

# Density dependent UCG code: theory and implementation

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November 12, 2015

*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.

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

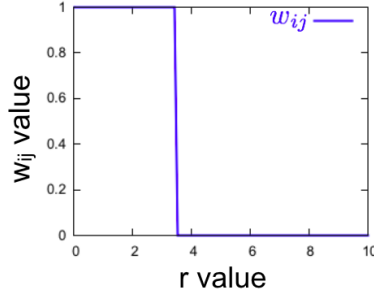
By using a [short-hand notation](#)

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

### 1.1.2 Choice of $r_{\text{cut}}$

We can set  $r_{\text{cut}}$  value arbitrarily less than  $r_{\text{ljcut}}$  to ensure that for  $r_{ij} \leq r_{\text{ljcut}}$   $w_{ij} \simeq 1$  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,  $r_{\text{cut}}$  is chosen as  $3.5 \text{ \AA}$ .

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



**Figure 1:** A behavior of  $w_i$  function by differing  $r$  value:  $r_{\text{cut}} = 3.5 \text{ \AA}$

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

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

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

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:

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

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

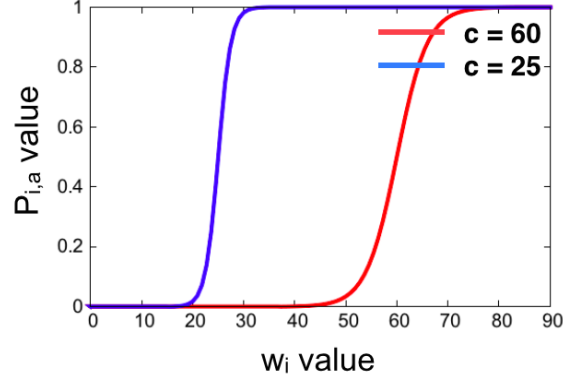
However, it is worth mentioning that the shape of these probabilities also determined by the  $c$  value.

### 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,

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

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

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

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

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

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

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

which is

$$t(r_{ij}) = \tanh\left(\frac{r_{ij} - r_{\text{cut}}}{0.001 r_{\text{cut}}}\right)$$

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,

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

Similarly,

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

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

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

## 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.

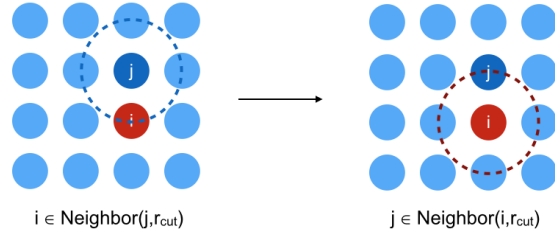
**Lemma:** if the particle  $j$  is in a neighbor of the particle  $i$ , then also particle  $i$  is in a neighbor of the particle  $j$ .

*Proof:*

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

□

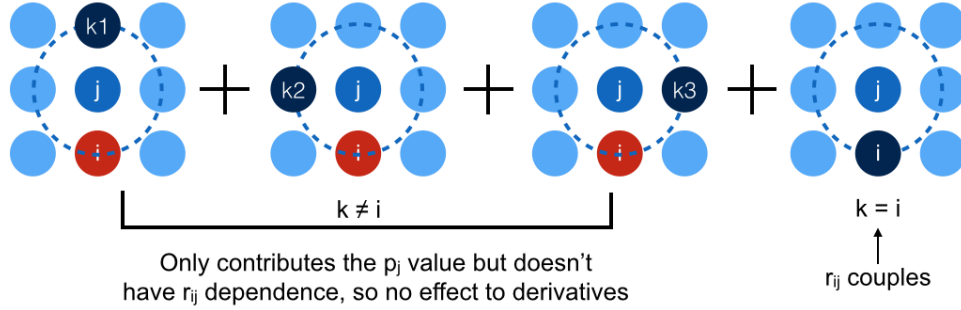
This Lemma is easily explained by the following diagram.



**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  $w^{\text{mix}}(\mathbf{r}^n)$ .

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

Thus, the force expression is

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

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

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

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

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

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

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

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

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

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

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

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  $\nabla_i$ . 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  $P_{j, \alpha/\beta}$ .

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

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

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

□

Thus, the first term can be expressed as

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

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

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



### 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

$$\begin{aligned} \mathbf{f}_i^{(2)} &= - \sum_j \sum_{\alpha\beta} p_{s_i,\alpha} p_{s_j,\beta} \nabla_i u_{\alpha\beta}(r_{ij}) \\ &= - \sum_j \left( p_{s_i,\alpha} p_{s_j,\alpha} \nabla_i u_{\alpha\alpha}(r_{ij}) + (p_{s_i,\alpha} p_{s_j,\beta} + p_{s_i,\beta} p_{s_j,\alpha}) \cdot \nabla_i u_{\alpha\beta}(r_{ij}) + p_{s_i,\beta} p_{s_j,\beta} \nabla_i u_{\beta\beta}(r_{ij}) \right) \end{aligned} \quad (15)$$

### 2.4 Third subforce term

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

$$\mathbf{f}_i^{(3)} = - \sum_{jk} \sum_{\alpha\beta} (\nabla_i (p_{s_j,\alpha} p_{s_k,\beta})) u_{\alpha\beta}(r_{jk}) \quad (16)$$

$$\begin{aligned} &= - \sum_{jk} \sum_{\alpha\beta} \left( (\nabla_i p_{s_j,\alpha} \cdot p_{s_k,\beta}) + (p_{s_j,\alpha} \cdot \nabla_i p_{s_k,\beta}) \right) u_{\alpha\beta}(r_{jk}) \\ &= - \sum_{jk} \sum_{\alpha\beta} (\mathbf{C}_{ijk}) \end{aligned} \quad (17)$$

Note that the above equation has  $\mathbf{C}_{ijk}$  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,

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

From the summation index above,  $t \in \mathcal{N}(j; r_{l_{\text{cut}}})$  means the particle  $t$  is the neighbor of particle  $j$  within cutoff radius  $r_{l_{\text{cut}}}$ . However, in this state probability case, the previous assumption that we used for the position dependent case  $\nabla_{i \neq j} \mathbf{p}_{s_j} = \mathbf{0}$  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.

$$\begin{aligned} \sum_{jk} \mathbf{C}_{ijk} &= \sum_{j \neq k, k=i} \mathbf{C}_{ijk} + \sum_{j=i, k \neq j} \mathbf{C}_{ijk} + \sum_{\substack{j \neq i \\ k \neq i}} \mathbf{C}_{ijk} \\ &= \left( \sum_{j \neq k, k=i} \mathbf{C}_{ijk} + \sum_{j=i, k \neq j} \mathbf{C}_{ijk} \right) + \left( \sum_{\substack{j \in \mathcal{N}(i; r_{\text{cut}}) \\ k \notin \mathcal{N}(i; r_{\text{cut}})}} \mathbf{C}_{ijk} + \sum_{\substack{j \notin \mathcal{N}(i; r_{\text{cut}}) \\ k \in \mathcal{N}(i; r_{\text{cut}})}} \mathbf{C}_{ijk} + \sum_{\substack{j \in \mathcal{N}(i; r_{\text{cut}}) \\ k \in \mathcal{N}(i; r_{\text{cut}})}} \mathbf{C}_{ijk} \right) \\ &\quad \text{two particles interaction} \quad \text{three particles interaction} \end{aligned} \quad (19)$$

#### 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.

$$\begin{aligned} \sum_{j \neq k, k=i} \mathbf{C}_{ijk} &= \sum_{j \neq i} \mathbf{C}_{ijk} \\ &= \sum_{j \neq i} \sum_{\alpha\beta} \left( (\nabla_i \mathbf{p}_{s_j, \alpha} \cdot \mathbf{p}_{s_i, \beta}) + (\mathbf{p}_{s_j, \alpha} \cdot \nabla_i \mathbf{p}_{s_i, \beta}) \right) \mathbf{u}_{\alpha, \beta}(\mathbf{r}_{ij}) \\ &= \sum_{j \neq i} \left( (\nabla_i \mathbf{p}_{s_j, \alpha} \cdot \mathbf{p}_{s_i, \alpha}) + (\mathbf{p}_{s_j, \alpha} \cdot \nabla_i \mathbf{p}_{s_i, \alpha}) + (\nabla_i \mathbf{p}_{s_j, \alpha} \cdot \mathbf{p}_{s_i, \beta}) + (\mathbf{p}_{s_j, \alpha} \cdot \nabla_i \mathbf{p}_{s_i, \beta}) \right. \\ &\quad \left. + (\nabla_i \mathbf{p}_{s_j, \beta} \cdot \mathbf{p}_{s_i, \alpha}) + (\mathbf{p}_{s_j, \beta} \cdot \nabla_i \mathbf{p}_{s_i, \alpha}) + (\nabla_i \mathbf{p}_{s_j, \beta} \cdot \mathbf{p}_{s_i, \beta}) + (\mathbf{p}_{s_j, \beta} \cdot \nabla_i \mathbf{p}_{s_i, \beta}) \right) \mathbf{u}_{\alpha, \beta}(\mathbf{r}_{ij}) \end{aligned} \quad (20)$$

The inner sum term can be reduced as

$$(\nabla_i \mathbf{p}_{s_j, \alpha} \cdot \mathbf{p}_{s_i, \alpha}) + (\mathbf{p}_{s_j, \alpha} \cdot \nabla_i \mathbf{p}_{s_i, \alpha}) := \mathbf{(1)} \quad (21)$$

$$(\nabla_i \mathbf{p}_{s_j, \alpha} \cdot \mathbf{p}_{s_i, \beta}) + (\mathbf{p}_{s_j, \alpha} \cdot \nabla_i \mathbf{p}_{s_i, \beta}) := \mathbf{(2)} \quad (22)$$

$$(\nabla_i \mathbf{p}_{s_j, \beta} \cdot \mathbf{p}_{s_i, \alpha}) + (\mathbf{p}_{s_j, \beta} \cdot \nabla_i \mathbf{p}_{s_i, \alpha}) := \mathbf{(3)} \quad (23)$$

$$(\nabla_i \mathbf{p}_{s_j, \beta} \cdot \mathbf{p}_{s_i, \beta}) + (\mathbf{p}_{s_j, \beta} \cdot \nabla_i \mathbf{p}_{s_i, \beta}) := \mathbf{(4)} \quad (24)$$

*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

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

Similarly,  $\sum_{j=i,k \neq j} C_{ijk} = \sum_{j \neq i} C_{ijk} = 0$ . 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.

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

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

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

$$\tag{27}$$

which doesn't reduced into simple expressions.

### 2.4.2 Three particles interaction term

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

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

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

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

*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:

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

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

$$\begin{aligned} \sum_{\substack{j \notin N(i; r_{\text{cut}}) \\ k \in N(i; r_{\text{cut}})}} C_{ijk} &= \sum_{\substack{j \notin N(i; r_{\text{cut}}) \\ k \in N(i; r_{\text{cut}})}} \sum_{\alpha\beta} (p_{s_j, \alpha} \cdot \nabla_i p_{s_k, \beta}) \cdot u_{\alpha\beta}(r_{ij}) \\ &= \sum_{\substack{j \notin N(i; r_{\text{cut}}) \\ k \in N(i; r_{\text{cut}})}} \left( (p_{s_j, \alpha} \cdot \nabla_i p_{s_k, \alpha}) \times (u_{\alpha\alpha} - u_{\alpha\beta}) + (p_{s_j, \alpha} \cdot \nabla_i p_{s_k, \beta}) \times (u_{\alpha\beta} - u_{\beta\beta}) \right) \end{aligned} \quad (29)$$

The last summation term has both two terms:

$$\sum_{\substack{j \in N(i; r_{\text{cut}}) \\ k \in N(i; r_{\text{cut}})}} C_{ijk} = \sum_{\substack{j \in N(i; r_{\text{cut}}) \\ k \in N(i; r_{\text{cut}})}} \left( (\nabla_i p_{s_j, \alpha} \cdot p_{s_k, \beta}) + (p_{s_j, \alpha} \cdot \nabla_i p_{s_k, \beta}) \right) \quad (30)$$

### 3 Implementation

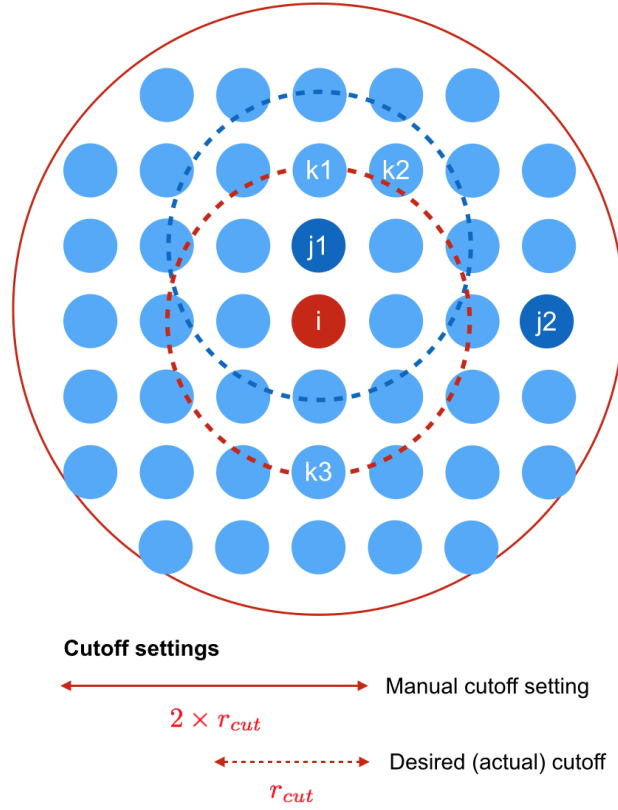
#### 3.1 Final force expression

From above discussion, the force acting on the particle  $i$ ,  $\mathbf{f}_i$  can be expressed as below equation.

$$\begin{aligned} \mathbf{f}_i &= - \left( \sum_{\alpha} (\nabla_i p_{s_i, \alpha}) \cdot (-kT \ln p_{s_i, \alpha}) + \sum_j \sum_{\alpha} \nabla_i p_{s_j, \alpha} \cdot (-kT \ln p_{s_j, \alpha}) - \sum_j \sum_{\alpha\beta} p_{s_i, \alpha} p_{s_j, \beta} \cdot \nabla_i u_{\alpha\beta} \right) \\ &\quad - \left( \sum_j \sum_{\alpha\beta} (\nabla_i p_{s_i, \alpha} p_{s_j, \beta}) + (p_{s_i, \alpha} \nabla_i p_{s_j, \beta}) u_{\alpha\beta} \right) \\ &\quad - \left( \sum_{jk} \sum_{\alpha\beta} (p_{s_j, \alpha} \nabla_i p_{s_k, \beta}) + \sum_{jk} \sum_{\alpha\beta} (\nabla_i p_{s_j, \alpha} p_{s_k, \beta}) + \sum_{jk} \sum_{\alpha\beta} (p_{s_j, \alpha} \nabla_i p_{s_k, \beta} + \nabla_i p_{s_j, \alpha} p_{s_k, \beta}) \right) \end{aligned}$$

#### 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  $2 \times r_{cut}$

- $r_{ij}$ : To calculate the distance to determine  $j \in N(i; r_{cut})$
- $r_{jk}$ : To calculate the distance to determine  $k \in N(j; r_{cut})$
- $r_{ik}$ : 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: $i$ - $j_1$ - $k_1$

From Figure 5,  $r_{ij_1} < r_{cut}$ ,  $r_{j_1k_1} < r_{cut}$ , and  $r_{ik_1} < r_{cut}$ . Thus the neighboring interaction is  $j_1 \in N(i; r_{cut})$ , and  $k_1 \in N(j_1; r_{cut})$  and  $k_1 \in N(i; r_{cut})$ , which is **valid**  $ijk$  pair.

#### 3.3.2 Case 2: $i$ - $j_1$ - $k_2$

From Figure 5,  $r_{ij_1} < r_{cut}$ ,  $r_{j_1k_2} < r_{cut}$ , and  $r_{ik_2} > r_{cut}$ . Thus the neighboring interaction is  $j_1 \in N(i; r_{cut})$ , and  $k_2 \in N(j_1; r_{cut})$  and  $k_2 \notin N(i; r_{cut})$ , which is **valid**  $ijk$  pair.

### 3.3.3 Case 3: i-j1-k3

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

### 3.3.4 Case 4: i-j2-k1

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

## 3.4 LAMMPS routine

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

$$\begin{aligned}
 \mathbf{f}_i = & - \left[ \sum_{\alpha} (\nabla_i p_{s_i, \alpha}) \cdot (-kT \ln p_{s_i, \alpha}) + \sum_j \sum_{\alpha} \nabla_i p_{s_j, \alpha} \cdot (-kT \ln p_{s_j, \alpha}) \right] - \left[ \sum_j \sum_{\alpha\beta} p_{s_i, \alpha} p_{s_j, \beta} \cdot \nabla_i u_{\alpha\beta} \right] \\
 & - \left[ \sum_j \sum_{\alpha\beta} (\nabla_i p_{s_i, \alpha} p_{s_j, \beta}) + (p_{s_i, \alpha} \nabla_i p_{s_j, \beta}) u_{\alpha\beta} \right] \quad \text{(3)} \\
 & - \left[ \sum_{jk} \sum_{\alpha\beta} (p_{s_j, \alpha} \nabla_i p_{s_k, \beta}) + \sum_{jk} \sum_{\alpha\beta} (\nabla_i p_{s_j, \alpha} p_{s_k, \beta}) + \sum_{jk} \sum_{\alpha\beta} (p_{s_j, \alpha} \nabla_i p_{s_k, \beta} + \nabla_i p_{s_j, \alpha} p_{s_k, \beta}) \right] \quad \text{(4)}
 \end{aligned}$$

**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.

### Inside of pair.cpp file

*Compute subroutine*

```

(1) term
for i
  for neighbor j
    ij entropic term
  i entropic term

```

```

(2,3,4) terms
for i
  for j in 2*rcut
    if rij < rcut
      ij interaction ((2)+(3))
    for k in 2*rcut
      if rjk < rcut
        if rij < rcut OR rik < rcut
          if rij < rcut
            if rik < rcut
              (4)-3 term
            elseif rik > rcut
              (4)-2 term
          elseif rij > rcut
            (4)-1 term

```

**Figure 7:** Force calculating subroutine