alpha,\beta}(r_{jk}) \end{aligned} \tag{5}$$

For the sake of concision, let's separate the force component into three parts from the natural order, i.e. $\mathbf{f}_i = \mathbf{f}_i^{(1)} + \mathbf{f}_i^{(2)} + \mathbf{f}_i^{(3)}$ where

$$\mathbf{f}_i^{(1)} = -\sum_j \sum_\alpha (\nabla_i p_{s_j,\alpha})(\mu_\alpha - kT\ln(p_{s_j,\alpha}) - kT) := -\sum_j \sum_\alpha \mathbb{A}_{ij} \tag{6}$$

$$\mathbf{f}_i^{(2)} = -\sum_{jk}\sum_{\alpha\beta} p_{s_j,\alpha}p_{s_k,\beta}\nabla_i u_{\alpha\beta}(r_{jk}) := -\sum_{jk}\sum_{\alpha\beta} \mathbb{B}_{ijk} \tag{7}$$

$$\mathbf{f}_i^{(3)} = -\sum_{jk}\sum_{\alpha\beta}(\nabla_i(p_{s_j,\alpha}p_{s_k,\beta}))u_{\alpha,\beta}(r_{jk}) := -\sum_{jk}\sum_{\alpha\beta} \mathbb{C}_{ijk} \tag{8}$$

The form of each subforce term will be examined on the following subsections.

2.2 First subforce term

The first subforce term $\mathbf{f}_i^{(1)}(\mathbf{r}^n)$, the entropic contribution, can be represented by using the short-hand notation that

$$\mathbb{A}_{ij} := (\nabla_i p_{s_j,\alpha})(\mu_\alpha - kT\ln(p_{s_j,\alpha}) - kT)$$

Then, the first subforce term can be decomposed into

$$\begin{aligned} \mathbf{f}_i^{(1)} &= -\sum_j \sum_\alpha (\nabla_i p_{s_j,\alpha})(\mu_\alpha - kT\ln(p_{s_j,\alpha}) - kT) \\ &= -\sum_{j\neq i}\sum_\alpha \mathbb{A}_{ij} - \sum_i \sum_\alpha \mathbb{A}_i \end{aligned} \tag{9}$$

Above expression is composed of two cases: particle j is i or is not i. The second term for the force component can be simply written as below because of the normalization of the probability, i.e. $\sum_i \nabla_i p_{s_i} = 0$, which gives

$$-\sum_i \sum_\alpha \mathbb{A}_i = -\sum_\alpha (\nabla_i p_{s_i,\alpha})(\mu_\alpha - kT\ln(p_{s_i,\alpha})) \tag{10}$$

However, for the first term, two things are worth mentioning: first, the simple cancellation cannot be applied, because it is summation of p_{s_j} over j with ∇_i. To retain the dependence of the r_i, only the term in the p_{s_j} which has r_i in the summation will be survived because of the summation index $j \neq i$. Also, $\forall j \neq i$, $\nabla_i p_{s_i,\alpha/\beta}$ doesn't have to be zero for the case, see the lemma 2 below.

Lemma 2: For this density-dependent state probability case, $\forall j \neq i$, $\nabla_i p_{s_i,\alpha/\beta}$ doesn't necessarily have to be zero.

Proof: To show that, let's first start with the derivative of $P_{j,\alpha/\beta}$.

$$
\begin{aligned}
\nabla_i P_{j,\alpha/\beta} &= \nabla_i \left(\frac{1}{2}\Big(1 \pm \tanh(\frac{w_j - c}{0.1c})\Big) \right) \\
&= \pm\frac{1}{2} \cdot \operatorname{sech}^2(\frac{w_j - c}{0.1c}) \times \frac{1}{0.1c} \cdot \nabla_i(w_j) \\
&= \pm\frac{1}{2} \cdot \operatorname{sech}^2(\frac{w_j - c}{0.1c}) \times \frac{1}{0.1c} \cdot \nabla_i \left(\sum_{t \in \mathcal{N}(j; r_{ljcut})} (\frac{1}{2}(1 - \tanh(\frac{r_{jt} - r_{cut}}{0.001 r_{cut}}))) \right) \\
&= \pm\frac{\operatorname{sech}^2(\frac{w_j - c}{0.1c})}{0.2c} \times \sum_{t \in \mathcal{N}(j; r_{ljcut})} \left(-\frac{1}{2}\operatorname{sech}^2(\frac{r_{jt} - r_{cut}}{0.001 r_{cut}}) \times \nabla_i (\frac{r_{jt}}{0.001 r_{cut}}) \right) \\
&= \mp\frac{\operatorname{sech}^2(\frac{w_j - c}{0.1c})}{0.004c \cdot r_{cut}} \times \sum_{t \in \mathcal{N}(j; r_{ljcut})} \left(\operatorname{sech}^2(\frac{r_{jt} - r_{cut}}{0.001 r_{cut}}) \times \Big[\frac{\Delta x}{r_{jt}}, \frac{\Delta y}{r_{jt}}, \frac{\Delta x}{r_{jt}}\Big] \right)
\end{aligned}
\tag{11}
$$

Therefore, for $j \neq i$, the necessary condition of $\nabla_i p_{s_j,\alpha/\beta} \neq 0$ is that $\exists i \in N(j; r_{ljcut})$. For that case, $\nabla_i p_{s_j,\alpha/\beta}$ reduces into

$$
\nabla_i p_{s_j,\alpha/\beta} = \mp\frac{\operatorname{sech}^2(\frac{w_j - c}{0.1c})}{0.004c \cdot r_{cut}} \times \operatorname{sech}^2(\frac{r_{ij} - r_{cut}}{0.001 r_{cut}}) \times \Big[\frac{\Delta x}{r_{ij}}, \frac{\Delta y}{r_{ij}}, \frac{\Delta x}{r_{ij}}\Big]
\tag{12}
$$

□

Thus, the first term can be expressed as

$$
-\sum_{j \neq i} \sum_{\alpha} \mathbb{A}_{ij} = -\sum_{j \neq i} \sum_{\alpha} \left(\mp\frac{\operatorname{sech}^2(\frac{w_j - c}{0.1c})}{0.004c \cdot r_{cut}} \times \operatorname{sech}^2(\frac{r_{ij} - r_{cut}}{0.001 r_{cut}}) \times \Big[\frac{\Delta x}{r_{ij}}, \frac{\Delta y}{r_{ij}}, \frac{\Delta x}{r_{ij}}\Big] \right) \times \big(\mu_\alpha - kT \ln(p_{s_i,\alpha}) - kT\big)
\tag{13}
$$

However, since $\nabla_i(p_{s_j,\alpha}) = -\nabla_i(p_{s_j,\beta})$, the only remained term is

$$
-\sum_{j \neq i} \sum_{\alpha} \mathbb{A}_{ij} = -\sum_{j \neq i} \sum_{\alpha} \left((\mp\frac{\operatorname{sech}^2(\frac{w_j - c}{0.1c})}{0.004c \cdot r_{cut}} \times \operatorname{sech}^2(\frac{r_{ij} - r_{cut}}{0.001 r_{cut}}) \times \Big[\frac{\Delta x}{r_{ij}}, \frac{\Delta y}{r_{ij}}, \frac{\Delta x}{r_{ij}}\Big]) \times \big(\mu_\alpha - kT \ln(p_{s_i,\alpha})\big) \right)
\tag{14}
$$

2.3 Second subforce term

From definition of $\mathbf{f}_i^{(2)}$,

$$\mathbf{f}_i^{(2)} = -\sum_{jk}\sum_{\alpha\beta} p_{s_j,\alpha}p_{s_k,\beta}\nabla_i u_{\alpha\beta}(r_{jk})$$

However, $u_{\alpha\beta}(r_{jk})$ only has dependency on $r_{jk} = |r_j - r_k|$ thus, to make the derivative term non-zero,

This subforce term is invariant under the first case, where the state probability is only dependent on the particle's position. Thus, for the two-state system, detailed expression for the second subforce term is

$$\begin{aligned}\mathbf{f}_i^{(2)} &= -\sum_{j}\sum_{\alpha\beta} p_{s_i,\alpha}p_{s_j,\beta}\nabla_i u_{\alpha\beta}(r_{ij}) \qquad (15)\\ &= -\sum_{j}\Big(p_{s_i,\alpha}p_{s_j,\alpha}\nabla_i u_{\alpha\alpha}(r_{ij}) + \big(p_{s_i,\alpha}p_{s_j,\beta} + p_{s_i,\beta}p_{s_j,\alpha}\big)\cdot\nabla_i u_{\alpha\beta}(r_{ij}) + p_{s_i,\beta}p_{s_j,\beta}\nabla_i u_{\beta\beta}(r_{ij})\Big)\end{aligned}$$

2.4 Third subforce term

From the definition of $\mathbf{f}_i^{(3)}$,

$$\begin{aligned}\mathbf{f}_i^{(3)} &= -\sum_{jk}\sum_{\alpha\beta}(\nabla_i(p_{s_j,\alpha}p_{s_k,\beta}))u_{\alpha,\beta}(r_{jk}) \qquad (16)\\ &= -\sum_{jk}\sum_{\alpha\beta}\Big((\nabla_i p_{s_j,\alpha}\cdot p_{s_k,\beta}) + (p_{s_j,\alpha}\cdot\nabla_i p_{s_k,\beta})\Big)u_{\alpha,\beta}(r_{jk})\\ &= -\sum_{jk}\sum_{\alpha\beta}(\mathbb{C}_{ijk}) \qquad (17)\end{aligned}$$

Note that the above equation has $\mathbb{C}_{ijk}$ term in short-hand notation for the sake of brevity. Since it is the force expression of the particle i, the only non-zero terms from either $\nabla_i p_{s_j,\alpha}$ or $\nabla_i p_{s_j,\beta}$ will be survived after a summation. However, from the probability function construction that,

$$\begin{aligned}P_{j,\alpha/\beta} &= \frac{1}{2}\left(\pm\tanh\Big(\frac{\sum_{t\in\mathcal{N}(j;r_{ljcut})}\frac{1}{2}(1-\tanh(\frac{\sqrt{(x_j-x_t)^2+(y_j-y_t)^2+(z_j-z_t)^2}-r_{cut}}{0.001r_{cut}})) - c}{0.1c}\Big)+1\right) \qquad (18)\\ &= \frac{1}{2}\Big(\pm\tanh(\frac{w_j-c}{0.1c})+1\Big)\end{aligned}$$

From the summation index above, $t \in \mathcal{N}(j; r_{ljcut})$ means the particle t is the neighbor of particle j within cutoff radius r_{ljcut}. However, in this state probability case, the previous assumption that we used for the position dependent case $\nabla_{\mathbf{i}\neq\mathbf{j}}\mathbf{p}_{\mathbf{s}_{j,,}} = \mathbf{0}$ is not valid in here.

Furthermore, from the **Lemma 2**, we know that the summation index $\sum_{jk}$ cannot be simply reduced into $\sum_i$ for $\mathbf{f}_i^{(3)}$. However, one can still decompose it by following scheme.

$$\sum_{jk} \mathbb{C}_{ijk} = \sum_{j\neq k, k=i} \mathbb{C}_{ijk} + \sum_{j=i, k\neq j} \mathbb{C}_{ijk} + \sum_{\substack{j\neq i \\ k\neq i}} \mathbb{C}_{ijk} \tag{19}$$

$$= \underbrace{\left(\sum_{j\neq k, k=i} \mathbb{C}_{ijk} + \sum_{j=i, k\neq j} \mathbb{C}_{ijk}\right)}_{\text{two particles interaction}} + \underbrace{\left(\sum_{\substack{j\in N(i;r_{cut}) \\ k\notin N(i;r_{cut})}} \mathbb{C}_{ijk} + \sum_{\substack{j\notin N(i;r_{cut}) \\ k\in N(i;r_{cut})}} \mathbb{C}_{ijk} + \sum_{\substack{j\in N(i;r_{cut}) \\ k\in N(i;r_{cut})}} \mathbb{C}_{ijk}\right)}_{\text{three particles interaction}}$$

2.4.1 Two particles interaction term

For the simple two-particle interaction term, the expression of third subforce term is simply from the first example case.

$$\sum_{j\neq k, k=i} \mathbb{C}_{ijk} = \sum_{j\neq i} \mathbb{C}_{ijk} \tag{20}$$

$$= \sum_{j\neq i} \sum_{\alpha\beta} \left((\nabla_i p_{s_j,\alpha} \cdot p_{s_i,\beta}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\beta}) \right) u_{\alpha,\beta}(r_{ij})$$

$$= \sum_{j\neq i} \Big((\nabla_i p_{s_j,\alpha} \cdot p_{s_i,\alpha}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\alpha}) + (\nabla_i p_{s_j,\alpha} \cdot p_{s_i,\beta}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\beta})$$

$$+ (\nabla_i p_{s_j,\beta} \cdot p_{s_i,\alpha}) + (p_{s_j,\beta} \cdot \nabla_i p_{s_i,\alpha}) + (\nabla_i p_{s_j,\beta} \cdot p_{s_i,\beta}) + (p_{s_j,\beta} \cdot \nabla_i p_{s_i,\beta}) \Big) u_{\alpha,\beta}(r_{ij})$$

The inner sum term can be reduced as

$$(\nabla_i p_{s_j,\alpha} \cdot p_{s_i,\alpha}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\alpha}) := (1) \tag{21}$$

$$(\nabla_i p_{s_j,\alpha} \cdot p_{s_i,\beta}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\beta}) := (2) \tag{22}$$

$$(\nabla_i p_{s_j,\beta} \cdot p_{s_i,\alpha}) + (p_{s_j,\beta} \cdot \nabla_i p_{s_i,\alpha}) := (3) \tag{23}$$

$$(\nabla_i p_{s_j,\beta} \cdot p_{s_i,\beta}) + (p_{s_j,\beta} \cdot \nabla_i p_{s_i,\beta}) := (4) \tag{24}$$

CASE 1: Two states with same potential parameters Case 1 is applied to the system with two states with its state probability, but has same potential parameter (e.g. same LJ parameters). This case can be regarded as a system of uniform potential, but has some system mixing among particles. Thus, in this case, there is no state dependency on the potentials, i.e. $u_{\alpha,\alpha}(r_{ij}) = u_{\alpha,\beta}(r_{ij}) = u_{\beta,\beta}(r_{ij}) = u(r_{ij})$. Furthermore, we know that $p_{s_i,\alpha} + p_{s_i,\beta} = p_{s_j,\alpha} + p_{s_j,\beta} = 1$, $\nabla_i p_{s_i,\alpha} = -\nabla_i p_{s_i,\beta}$ and $\nabla_i p_{s_j,\alpha} = -\nabla_i p_{s_j,\beta}$, the summation can be reduced as

$$
\begin{aligned}
(1)+(2)+(3)+(4) = \Bigg(& \left(\nabla_i p_{s_j,\alpha} \cdot p_{s_i,\alpha}\right) + \left(p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\alpha}\right) + \left(\nabla_i p_{s_j,\alpha} \cdot (1 - p_{s_i,\alpha})\right) \\
& + \left(p_{s_j,\alpha} \cdot (-\nabla_i p_{s_i,\alpha})\right) + \left((-\nabla_i p_{s_j,\alpha}) \cdot p_{s_i,\alpha}\right) + \left((1 - p_{s_j,\alpha}) \cdot \nabla_i p_{s_i,\alpha}\right) \\
& + \left((-\nabla_i p_{s_j,\alpha}) \cdot (1 - p_{s_i,\alpha})\right) + \left((1 - p_{s_j,\alpha}) \cdot (-\nabla_i p_{s_i,\alpha})\right) \Bigg) u(r_{ij}) \\
= \Big(& \nabla_i p_{s_j,\alpha} - \nabla_i p_{s_j,\alpha} \cdot p_{s_i,\alpha} + \nabla_i p_{s_i,\alpha} - \nabla_i p_{s_i,\alpha} \cdot p_{s_j,\alpha} \\
& - \nabla_i p_{s_j,\alpha} + \nabla_i p_{s_j,\alpha} \cdot p_{s_i,\alpha} - \nabla_i p_{s_i,\alpha} + \nabla_i p_{s_i,\alpha} \cdot p_{s_j,\alpha} \Big) u(r_{ij}) \\
= 0 &
\end{aligned}
$$

Similarly, $\sum_{j=i,k\neq j} \mathbb{C}_{ijk} = \sum_{j\neq i} \mathbb{C}_{ijk} = 0$. Therefore, there is no effective mixing effect for the uniform potential case.

CASE 2: Two states with different potential parameters In this case, the two body term can be survived due to $u_{\alpha,\alpha}(r_{ij}) \neq u_{\alpha,\beta}(r_{ij}) \neq u_{\beta,\beta}(r_{ij})$ and by mixing law, only $u_{\alpha,\beta}(r_{ij}) = u_{\beta,\alpha}(r_{ij})$. However, this inter-state term is not vanished, see below.

$$
\begin{aligned}
\Big((2)+(3)\Big) &= \Big(\left(\nabla_i p_{s_j,\alpha} \cdot (1 - p_{s_i,\alpha})\right) + \left(p_{s_j,\alpha} \cdot (-\nabla_i p_{s_i,\alpha})\right) + \left((-\nabla_i p_{s_j,\alpha}) \cdot p_{s_i,\alpha}\right) + \left((1 - p_{s_j,\alpha}) \cdot \nabla_i p_{s_i,\alpha}\right) \Big) \\
&= \Big(\nabla_i p_{s_j,\alpha} - p_{s_i,\alpha} \cdot \nabla_i p_{s_j,\alpha} - p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\alpha} + \nabla_i p_{s_i,\alpha} \\
&\quad - p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\alpha} - \nabla_i p_{s_j,\alpha} + p_{s_i,\alpha} \cdot \nabla_i p_{s_j,\alpha} \Big) \cdot u_{\alpha,\beta}(r_{ij}) \\
&= \Big(\nabla_i p_{s_i,\alpha} - 2 p_{s_j,\alpha} \cdot \nabla_i p_{s_i,\alpha} \Big) \cdot u_{\alpha,\beta}(r_{ij}) \\
&= \Big(\nabla_i p_{s_i,\alpha} (1 - 2 p_{s_j,\alpha}) \Big) \cdot u_{\alpha,\beta}(r_{ij}) \\
&= \nabla_i p_{s_i,\alpha} \times (1 - 2 p_{s_j,\alpha}) \times u_{\alpha,\beta}(r_{ij})
\end{aligned} \tag{25}
$$

Furthermore, plugging the probability and its derivative definition, it gives

$$\textbf{(LHS)} = -\frac{\mathrm{sech}^2(\frac{w_i - c}{0.1c})}{0.004c \cdot r_{cut}} \times \left(\sum_j \mathrm{sech}^2(\frac{r_{ij} - r_{cut}}{0.001 r_{cut}})\right) \times \left[\frac{\Delta x}{r_{ij}}, \frac{\Delta y}{r_{ij}}, \frac{\Delta x}{r_{ij}}\right] \times \left(-\tanh(\frac{w_j - c}{0.1c})\right) \times u_{\alpha,\beta}(r_{ij}) \tag{26}$$

$$= \frac{\tanh(\frac{w_j - c}{0.1c}) \cdot \mathrm{sech}^2(\frac{w_i - c}{0.1c})}{0.004c \cdot r_{cut}} \times \left(\sum_j \mathrm{sech}^2(\frac{r_{ij} - r_{cut}}{0.001 r_{cut}})\right) \times \frac{u_{\alpha,\beta}(r_{ij})}{r_{ij}} \left[\Delta x, \Delta y, \Delta z\right] \tag{27}$$

which doesn't reduced into simple expressions.

2.4.2 Three particles interaction term

For the three-particle interaction term, The first summation term,

$$\sum_{\substack{j \in N(i; r_{cut}) \\ k \notin N(i; r_{cut})}} \mathbb{C}_{ijk} = \sum_{\substack{j \in N(i; r_{cut}) \\ k \notin N(i; r_{cut})}} \sum_{\alpha\beta} \left((\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_k,\beta}) \right) \cdot u_{\alpha\beta}(r_{ij}) \tag{28}$$

Since $k \notin N(i; r_{cut})$, $\nabla_i P_{s_k,\alpha/\beta} = 0$, thus

$$\begin{aligned}
\textbf{(LHS)} &= \sum_{\substack{j \in N(i; r_{cut}) \\ k \notin N(i; r_{cut})}} \sum_{\alpha\beta} (\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) \cdot u_{\alpha\beta}(r_{ij}) \\
&= \sum_{\substack{j \in N(i; r_{cut}) \\ k \notin N(i; r_{cut})}} \Big((\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\alpha}) u_{\alpha\alpha} + (\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) u_{\alpha\beta} + (\nabla_i p_{s_j,\beta} \cdot p_{s_k,\alpha}) u_{\beta\alpha} + (\nabla_i p_{s_j,\beta} \cdot p_{s_k,\beta}) u_{\beta\beta} \Big) \\
&= \sum_{\substack{j \in N(i; r_{cut}) \\ k \notin N(i; r_{cut})}} \Big((\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\alpha}) u_{\alpha\alpha} + (\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) u_{\alpha\beta} \\
&\qquad + (-\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\alpha}) u_{\beta\alpha} + (-\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) u_{\beta\beta} \Big) \\
&= \sum_{\substack{j \in N(i; r_{cut}) \\ k \notin N(i; r_{cut})}} \Big((\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\alpha}) \times \big(u_{\alpha\alpha} - u_{\alpha\beta}\big) + (\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) \times \big(u_{\alpha\beta} - u_{\beta\beta}\big) \Big)
\end{aligned}$$

Note: The equation above is the most reduced form. One can write it down much in detail by using $p_{s_k,\alpha} + p_{s_k,\beta} = 1$, but that expression can only give following terms:

$$\textbf{(LHS)} = \sum_{\substack{j \in N(i; r_{cut}) \\ k \notin N(i; r_{cut})}} \left(\nabla_i p_{s_j,\alpha} \Big(p_{s_k,\alpha} (u_{\alpha\alpha} - 2u_{\alpha\beta} + u_{\beta\beta}) + u_{\alpha\beta} - u_{\beta\beta} \Big) \right)$$

Likewise, the second summation term is followed as equation below due to $\nabla_i P_{s_j,\alpha/\beta} = 0 \; (\because j \notin N(i; r_{cut}))$

$$\sum_{\substack{j\notin N(i;r_{cut})\\ k\in N(i;r_{cut})}} \mathbb{C}_{ijk} = \sum_{\substack{j\notin N(i;r_{cut})\\ k\in N(i;r_{cut})}} \sum_{\alpha\beta} (p_{s_j,\alpha} \cdot \nabla_i p_{s_k,\beta}) \cdot u_{\alpha\beta}(r_{ij}) \tag{29}$$

$$= \sum_{\substack{j\notin N(i;r_{cut})\\ k\in N(i;r_{cut})}} \Big((p_{s_j,\alpha} \cdot \nabla_i p_{s_k,\alpha}) \times \big(u_{\alpha\alpha} - u_{\alpha\beta}\big) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_k,\beta}) \times \big(u_{\alpha\beta} - u_{\beta\beta}\big) \Big)$$

The last summation term has both two terms:

$$\sum_{\substack{j\in N(i;r_{cut})\\ k\in N(i;r_{cut})}} \mathbb{C}_{ijk} = \sum_{\substack{j\in N(i;r_{cut})\\ k\in N(i;r_{cut})}} \Big((\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_k,\beta}) \Big) \tag{30}$$

3 Implementation

3.1 Final force expression

From above discussion, the force acting on the particle i, $\mathbf{f}_i$ can be expressed as below equation. For the sake of the clarity, use $N(i) := N(i; r_{cut})$. Also, it is obvious that if $j \in N(i)$ then, $j \neq i$. In the equation below, I didn't fully write down the $\sum_\alpha \sum_{\alpha\beta}$ terms, but one can relate each subforce term from previous sections.

$$\begin{aligned}
\mathbf{f}_i = &- \Big(\sum_{\alpha} (\nabla_i p_{s_i,\alpha}) \cdot (\mu_\alpha - kT \ln p_{s_i,\alpha}) + \sum_{j\in N(i)} \sum_{\alpha} \nabla_i p_{s_j,\alpha} \cdot (\mu_\alpha - kT \ln p_{s_j,\alpha}) \Big) \\
&- \Big(\sum_{j\in N(i)} \sum_{\alpha\beta} p_{s_i,\alpha} p_{s_j,\beta} \cdot \nabla_i u_{\alpha\beta} \Big) \\
&- \Big(\Big\{ \sum_{j\in N(i)} \sum_{\alpha\beta} (\nabla_i p_{s_i,\alpha} p_{s_j,\beta} + p_{s_i,\alpha} \nabla_i p_{s_j,\beta}) \cdot u_{\alpha\beta} \Big\} \\
&\quad + \Big\{ \Big(\sum_{\substack{j\notin N(i)\\ k\in N(i)}} \sum_{\alpha\beta} (p_{s_j,\alpha} \nabla_i p_{s_k,\beta}) + \sum_{\substack{j\in N(i)\\ k\notin N(i)}} \sum_{\alpha\beta} (\nabla_i p_{s_j,\alpha} p_{s_k,\beta}) + \sum_{\substack{j\in N(i)\\ k\in N(i)}} \sum_{\alpha\beta} (p_{s_j,\alpha} \nabla_i p_{s_k,\beta} \\
&\qquad + \nabla_i p_{s_j,\alpha} p_{s_k,\beta}) \cdot u_{\alpha\beta} \Big) \Big\} \Big)
\end{aligned}$$

From above equation, $\Big(\Big)$ denote the first, second and third subforce terms and parenthesis $\Big\{\Big\}$ shows that the two-particle term and three-particle term in the third subforce term. (See the summation index.)

3.2 three particle interaction

To consider three particles i, j, k, following figure shows the implementation to LAMMPS.

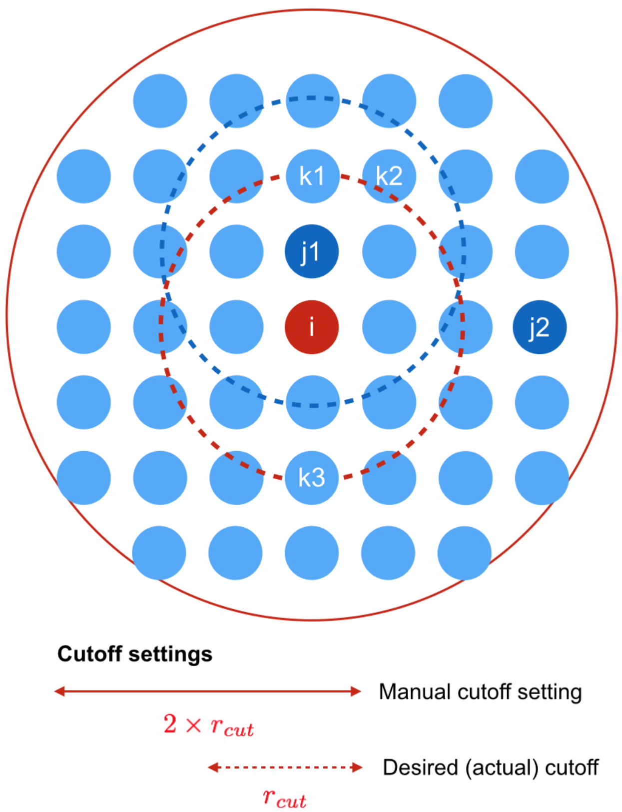

Figure 5: Three particles pairs i, j, k from an enhanced cutoff $2 \times r_{cut}$

- $\mathbf{r_{ij}}$: To calculate the distance to determine $j \in N(i; r_{cut})$
- $\mathbf{r_{jk}}$: To calculate the distance to determine $k \in N(j; r_{cut})$
- $\mathbf{r_{ik}}$: To calculate the distance to determine $k \in N(i; r_{cut})$ or $k \notin N(i; r_{cut})$

3.3 Case study

3.3.1 Case 1: i–j1–k1

From Figure 5, $r_{ij1} < r_{cut}$, $r_{j1k1} < r_{cut}$, and $r_{ik1} < r_{cut}$. Thus the neighboring interaction is $j1 \in N(i; r_{cut})$, and $k1 \in N(j1; r_{cut})$ and $k1 \in N(i; r_{cut})$, which is **valid** ijk pair.

3.3.2 Case 2: i–j1–k2

From Figure 5, $r_{ij1} < r_{cut}$, $r_{j1k2} < r_{cut}$, and $r_{ik2} > r_{cut}$. Thus the neighboring interaction is $j1 \in N(i; r_{cut})$, and $k2 \in N(j1; r_{cut})$ and $k2 \notin N(i; r_{cut})$, which is **valid** ijk pair.

3.3.3 Case 3: i–j1–k3

From Figure 5, $r_{ij1} < r_{cut}$, $r_{j1k3} > r_{cut}$, and $r_{ik1} < r_{cut}$. Thus the neighboring interaction is $j1 \in N(i; r_{cut})$, and $k3 \notin N(j1; r_{cut})$ and $k3 \notin N(i; r_{cut})$, which is **invalid** ijk pair.

3.3.4 Case 4: i–j2–k1

From Figure 5, $r_{ij2} > r_{cut}$, $r_{j2k1} > r_{cut}$, and $r_{ik1} < r_{cut}$. Thus the neighboring interaction is $j2 \notin N(i; r_{cut})$, and $k1 \in N(j2; r_{cut})$ and $k1 \in N(i; r_{cut})$, which is **invalid** ijk pair.

3.4 LAMMPS routine

Therefore, from above sections, one can decompose the $\mathbf{f}_i$ component as below.

$$
\begin{aligned}
\mathbf{f}_i = &-\overset{\textbf{(1)}}{\boxed{\left(\sum_{\alpha}(\nabla_i p_{s_i,\alpha})\cdot(-kT\ln p_{s_i,\alpha}) + \sum_{j}\sum_{\alpha}\nabla_i p_{s_j,\alpha}\cdot(-kT\ln p_{s_j,\alpha})\right)}} - \overset{\textbf{(2)}}{\boxed{\left(\sum_{j}\sum_{\alpha\beta} p_{s_i,\alpha}p_{s_j,\beta}\cdot\nabla_i u_{\alpha\beta}\right)}} \\
&-\boxed{\left(\sum_{j}\sum_{\alpha\beta}\left(\nabla_i p_{s_i,\alpha}p_{s_j,\beta}\right) + \left(p_{s_i,\alpha}\nabla_i p_{s_j,\beta}\right)u_{\alpha\beta}\right)}\ \textbf{(3)} \\
&-\underset{\textbf{(4)}}{\boxed{\left(\sum_{jk}\sum_{\alpha\beta}\left(p_{s_j,\alpha}\nabla_i p_{s_k,\beta}\right)^{\textbf{(4)-1}} + \sum_{jk}\sum_{\alpha\beta}\left(\nabla_i p_{s_j,\alpha}p_{s_k,\beta}\right)^{\textbf{(4)-2}} + \sum_{jk}\sum_{\alpha\beta}\left(p_{s_j,\alpha}\nabla_i p_{s_k,\beta} + \nabla_i p_{s_j,\alpha}p_{s_k,\beta}\right)^{\textbf{(4)-3}}\right)}}
\end{aligned}
$$

Figure 6: Force decomposition into four parts

To implement this, from, section 3.2, the subroutine *Compute* in pair style can be composed of these two for loops.

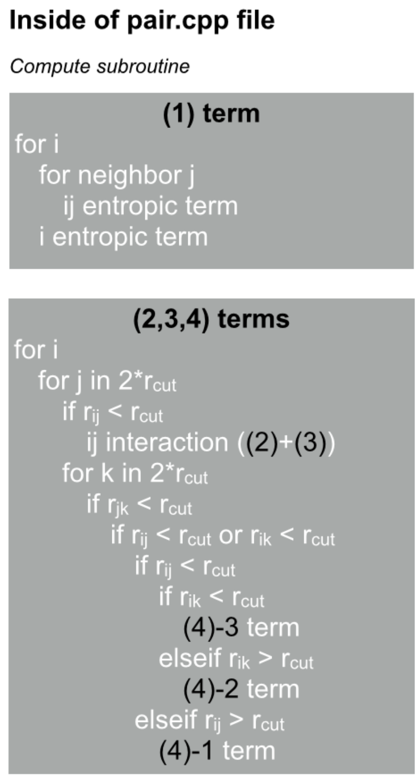

Figure 7: Force calculating subroutine