

Density dependent UCG code: theory and implementation

Jaehyeok Jin

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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.

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

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_{cut}

We can set r_{cut} value arbitrarily less than r_{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_{cut} is chosen as 3.5 Å.

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

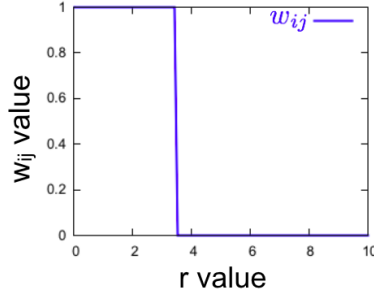


Figure 1: A behavior of w_i function by differing r value: $r_{\text{cut}} = 3.5\text{Å}$

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.

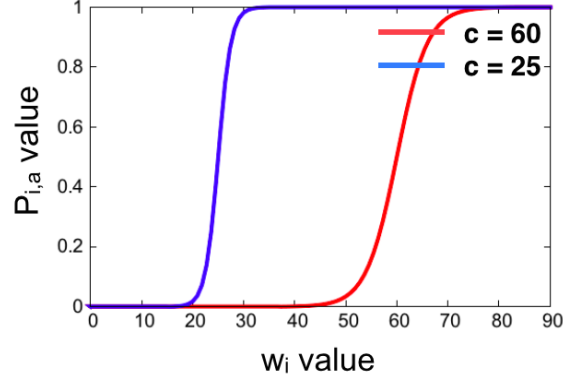


Figure 2: A dependence of state probability function $P_{i,a}$ on the coefficient c value

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.

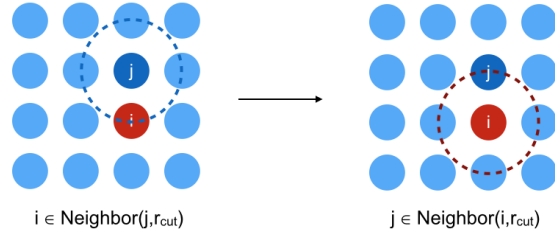


Figure 3: A relation about neighboring particles

1.3 Summation scheme

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

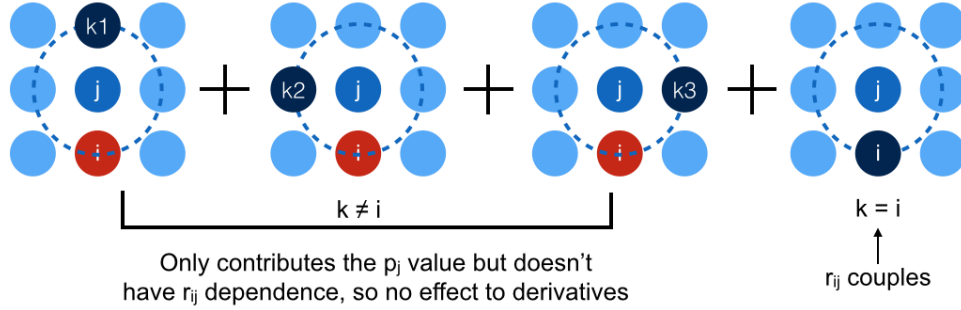


Figure 4: Summation among three particles i, j, k

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 ∇_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. For the sake of the clarity, use $N(i) := N(i; r_{\text{cut}})$. 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.

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

From above equation, $\left(\right)$ denote the first, second and third subforce terms and parenthesis $\{ \}$ 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.

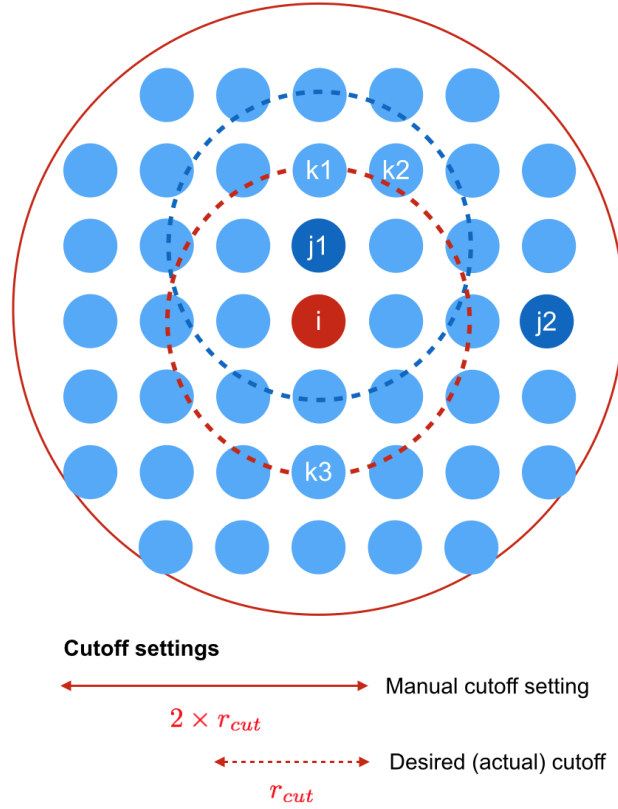


Figure 5: Three particles pairs i, j, k from an enhanced cutoff $2 \times r_{cut}$

- 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-j1-k1

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

3.3.2 Case 2: i-j1-k2

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

$$\begin{aligned}
 \mathbf{f}_i = & \text{(1)} \left[\left(\sum_{\alpha} (\nabla_i p_{s_i, \alpha}) \cdot (\mu_{\alpha} - kT \ln p_{s_i, \alpha}) + \sum_{j \in N(i)} \sum_{\alpha} \nabla_i p_{s_j, \alpha} \cdot (\mu_{\alpha} - kT \ln p_{s_j, \alpha}) \right) \right. \\
 & \text{(2)} \left. - \left(\sum_{j \in N(i)} \sum_{\alpha \beta} p_{s_i, \alpha} p_{s_j, \beta} \cdot \nabla_i u_{\alpha \beta} \right) \right] \\
 & \text{(3)} \left[- \left\{ \sum_{j \in N(i)} \sum_{\alpha \beta} (\nabla_i p_{s_i, \alpha} p_{s_j, \beta} + p_{s_i, \alpha} \nabla_i p_{s_j, \beta}) \cdot u_{\alpha \beta} \right\} \right] \\
 & \text{(4)} \left[+ \left\{ \left(\sum_{\substack{j \notin N(i) \\ k \in N(i)}} \sum_{\alpha \beta} (p_{s_j, \alpha} \nabla_i p_{s_k, \beta}) \right) + \sum_{\substack{j \in N(i) \\ k \notin N(i)}} \sum_{\alpha \beta} (\nabla_i p_{s_j, \alpha} p_{s_k, \beta}) + \sum_{\substack{j \in N(i) \\ k \in N(i)}} \sum_{\alpha \beta} (p_{s_j, \alpha} \nabla_i p_{s_k, \beta} \right. \right. \\
 & \quad \left. \left. + \nabla_i p_{s_j, \alpha} p_{s_k, \beta}) \cdot u_{\alpha \beta} \right\} \right]
 \end{aligned}$$

(4)-1 (4)-2 (4)-3

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