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從力學觀點探討一維有交互作用之氣體：一個從力學觀點探討弱相互作用之多體系統的示範

A Mechanical Approach to One-dimensional Interacting Gas: A Demonstration of Investigating Weakly Interacting N-body Systems from A Mechanical Viewpoint

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A mechanical approach to one-dimensional interacting gas: a demonstration of investigating weakly interacting N-body systems from a mechanical viewpoint

本論文係王重陽君（r03222014）在國立臺灣大學物理學系、所完成之碩士學位論文，於民國 106 年 03 月 13 日承下列考試委員審查通過及口試及格，特此證明

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在研究的過程中，老師的風格是對底下的學生非常放任，讓我們有很大的自由度(like degrees of freedom in a N-body system)嘗試自己的想法。從事後的先見之明來看，有些嘗試雖然錯得離譜，但卻讓我從這樣一團糟的東西裡面想到一些日後很有用的想法。在老師的團隊裡面，這樣自由放任的模式，讓我這三年來過得很愉快。

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摘要

著名的凡得瓦方程式(van der Waals equation)是用來描述一箱有弱相互作用、而且在特定條件下(高溫極限以及低密度極限)的氣體的狀態方程式。傳統上對凡得瓦方程式的推導是採取統計力學中的標準做法，其中會牽涉到系綜的平均(ensemble average)。在我們的研究中，我們從純粹力學的觀點切入，來探討在一維空間中，一箱有弱相互作用之氣體的行為。因此，在我們的架構中，三個核心的概念為：粒子的軌跡、粒子交互作用的次數、每一次交互作用產生的效果。這樣的力學架構的優點是，除了推導出凡得瓦方程式，我們還可以得到一些在標準的統計力學中無法告訴我們的有趣的物理。例如，目前對於凡得瓦方程式的詮釋與圖像是採取了平均場(mean field approximation)的想法，在力學的觀點中，我們發現這樣的標準圖樣其實是錯誤的。傳統上，對於一個古典的多體系統，物理學家通常是採用統計力學或是分子動力論(kinetic theory)的框架。在這份研究中，我們除了探討一維的有交互作用之氣體，也展示了如何從力學的觀點來探討有弱相互作用的多體系統，並對於粒子之間的交互作用所產生的第一階的物理效應有更深刻的理解。

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Abstract

The famous van der Waals equation is the equation of state for a box of weakly interacting gas particles under certain limits (high temperature and low density). Traditional derivations of the van der Waals equation typically use standard recipes involving ensemble averages of statistical mechanics. In this work, we study a box of weakly interacting gas particles in one-dimension from a purely mechanical point of view. Thus, trajectories, number of particle-particle interactions, and effect of each particle-particle interaction are at the heart of the present approach. This has the merit that it not only reproduces the van der Waals equation but also tells us some extra interesting physics not immediately clear from a pure statistical mechanical approach. For example, we find that the traditional handwaving interpretation of the van der Waals equation adopting mean field approximation is actually incorrect. In this investigation of one-dimensional interacting gas, we demonstrate the possibility taking a mechanical point of view and having deeper understanding for the physics of leading order effect of particle-particle interaction, for weakly interacting N-body systems that are usually studied in the framework of statistical mechanics or kinetic theory.

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1 Introduction

Statistical mechanics and kinetic theory are two main frameworks one adopts when studying a system containing a huge number of degrees of freedom. Researches in this field study hard sphere systems [2, 12, 14, 15, 16, 17, 19, 20], hard ellipse systems [4], hard needle systems [6, 7], van der Waals theory [8], granular particle systems [1, 5, 11], etc. There are also researches concerning fundamental issues [9, 10].

Statistical mechanics and kinetic theory are powerful and systematic, but it often amounts to meaning that one has to pay the price of losing certain detailed dynamical information about the interparticular interactions. In order to study a weakly interacting N-body system, besides statistical mechanics, kinetic theory and numerical simulation, do we have other choice? At first glance, the idea of particle trajectory is useful only for systems containing small degrees of freedom. However, we can actually bring in the idea of trajectory for a N-body system if the effect of particle-particle interaction is weak. In this work, we study a weakly interacting one-dimensional gas to see how a direct approach investigating the detailed mechanical interaction between particles might shed some light on its merits as opposed to the traditional approach.

Before describing our mechanical approach, we first give a brief review of how one understands a weakly interacting one-dimensional gas in statistical mechanics. For a one-dimensional classical gas in the box, the equation of state at thermal equilibrium can be calculated by standard recipes in statistical mechanics. Specifically, one can start with a given Hamiltonian of the gas system and computes its partition function, then following through the standard recipes [3, 13] to arrive at the following equation of state

$$F = \rho(k_B T) - \rho^2(k_B T)\int_0^\infty dr\left[e^{-\frac{U(r)}{k_B T}} - 1\right] + \mathcal{O}(\rho^3), \tag{1}$$

where F is the force exerted on each side of the confining box, $\rho \equiv \frac{N}{L}$ is the linear number density (N and L are the particle number and the size of the one-dimensional

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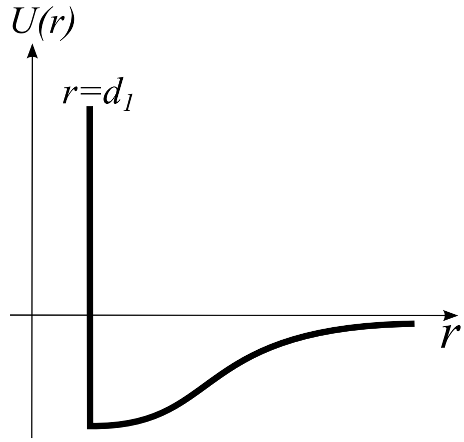

Figure 1: Particle-particle interaction consisting of a hard core (at $r = d_1$) and an interaction tail. $U(r)$ is the potential describing the interaction between two particles.

box, respectively), k_B is Boltzmann's constant, T is the temperature of the system, and $U(r)$ is the potential between two gas particles with r being their separation. In the above, one has assumed a low density limit so that a Taylor expansion in ρ is possible.

We will specialize to the case when the potential representing particle-particle interaction is consisted of a hard core and an interaction tail, as shown in Fig. 1.

By Eq.1, the equation of state for such a potential is given by

$$F = \rho(k_B T) + \rho^2(k_B T)d_1 - \rho^2(k_B T)\int_{d_1}^{\infty} dr \left[e^{-\frac{U(r)}{k_B T}} - 1\right] + \mathcal{O}(\rho^3). \tag{2}$$

Consider only the low density limit and keep up to the second order in the number density, and further assume the high temperature limit and weakly interacting limit. Approximate Eq.2 to first order of $\frac{U(r)}{k_B T}$ under these limits, and the equation of state becomes

$$F = \rho(k_B T) + \rho^2(k_B T)d_1 - \rho^2 \int_{d_1}^{\infty} dr\,[-U(r)] = \rho(k_B T)\left(1 + \rho d_1 - \rho\int_{d_1}^{\infty} dr \left[\frac{-U(r)}{k_B T}\right]\right) \tag{3}$$

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After rearrangement, the equation of state is given by

$$\left(F + (\frac{N}{L})^2 \int_{d_1}^{\infty} dr\,[-U(r)]\right)(L - d_1 N) = N k_B T, \tag{4}$$

which is the van der Waals equation in one-dimension.

This is the statistical mechanics approach to the van der Waals equation, the equation of state for interacting gas under the conditions of low density, high temperature and weak interaction. The derivation provided by statistical mechanics is simple, and in one scoop it easily relates the force with the temperature, the density and the potential describing particle-particle interaction. On the other hand, one also loses track of exactly what has happened to the *dynamical* behavior of the constituent particles. For example, if we "turn on" the interparticular interactions of an otherwise ideal gas, will that make the gas particle move faster or slower? And, does the answer depend on the original velocity of a particle? Statistical mechanics by itself doesn't provide such information. In this regard, the physics contained in an equation of state is quite limited.

In this work, we adopt an approach different from statistical mechanics. We take a mechanical point of view, considering the detailed mechanics of the gas particles. In order to deal with a system of an essentially infinite number of degrees of freedom, statistical mechanics hides the complexity in its fundamental principles and assumptions (such as the notion of partition function), so that we can focus on things like the equation of state that can be more readily measured. In our mechanical approach, in order to deal with the complex one-dimensional interacting gas system, we still need to put in by hand some basic assumptions. We are not pretending that we are going to derive the equation of state for a one-dimensional interacting gas from scratch and nothing else. However, we will do our best making assumptions that seem at least reasonable. Besides rebuilding the equation of state, we will have some physics that standard statistical mechanics doesn't tell us. For example, we will try to answer the

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two previous questions in our mechanical approach.

The thesis is organized as follows. In Chapter 2, we discuss the foundation of our mechanical point of view. In Chapter 3, we consider a special case of square well particle-particle interaction and show how the mechanical model is built. In Chapter 4, we generalize the previous results to generic interacting gas, with the help of physics insight we developed in Chapter 3. Finally, we summarize the result and give some possible implications in Chapter 5.

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2 Mechanical picture for one-dimensional interacting gas

Consider a bunch of particles flying in a one-dimensional box, as shown in Fig. 2. As a particle hits the wall of the box, the wall experiences a force. The collision between the particle and the wall is assumed to be perfectly elastic. Because our description is a bit unorthodox, we first describe how we view the momentum transferred to the right-hand wall by the right-most particle in a one-dimensional box.

Physically we know the right-most particle is the only particle that is constantly bombarding the wall. But the momentum it transfers to the wall after each collision varies in time, because, prior to the collision, this particle gets its momentum from a collision with the particle immediate to its left. But where does that neighboring particle pick up that particular momentum? Clearly, It gets it through an even earlier collision with the immediate neighbor to its left. In this sense, we see that we may assign an arrow to the momentum carried by each particle, and think of each collision happening between two particles as a mechanism of exchanging the arrows of momentum. In other words, an arrow gets pushed to its right after each collision, all the way until it hits the right-hand wall.

In the picture described above, we see that the total force felt by the wall is the summation of the contributions of all particles in the box, namely

$$F = \sum_j F_j = \sum_j \frac{(\text{momentum transferred})_j}{(\text{flying time period})_j} = \sum_j \frac{2mv_j}{T_j} \tag{5}$$

where j is the index of particle, T_j is the time period it takes for an arrow to complete one round trip (between the two walls), and v_j is the velocity of a particle when it hits the wall, called collision velocity. By the lower index j, we actually label the velocity arrow, but not the particle itself, since a particle cannot pass through another particle in

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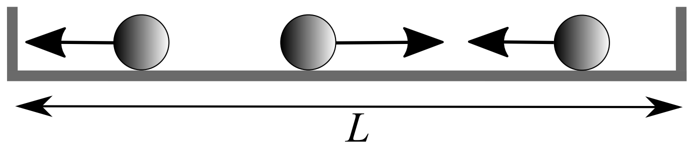

Figure 2: Particles flying in a one-dimensional box of length L.

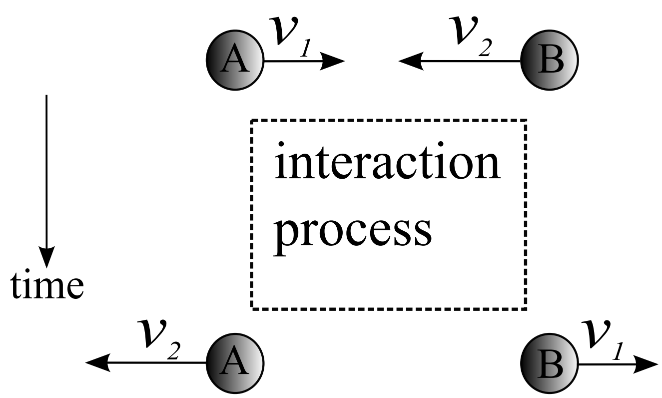

Figure 3: Interaction between particle A and particle B. Particle A is always on the left hand side of particle B, while the velocity arrow v_1 can penetrate.

one-dimensional space. When two particles collide, the velocity arrows will penetrate, but the left particle stays always on the left and the right particle stays always on the right, as shown in Fig. 3. A particle is just a mediator of a velocity arrow.

For a box of ideal gas, that is, the particles have no size and there is no particle-particle interaction, the particles are free, and the force is given by

$$F = \sum_j \frac{2mv_j^0}{T_j^0} = \sum_j \frac{2mv_j^0}{\frac{2L}{v_j^0}} = \frac{2}{L} \sum_j \frac{1}{2} m \left(v_j^0\right)^2 \tag{6}$$

Here the upper index of 0 stands for free particle. The notion of temperature is introduced via Maxwell's velocity distribution

$$f(v) \equiv \frac{1}{\sqrt{\frac{2k_BT}{m}\pi}} e^{-\frac{\frac{1}{2}mv^2}{k_BT}} = \frac{1}{\sqrt{a\pi}} e^{-\frac{v^2}{a}}, \int_{-\infty}^{\infty} dv f(v) = 2\int_0^{\infty} dv f(v) = 1 \tag{7}$$

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where $a \equiv \frac{2k_BT}{m}$. Summation over j is given by

$$\sum_j = N\left(2\int_0^\infty dv_j^0 f(v_j^0)\right) = \frac{2N}{\sqrt{a\pi}}\int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}} \tag{8}$$

The factor of two comes from the fact that we consider the force felt by the right wall. Since particle hits the right wall only if its velocity is positive, we consider the right half part (positive velocity) of Maxwell's velocity distribution and then multiply a factor of two to recover the true particle number. Plugging Eq.8 into Eq.6, the force for an ideal gas is

$$F = \frac{2}{L}\frac{2N}{\sqrt{a\pi}}\int_0^\infty dv e^{-\frac{v^2}{a}}\frac{1}{2}mv^2 = \frac{Nk_BT}{L} = \rho k_B T \tag{9}$$

which is the one-dimensional version for $PV = Nk_BT$, the equation of state for an ideal gas. Note that Maxwell's velocity distribution is put in by hand at the last stage just so that the population of particles with a specific velocity can be connected with temperature, provided that thermal equilibrium is reached.

What happens when particle-particle interaction is turned on? In order to study the force felt by the wall, which is equivalent to the equation of state, there are three elements: summation over all particles ($\sum_j$), flying time period (T_j), and momentum transferred ($2mv_j$). For the summation over all the particles, we will make the explicit assumption that Maxwell's velocity distribution is valid for our system. When particle-particle interaction is turned on, a particle interacts with other particles and hence its velocity is no longer a constant but influenced by particle-particle interactions. Therefore, we expect that the travel time period will be modified. For momentum transferred, due to particle-particle interaction, the velocity of a particle at the moment hitting the wall (collision velocity) may differ from its free particle velocity, and hence the momentum collected by the wall should be modified in the presence of particle-particle interaction. The question we want to ask is, when there is particle-particle interaction, how do flying time period (physics in the bulk) and momentum transferred (physics on

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the boundary) change, and hence lead to the modification of the equation of state? And if we stick with our mechanical approach (but with a set of extra assumptions), how far can we go? Note that standard statistical mechanics cannot tell us "what happens in the bulk" and "what happens on the boundary." It just gives us the equation of state, the total result after combining "physics in the bulk" and "physics on the boundary."

If the system has a high density or a long range interaction, many particles in the box are simultaneously coupled together. This makes things rather hard to track. In order to have a working mechanical approach, we therefore consider the case of low density and particle-particle interaction being short-ranged and weak. Of course, particle-particle interaction by itself has a dimension, and we will see later that a more appropriate statement is that we consider $\frac{U(r)}{k_B T}$, a dimensionless quantity, to be small. This requirement corresponds to assuming a weak particle-particle interaction and high temperature. Since $\frac{1}{2}k_B T$ stands for average kinetic energy, $\mathcal{O}\left(\frac{U(r)}{k_B T}\right) < \mathcal{O}(1)$ means that average kinetic energy is much larger than potential energy describing particle-particle interaction. So we consider one-dimensional interacting gas systems under the limits of low density (dilute gas), short-ranged and weak particle-particle interaction (weakly interacting) and high temperature. Note that these conditions are also required by the van der Waals equation. In this sense, then, we are not imposing more conditions than the standard statistical mechanics approaches require. Since the interaction is small in some sense, we treat the effect of particle-particle interaction as a perturbation, and a particle is a free particle like ideal gas most of the time.

Compared with ideal gas, namely $F = \rho k_B T$, the correction due to particle-particle interaction in van der Waals equation of state is kept to order one, which can be seen in Eq.3. Therefore, in order to construct an equation of state from a mechanical model that can be compared with the van der Waals equation, we only need to retain the accuracy up to the first order in the particle-particle interaction. In other words, we consider the physics perturbed around the ideal gas (free particle) regime and need only

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retain the perturbation up to the first order correction.

To be more concrete, our goal is to study the equation of state, which is equivalent to the force felt by the wall, and is given by

$$F = \sum_j \frac{2mv_j}{T_j} = \sum_j \frac{2m(v_j^0 + \Delta v_j^0)}{T_j^0 + \Delta T_j^0} \tag{10}$$

where v_j^0 is the free particle velocity, $v_j = v_j^0 + \Delta v_j^0$ is the collision velocity, $T_j^0 = \frac{2L}{v_j^0}$ is the flying time period without interaction, and $T_j = T_j^0 + \Delta T_j^0$ is the flying time period in the presence of interaction. Expanding things out to first order in the small corrections, we see that Eq.10 becomes

$$F = \sum_j \frac{2mv_j^0}{T_j^0} - \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0} \tag{11}$$

What we are going to do is trying to study the three terms in Eq.11 with the notion of particle trajectories. The first term corresponds to ideal gas, namely the unperturbed part. The second term arises from the modification of flying time period (physics in the bulk). The third term comes from the modification of collision velocity (physics on the boundary). The strategy is tracking a particle label by j (which means that its free particle velocity is v_j^0), called the main particle, and find out the influence of the other particles, called the background particles, on the main particle. Apparently, the main particle is not special but just a notion for bookkeeping.

Here we want to mention that the idea of *temperature* is actually a subtle concept. When there is particle-particle interaction, the velocity of a particle is no longer a constant, but fluctuates as the particle interacts with other particles. How do we introduce the idea of Maxwell's velocity distribution, and hence the temperature of the system, in this situation? The idea is, the velocity distribution of v_j^0 (the unperturbed part) is described by Maxwell's velocity distribution with temperature T. That is, we identify the first term of the right hand side of Eq.11 with $\rho k_B T$, since the picture in

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mind is that we are doing perturbation and things should go back to ideal gas when there is no particle-particle interaction. But is this T equal to "the real temperature of the box of interacting gas?" We don't know. At this stage, the relation between "T" and "the real temperature of the box of interacting gas" is unclear in our mechanical model. Later (Section 3.3) we will find out what is *the real temperature of the box of interacting gas*. At this stage, T is just a parameter appears in $\sum_j$ (Eq.8), and we don't know how to deal with the real temperature of the system. However, we want to point out that temperature is a thermodynamic concept instead of a mechanical concept, and hence calculations of the effect of particle-particle interaction can be done in our mechanical approach, without dealing with the thermodynamic issue of "What is the real temperature of the system?"

To avoid possible confusion, we should emphasize that we are talking about the real temperature of the system when taking standard statistical mechanics. Therefore, although we don't know how to introduce the idea of temperature in our mechanical approach (the real temperature of the system may be larger or smaller than T in our mechanical approach), the symbol T in Eq.1 to Eq.4 is the real temperature of the system. Later we will use T_{real} for the real temperature of the system in our mechanical approach. Note that if we have $T \neq T_{real}$, then we have $\sum_j \frac{2mv_j^0}{T_j^0} \neq \rho k_B T_{real}$, which means that it is too naive to identify $\sum_j \frac{2mv_j^0}{T_j^0}$ (our mechanical approach) with the ideal gas part in Eq.1 to Eq.4 (standard statistical mechanics). Of course, T is close to T_{real} even if $T \neq T_{real}$, since the effect of particle-particle interaction is weak.

At the end of this chapter, we want to point out that interacting gas is different from ideal gas due to particle-particle interaction. Therefore, it is not surprising that "how many particle-particle interactions are there" and "what is the influence of a particle-particle interaction" are at the heart of our mechanical approach when studying interacting gas. We will see how to understand the behavior of a box of interacting gas by these two central ideas.

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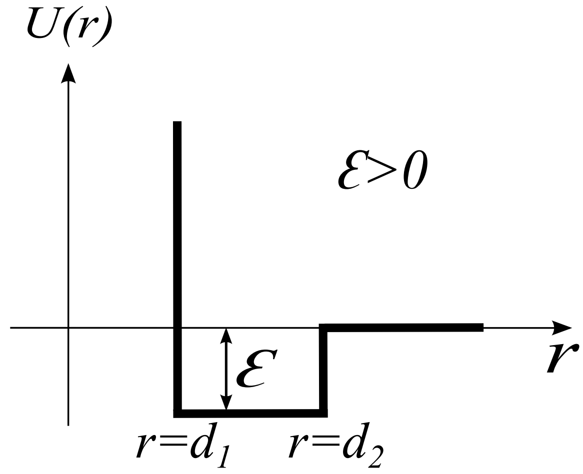

Figure 4: Square well potential.

3 One-dimensional interacting gas with square well potential

In this chapter, we consider one-dimensional non-ideal gas with square well interparticular potential, as shown in Fig. 4. We work out the details in the mechanical model for this specific particle-particle interaction. The advantage of square well potential is that when two particles come close enough and interact, the motion is easy to analyze, since the two particles are actually two free particles inside the potential well (namely, they are free particles for $d_1 < r < d_2$). Interaction is nonvanishing only at $r = d_2$ and $r = d_1$. This is why we choose square well potential. In the next chapter, a more general potential is considered.

By the recipe in standard statistical mechanics (Eq.3), equation of state for square well potential is

$$F = \rho\,(k_B T) + \rho^2\,(k_B T)\,d_1 - \rho^2\,(d_2 - d_1)\,\epsilon. \tag{12}$$

Eq.12 is what we are going to compare with when obtaining an equation of state by our mechanical approach.

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3.1 Mechanics of interaction between two particles

Consider the interaction between two particles described by a generic potential with the only condition that the interaction has a finite range r_0. Since there is no interaction for $r > r_0$, we consider the physics with the initial state being the start of the interaction ($r = r_0$)(incoming) and the final state being the end of the interaction ($r = r_0$)(outgoing), as shown in Fig. 5. Suppose the interaction takes time interval of $\Delta t_{interaction}$, which is a function of the two input velocities and the form of the potential. Now we want to ask, what are the displacements of the two particles during $\Delta t_{interaction}$? In center-of-mass frame, the left particle takes a displacement of r_0 and the right particle takes a displacement of $-r_0$. We want to emphasize again that by particle we actually mean the velocity arrow, but not the particle itself. In the lab frame (of the confining box), the displacements are given by

$$\text{displacement of left particle} = r_0 + v_{CM}\Delta t_{interaction} \tag{13}$$

$$\text{displacement of right particle} = -r_0 + v_{CM}\Delta t_{interaction} \tag{14}$$

where v_{CM} is the center-of-mass velocity.

What is this $\Delta t_{interaction}$? Consider a potential having a hard core shown in Fig. 1. By conservation of energy, the speed of the two particles in their center-of-mass frame is given by

$$v(r) = \sqrt{\left(\frac{v_1 - v_2}{2}\right)^2 + \frac{U(r_0) - U(r)}{m}} \tag{15}$$

where m is the mass of the particle, r is the separation of the two particles. So $\Delta t_{interaction}(v_1, v_2)$ is given by

$$\Delta t_{interaction}(v_1, v_2) = \int_{d_1}^{r_0} \frac{dr}{\sqrt{\left(\frac{v_1-v_2}{2}\right)^2 - \frac{U(r)}{m}}} \tag{16}$$

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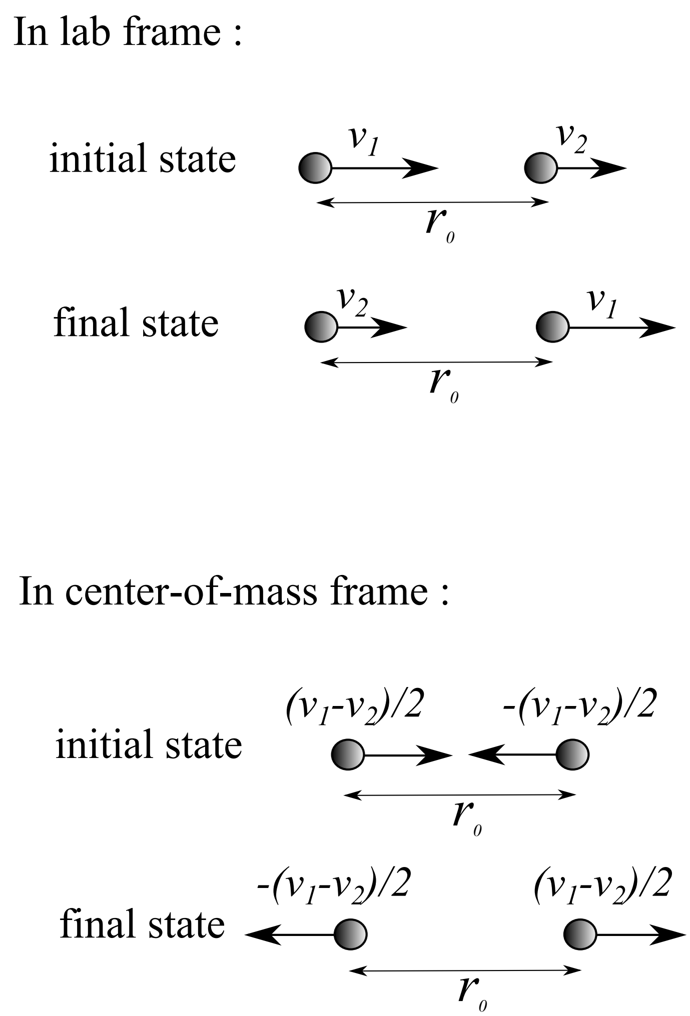

Figure 5: A particle with velocity v_1 interacts with a particle with velocity v_2. The interaction range is denoted as r_0. The upper half part shows the situation in the lab frame. The lower half part shows the situation in center-of-mass frame.

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where we have used the condition of $U(r_0) = 0$.

For particle-particle interaction that is repulsive, $\Delta t_{interaction}$ is more complicated in the sense that the lower bound of d_1 of the integral in Eq.16 should be replaced by a function of v_1 and v_2. For example, when the two particles are not energetic enough in the center-of-mass frame (that is, $v_1 - v_2$ is small), they don't have enough kinetic energy to overcome the potential barrier and reach $r = d_1$. Particle-particle repulsion will be studied later when we study generic particle-particle interaction (Section 4.3).

3.2 Flying time period

Without loss of generality, we may track a main "particle" (in fact, a velocity arrow) which flies from the left wall to the right wall. When particle-particle interactions are taken into account, the main particle changes its velocity along the trip from the left wall to the right wall, and hence its flying time period is changed. Since low density limit (dilute gas) is considered, it is a free particle moving with its free particle velocity v_j^0 for most of the time.

How is the flying time period modified by particle-particle interaction? Well, we may separate the effect into two parts, that is, how many collisions there are in total, and what is the effect of each collision. So there are two steps. First, we find out how many collisions there are for the main particle to fly from the left wall to the right wall during the trip (Section 3.2.1 to Section 3.2.2). This number turns out *not* to have anything to do with the form of the particle-particle interaction, as we will show in the following. The details of the particle-particle interaction comes in only when we are dealing with the effect of each collision (Section 3.2.3).

We separate the flying time period into free particle part and interaction part. The

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flying time period is the sum of the two parts, which is given by

$$\begin{aligned}\frac{1}{2}T_j &= \frac{L - \text{total displacement of } v_j^0 \text{ in interaction}}{v_j^0} + \sum_k \Delta t_{interaction}(v_j^0, v_k) \\ &= \frac{L}{v_j^0} + \sum_k \Delta t_{interaction}(v_j^0, v_k) - \frac{\text{total displacement of } v_j^0 \text{ in interaction}}{v_j^0} \end{aligned} \tag{17}$$

where the background particles are labeled by k, and v_k is the velocity of the background particle when colliding with the main particle.

Particle-particle interactions can be classified as forward collision and backward collision. By forward collision, we mean the background particle collides with the main particle from the right. By backward collision, we mean the background particle collides with the main particle from the left. The number of forward collisions and backward collisions are denoted as $\#_R$ (R stands for right) and $\#_L$ (L stands for left), respectively. For forward collision, by Eq.13, we have

$$\begin{aligned} &\Delta t_{interaction}(v_j^0, v_k) - \frac{\text{displacement of } v_j^0 \text{ in interaction}}{v_j^0} \\ &= \Delta t_{interaction}(v_j^0, v_k) - \frac{r_0 + \frac{v_j^0 + v_k}{2}\Delta t_{interaction}(v_j^0, v_k)}{v_j^0} \\ &= -\frac{r_0}{v_j^0} + \frac{v_j^0 - v_k}{2v_j^0}\Delta t_{interaction}(v_j^0, v_k) \end{aligned} \tag{18}$$

Similarly, for backward collision, by Eq.14, we have

$$\begin{aligned} &\Delta t_{interaction}(v_j^0, v_k) - \frac{\text{displacement of } v_j^0 \text{ in interaction}}{v_j^0} \\ &= \Delta t_{interaction}(v_j^0, v_k) - \frac{-r_0 + \frac{v_j^0 + v_k}{2}\Delta t_{interaction}(v_j^0, v_k)}{v_j^0} \\ &= \frac{r_0}{v_j^0} + \frac{v_j^0 - v_k}{2v_j^0}\Delta t_{interaction}(v_j^0, v_k) \end{aligned} \tag{19}$$

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Plug Eq.18 and Eq.19 into Eq.17, and so ΔT_j^0 is given by

$$
\begin{aligned}
\frac{1}{2}\Delta T_j^0 = \frac{1}{2}\left(T_j - T_j^0\right) &= \frac{1}{2}T_j - \frac{L}{v_j^0} \\
&= \#_R\left(-\frac{r_0}{v_j^0} + \frac{v_j^0 - v_k}{2v_j^0}\Delta t_{interaction}(v_j^0, v_k)\right) \\
&+ \#_L\left(\frac{r_0}{v_j^0} + \frac{v_j^0 - v_k}{2v_j^0}\Delta t_{interaction}(v_j^0, v_k)\right)
\end{aligned} \tag{20}
$$

So we need to find out $\#_R$, $\#_L$, v_k and $\Delta t_{interaction}(v_j^0, v_k)$. Now we are going to build a mechanical model to find out $\#_R$ and $\#_L$.

3.2.1 The idea of "mirror diagram"

In order to proceed, we now introduce the idea of "mirror diagram" as a useful graphical tool we will use frequently in later analysis. The idea is quite simple. Mirror diagram is a diagram helping us visualize the trajectory of a particle in the one-dimensional box. Consider the case of an ideal gas, namely a box of free particles. For a particle flying in the box, it changes its direction when it hits the walls (the left wall and the right wall) due to the reflection provided by the walls. For a particle having a positive velocity at $t = 0$, as time goes on, the velocity will change from positive to negative, and negative to positive, and then positive to negative, so on and so forth. To visualize the motion of a particle, a common way is drawing its $x - t$ diagram. Mirror diagram is an idea built on ordinary $x - t$ diagram. An example of mirror diagram is presented in Fig. 6. It turns out that such diagram is quite helpful in dealing with one-dimensional particle system.

3.2.2 Counting the number of collisions

Back to the issue of computing $\#_R$ and $\#_L$. Consider the case of an ideal gas. How many collisions does the main particle experience in the whole trip flying from the left wall to the right wall? For a background particle with high speed, it can hit the main

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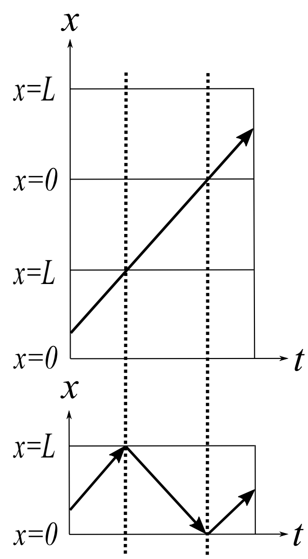

Figure 6: An example of mirror diagram. The lower diagram is an ordinary $x - t$ diagram. The upper diagram is the mirror diagram of the lower diagram. To construct a mirror diagram, we just reflect line segments in ordinary $x - t$ diagram with $x = 0$ and $x = L$, as they are two mirrors.

particle several times. On the contrary, for a background particle with low speed, it may hit the main particle only once. For a background particle with specified velocity and initial position, the numbers of forward collisions and backward collisions provided by the background particle are completely determined, as schematically shown in Fig. 7.

So much for the case of an ideal gas. But what about interacting gas particles? Because we are only computing corrections correct to the first order of particle-particle interaction, it turns out that the counting of the number of particle collisions can be essentially done by assuming that the particles behave just like ideal gas particles! To be more precise, let's look at Fig. 8.

Fig. 8 is the mirror diagram of the main particle and a background particle, in time interval $t = \frac{1}{2}T_j^0$. The trajectory of the main particle in the bottom block is the real trajectory, and the other above trajectories are its mirror images. We also draw two kinds of trajectory for the background particle: one being the trajectory of a free particle (ideal gas trajectory) and the other being the trajectory when particle-particle

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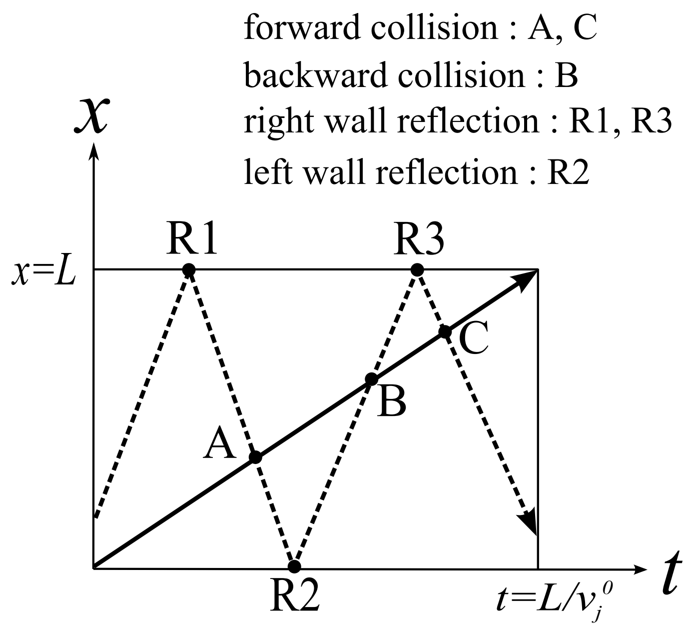

Figure 7: The $x - t$ diagram for a typical motion of the main particle (solid line) and a background particle (dash line) in the time interval that the main particle flying from the left wall to the right wall. There are two forward collisions and one backward collision in this figure.

interaction is turned on (real trajectory). Due to particle-particle interaction, the real background particle trajectory is different from its ideal gas trajectory. With the help of Fig. 8, we can see two things.

The first thing is: The number of collisions for the case when the background particle trajectory is that for an ideal gas is essentially the same as that for the case when the weak and short-ranged interaction is turned on. Their difference is expected to be of first order of particle-particle interaction. Referring back to Eq.(11), we see that this difference does not need to be explicitly included while performing the various summations, which themselves are already of first order in accuracy. For instance, to compute ΔT_j^0, which in itself is already a first order correction, we can use ideal gas particles as the background for the main "particle." Reprise: One can safely use the free particle model in counting the number of forward collisions and the number of backward collisions in our theory.

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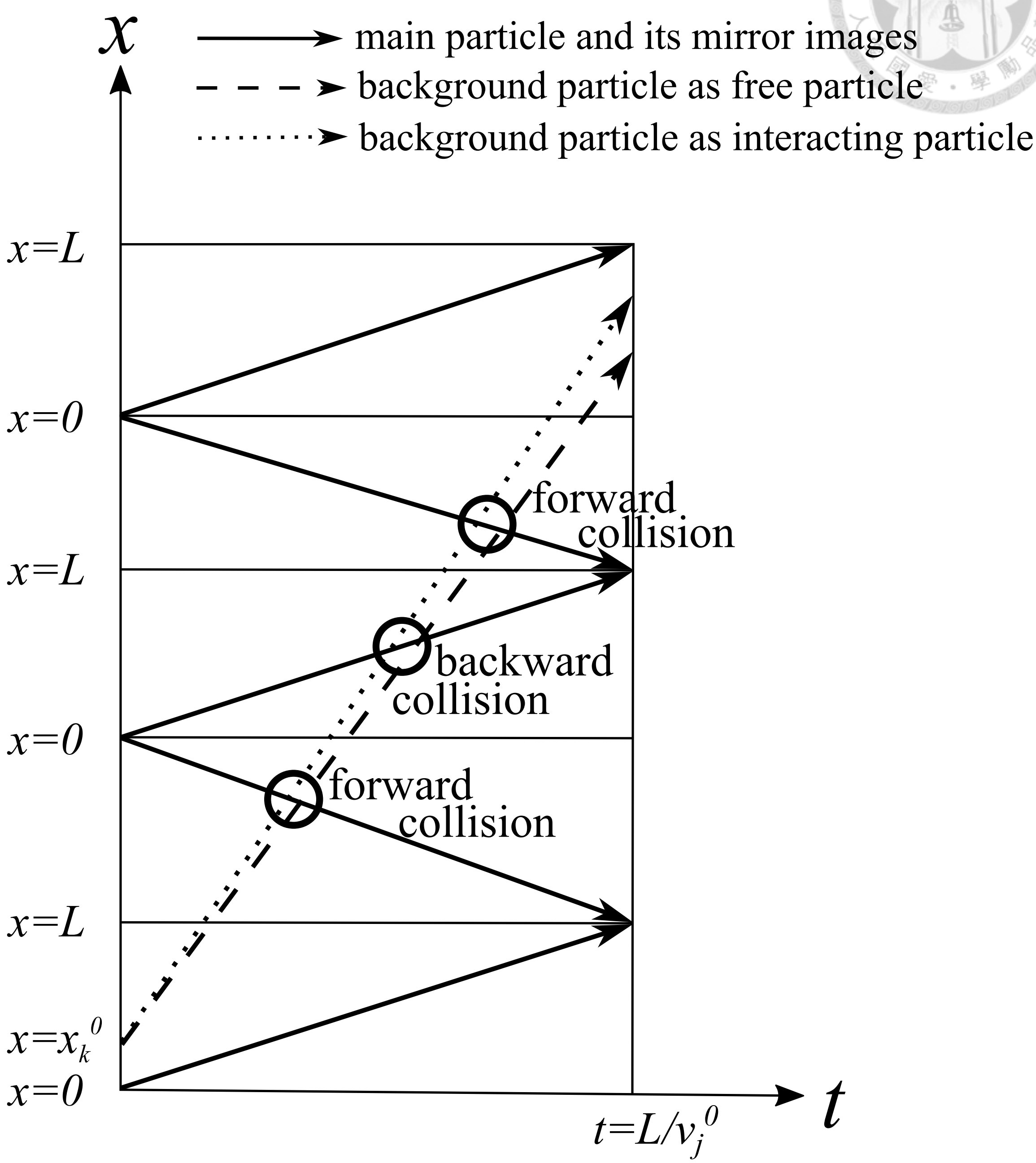

Figure 8: An example of mirror diagram containing the main particle and a background particle. For the background particle, we consider two kinds of trajectory: one is the trajectory being a free particle (ideal gas trajectory) and the other is the trajectory when particle-particle interaction is turned on (real trajectory). The initial position of the background particle is denoted as x_k^0.

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Mathematically speaking, consider a function $A(\delta) = B(\delta)C(\delta)$, where δ is small. Expand $A(\delta)$ with δ

$$A(\delta) = \left(B_0 + \delta B_1 + \mathcal{O}(\delta^2)\right)\left(C_0 + \delta C_1 + \mathcal{O}(\delta^2)\right) \tag{21}$$

If $B_0 = 0$ and $A(\delta)$ is kept to $\mathcal{O}(\delta)$, we have

$$A(\delta) = (\delta B_1)\, C_0 \tag{22}$$

Since $B(\delta)$ contributes at least one order of δ, it is sufficient to preserve $C(\delta)$ to the zeroth order of δ.

Total effect of particle-particle interaction, effect of each collision, number of collisions and strength of particle-particle interaction play the role of $A(\delta)$, $B(\delta)$, $C(\delta)$ and δ in Eq.21 and Eq.22, respectively. When the effect of particle-particle interaction is kept to order one, in order to count the number of collisions, the free particle model (ideal gas) is sufficient.

The second thing is: Based on the above, we see that, in order to count the number of collisions, we can just resort to the mirror diagram and count the numbers of crossing between the straight line of Fig. 8 (corresponding to the background particle) and the mirror-reflected arrows of the main particle of Fig. 8. To do the actual counting, we proceed as follows.

The number of collisions provided by a background particle depends on its velocity and initial position, that is, $\#_R = \#_R\left(v_j^0, v_k^0, x_k^0\right) = \#_R\left(\frac{v_k^0}{v_j^0}, x_k^0\right)$ and $\#_L = \#_L\left(v_j^0, v_k^0, x_k^0\right) = \#_L\left(\frac{v_k^0}{v_j^0}, x_k^0\right)$. With the help of mirror diagrams and some elementary counting of the intersection points of some straight lines (for example, there are two forward collisions and one backward collision in Fig. 8), $\frac{1}{L}\int_0^L dx_k^0 \#_L\left(v_j^0, v_k^0, x_k^0\right)$ is

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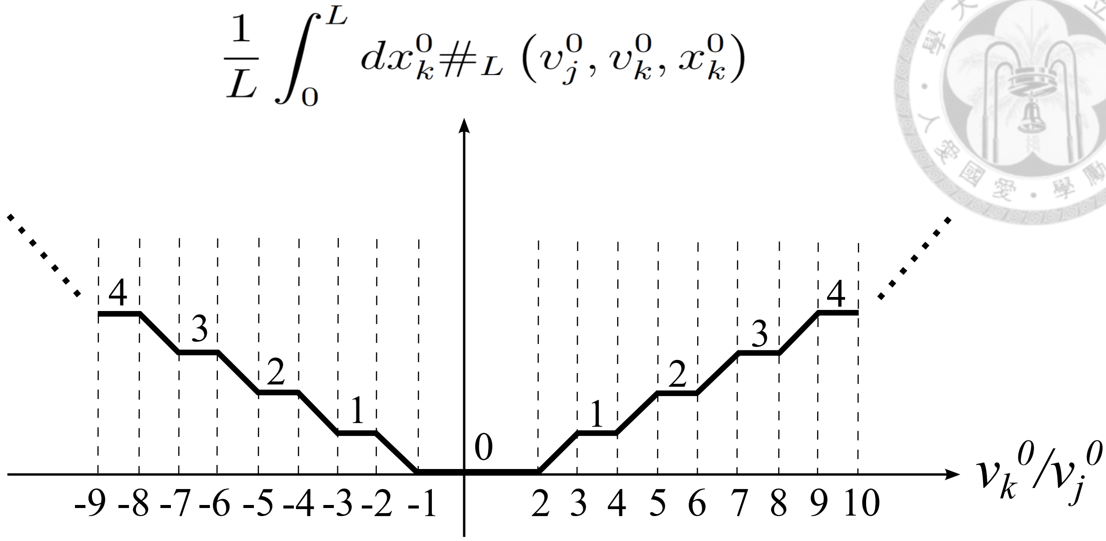

Figure 9: $\frac{1}{L}\int_0^L dx_k^0 \#_L\left(v_j^0, v_k^0, x_k^0\right)$ as a function of $\frac{v_k^0}{v_j^0}$. The line segments connecting two adjacent flat parts are straight lines with slopes being ± 1.

calculated and the result is shown in Fig. 9. For $\#_R$, we have

$$\frac{1}{L}\int_0^L dx_k^0 \#_R\left(v_j^0, v_k^0, x_k^0\right) = 1 + \frac{1}{L}\int_0^L dx_k^0 \#_L\left(v_j^0, v_k^0, x_k^0\right) \tag{23}$$

Let's see what Fig. 9 and Eq.23 mean. Without loss of generality, the main particle is set to start from $x = 0$ flying to $x = L$ in our construction. At $t = 0$, all background particles are between the right wall ($x = L$) and the initial position of the main particle ($x = 0$). Therefore, in the trip of the main particle flying from the left wall to the right wall, all background particles collide with the main particle at least one time, being forward collision of the main particle. To have a backward collision with the main particle, a background particle needs to fly fast enough to catch up with the main particle again, which can be seen from $\frac{1}{L}\int_0^L dx_k^0 \#_L\left(v_j^0, v_k^0, x_k^0\right) = 0$ for $-1 < \frac{v_k^0}{v_j^0} < 2$ in Fig. 9. Furthermore, a backward collision implies that the background particle hits the main particle from the left side and then passes through the main particle to its right side. Since now the background particle is between the main particle and the right wall, there will be a forward collision before the main particle arrives at the right wall. In

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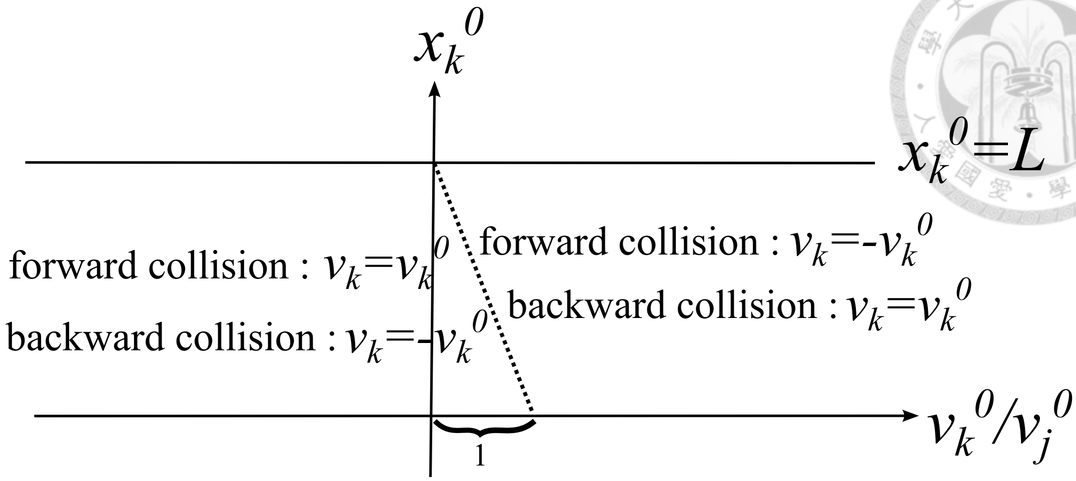

Figure 10: Velocity of a background particle when colliding with the main particle. It is a function of x_k^0 and $\frac{v_k^0}{v_j^0}$.

other words, a backward collision is always followed by a forward collision, due to the construction that the end of the trip of the main particle is hitting the right wall, which implies that no one can exist between the main particle and the right wall at the end of the trip. Comparing the initial situation at $t = 0$ and the final situation at $t = \frac{1}{2}T_j^0$, all the background particles change from sitting at the right side of the main particle to its left side, and hence the number of forward collisions is larger than the number of backward collisions by one.

Now we have $\#_R$ and $\#_L$. In view of Eq.20, the next thing to study is v_k, the velocity of a background particle when colliding with the main particle.

A background particle is specified by its initial position and free particle velocity, namely labeled by (x_k^0, v_k^0). For a given (x_k^0, v_k^0), what is the velocity of the background particle when it collides with the main particle? For example, consider a background particle with $v_k^0 = \frac{1}{2}v_j^0$. If $x_k^0 \sim 0$, forward collision occurs when the velocity of the background particle is v_k^0. On the other hand, if $x_k^0 \sim L$, that is, the background particle takes an initial position near the right wall, forward collision occurs when the velocity of the background particle is $-v_k^0$. The minus sign comes from the reflection provided

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by the right wall. The velocity of the background particle when it collides with the main particle depends on both x_k^0 and v_k^0. With the help of mirror diagram, we can easily find out the result shown in Fig. 10.

With Fig. 10, we define

$$H\left(v_k^0\right) \equiv \begin{cases} -v_k^0 & \text{for } \frac{v_k^0}{v_j^0} + \frac{x_k^0}{L} > 1 \\ v_k^0 & \text{for } \frac{v_k^0}{v_j^0} + \frac{x_k^0}{L} < 1 \end{cases} \tag{24}$$

For forward collision, $v_k = H\left(v_k^0\right)$. For backward collision, $v_k = -H\left(v_k^0\right)$.

Substituting the position distribution, the velocity distribution, and $H\left(v_k^0\right)$ into Eq.20, we have

$$\frac{1}{2}\Delta T_j^0 = \frac{1}{L}\int_0^L dx_k^0 \int_{-\infty}^{\infty} dv_k^0 \left(Nf(v_k^0)\right)\left[\#_R\left(-\frac{r_0}{v_j^0} + \frac{v_j^0 - H\left(v_k^0\right)}{2v_j^0}\Delta t_{interaction}\left(v_j^0, H\left(v_k^0\right)\right)\right)\right.$$
$$\left. +\#_L\left(\frac{r_0}{v_j^0} + \frac{v_j^0 + H\left(v_k^0\right)}{2v_j^0}\Delta t_{interaction}\left(v_j^0, -H\left(v_k^0\right)\right)\right)\right] \tag{25}$$

Since the dependence of x_k^0 appears only in $\#_R$ and $\#_L$, we may rearrange the integral as

$$\begin{aligned}\frac{1}{2}\Delta T_j^0 \quad = \quad & \frac{N}{v_j^0}\int_{-\infty}^{\infty} dv_k^0 f(v_k^0)\frac{1}{L}\int_0^L dx_k^0 \left[(-r_0)\left(\#_R - \#_L\right)\right. \\ & +\#_R\frac{v_j^0 - H\left(v_k^0\right)}{2}\Delta t_{interaction}\left(v_j^0, H\left(v_k^0\right)\right) \\ & \left.+\#_L\frac{v_j^0 + H\left(v_k^0\right)}{2}\Delta t_{interaction}\left(v_j^0, -H\left(v_k^0\right)\right)\right]\end{aligned} \tag{26}$$

With $\#_R$, $\#_L$ and $H\left(v_k^0\right)$ in hand, the remaining task is putting them together and calculating $\frac{1}{2}\Delta T_j^0$. The calculation is done in Appendix A. The result is

$$\frac{1}{2}\Delta T_j^0 = -r_0\frac{N}{v_j^0} + \frac{N}{2}\frac{1}{\sqrt{a\pi}\left(v_j^0\right)^2}\int_0^{\infty} dv_k^0 \left[e^{-\frac{\left(v_k^0 - v_j^0\right)^2}{a}} - e^{-\frac{\left(v_k^0 + v_j^0\right)^2}{a}}\right]\left(v_k^0\right)^2 \Delta t_{interaction}\left(0, v_k^0\right) \tag{27}$$

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3.2.3 Correction of the flying time period

Next we include the effect of the square well potential. For square well potential, in view of Eq.16, we see that $\Delta t_{interaction}\left(0, v_k^0\right)$ is given by

$$\Delta t_{interaction}\left(0, v_k^0\right) = \int_{d_1}^{d_2} \frac{dr}{\sqrt{\left(\frac{v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} + \int_{d_2}^{r_0} \frac{dr}{\sqrt{\left(\frac{v_k^0}{2}\right)^2}} = \frac{d_2 - d_1}{\sqrt{\left(\frac{v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} + \frac{r_0 - d_2}{\mid \frac{v_k^0}{2} \mid} \quad (28)$$

Plugging Eq.28 into Eq.27, we have

$$\begin{aligned}
\frac{1}{2}\Delta T_j^0 &= -r_0 \frac{N}{v_j^0} + \frac{N}{2} \frac{1}{\sqrt{a\pi}\left(v_j^0\right)^2} \int_0^\infty dv_k^0 \left[e^{-\frac{\left(v_k^0 - v_j^0\right)^2}{a}} - e^{-\frac{\left(v_k^0 + v_j^0\right)^2}{a}} \right] \\
&\quad \times \left(v_k^0\right)^2 \left[\frac{d_2 - d_1}{\sqrt{\left(\frac{v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} + \frac{r_0 - d_2}{\mid \frac{v_k^0}{2} \mid} \right] \\
&= -\frac{N d_2}{v_j^0} + \frac{N\left(d_2 - d_1\right)}{\sqrt{a\pi}\left(v_j^0\right)^2} \int_0^\infty dv_k^0 \left[e^{-\frac{\left(v_k^0 - v_j^0\right)^2}{a}} - e^{-\frac{\left(v_k^0 + v_j^0\right)^2}{a}} \right] \frac{\left(v_k^0\right)^2}{\sqrt{\left(v_k^0\right)^2 + \frac{4\epsilon}{m}}} \quad (29)
\end{aligned}$$

To expand a physical quantity, we should take something dimensionless as our perturbation parameter. Thus, we define the dimensionless velocity u to be

$$u_i^0 \equiv \sqrt{\frac{\frac{1}{2}m\left(v_i^0\right)^2}{k_B T}} = \frac{v_i^0}{\sqrt{\frac{2k_B T}{m}}} = \frac{v_i^0}{\sqrt{a}}. \quad (30)$$

In passing, we would like to emphasize that the introduction of this dimensionless velocity is quite helpful when dealing with the population in velocity distribution. With this dimensionless velocity, there is no parameter like temperature in Maxwell's velocity distribution, and the Boltzmann factor just reads e^{-u^2}. We will see the advantage of this dimensionless velocity later when we need to figure out the order of magnitude of some populations.

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With this dimensionless velocity, Eq.29 can be written as

$$\frac{1}{2}\Delta T_j^0 = -\frac{Nd_2}{v_j^0} + \frac{N\left(d_2-d_1\right)\sqrt{a}}{\sqrt{\pi}\left(v_j^0\right)^2}\int_0^\infty du_k^0\left[e^{-\left(u_k^0-u_j^0\right)^2}-e^{\left(u_k^0+u_j^0\right)^2}\right]\frac{\left(u_k^0\right)^2}{\sqrt{\left(u_k^0\right)^2+\frac{2\epsilon}{k_BT}}} \tag{31}$$

Expand the integrand in $\frac{\epsilon}{k_BT}$ and keep up to order $\mathcal{O}\left(\frac{\epsilon}{k_BT}\right)$, we have

$$\begin{aligned}
&\int_0^\infty du_k^0\left[e^{-\left(u_k^0-u_j^0\right)^2}-e^{\left(u_k^0+u_j^0\right)^2}\right]\frac{\left(u_k^0\right)^2}{\sqrt{\left(u_k^0\right)^2+\frac{2\epsilon}{k_BT}}}\\
&=\int_0^\infty du_k^0\left[e^{-\left(u_k^0-u_j^0\right)^2}-e^{\left(u_k^0+u_j^0\right)^2}\right]\left[\left(u_k^0\right)-\left(\frac{1}{u_k^0}\right)\frac{\epsilon}{k_BT}\right]\\
&=\int_0^\infty du_k^0\left[e^{-\left(u_k^0-u_j^0\right)^2}-e^{\left(u_k^0+u_j^0\right)^2}\right]u_k^0-\left(\int_0^\infty du_k^0\frac{e^{-\left(u_k^0-u_j^0\right)^2}-e^{\left(u_k^0+u_j^0\right)^2}}{u_k^0}\right)\frac{\epsilon}{k_BT}\\
&=\sqrt{\pi}u_j^0-\pi e^{-\left(u_j^0\right)^2}\mathrm{erfi}(u_j^0)\frac{\epsilon}{k_BT}\\
&=\sqrt{\frac{\pi}{a}}v_j^0-\pi e^{-\frac{\left(v_j^0\right)^2}{a}}\mathrm{erfi}\left(\frac{v_j^0}{\sqrt{a}}\right)\frac{\epsilon}{k_BT}
\end{aligned} \tag{32}$$

Plugging Eq.32 into Eq.31, we have

$$\frac{1}{2}\Delta T_j^0 = -\frac{Nd_1}{v_j^0} - \frac{N\left(d_2-d_1\right)\sqrt{a\pi}}{\left(v_j^0\right)^2}e^{-\frac{\left(v_j^0\right)^2}{a}}\mathrm{erfi}\left(\frac{v_j^0}{\sqrt{a}}\right)\frac{\epsilon}{k_BT} \tag{33}$$

This is the flying time correction due to a square well potential in the particle-particle interaction.

Let's try to figure out what Eq.33 is telling us. The first term is the effect of the hard core, whose meaning is as expected. The effect of the hard core is decreasing the space that a particle can move. The length of the box, namely L, is replaced by $L - Nd_1$, and the corresponding flying time correction is $\frac{1}{2}\Delta T_j^0 = -\frac{Nd_1}{v_j^0}$. The second term is the effect of the attraction potential, which can be seen from the feature that there are $d_2 - d_1$ and $\frac{\epsilon}{k_BT}$ in this term. The second term is always negative for any v_j^0 (recall that $v_j^0 \geq 0$ by construction). It means that the effect of the attraction tail in

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the square well potential is decreasing the flying time period and thus increasing the average velocity (average velocity is larger than free particle velocity), for all particles in the box. But why?

Consider what happens when two particles interact. A negative potential means there is an attractive force between the two particles. When the two particles interact, the left particle is attracted by the right particle and hence gets a positive acceleration; the right particle is attracted by the left particle and hence gets a negative acceleration. In the language of forward collision and backward collision, when the main particle has a forward collision, the background particle increases the velocity of the main particle by providing an attraction from the front. And when the main particle has a backward collision, the background particle decreases the velocity of the main particle by providing an attraction from the back. By Eq.23, the number of forward collisions is one more than that of backward collisions. Combining the numbers of forward collisions and backward collisions and their effects on the main particle, we now understand why a particle is sped up when particle-particle attraction is turned on.

We can analyze the effect with the help of average velocity. For square well potential, by Eq.33, the average velocity is given by

$$v_j \mid_{average} = \frac{2\left(L - Nd_1\right)}{T_j^0 + \Delta T_j^0} = \frac{2L}{T_j^0}\left(1 - \rho d_1\right)\left(1 - \frac{\Delta T_j^0}{T_j^0}\right) = v_j^0\left(1 - \rho d_1 - \frac{\Delta T_j^0}{T_j^0}\right)$$
$$= v_j^0\left(1 + \frac{\sqrt{\pi}\rho\left(d_2 - d_1\right)}{\frac{v_j^0}{\sqrt{a}}} e^{-\frac{\left(v_j^0\right)^2}{a}} \mathrm{erfi}\left(\frac{v_j^0}{\sqrt{a}}\right)\frac{\epsilon}{k_B T}\right) \tag{34}$$

where $\frac{\epsilon}{k_B T}$ is kept up to first order. In dimensionless form, the effect of attraction tail in square well potential is

$$u_j \mid_{average} - u_j^0 = \frac{v_j \mid_{average} - v_j^0}{\sqrt{a}} = \rho\left(d_2 - d_1\right)\frac{\epsilon}{k_B T}\left(\sqrt{\pi} e^{-\left(u_j^0\right)^2}\mathrm{erfi}(u_j^0)\right) \tag{35}$$

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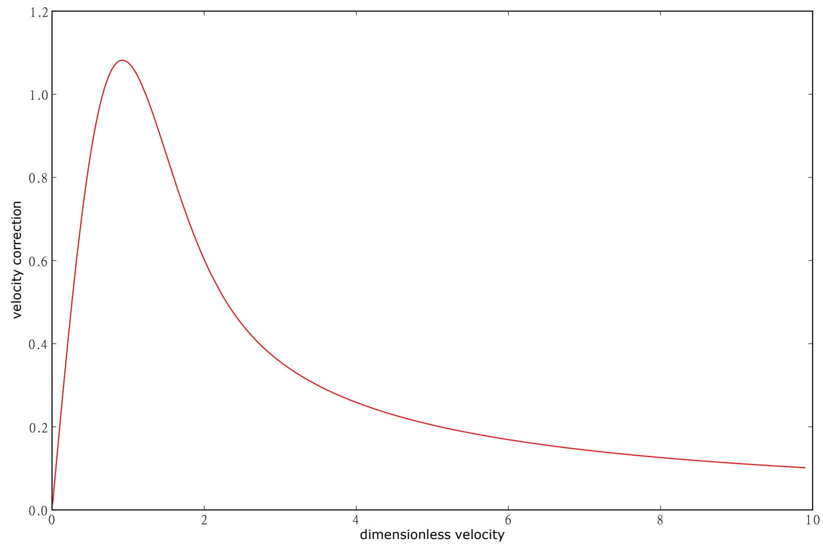

Figure 11: Correction of average velocity due to particle-particle attraction for square well potential. The x-axis is u_j^0 and the y-axis is $\frac{u_j|_{average} - u_j^0}{\rho(d_2-d_1)\frac{\epsilon}{k_BT}}$.

as shown in Fig. 11. The y-axis in Fig. 11 is

$$\frac{u_j \mid_{average} - u_j^0}{\rho\left(d_2 - d_1\right)\frac{\epsilon}{k_BT}} = \sqrt{\pi}e^{-\left(u_j^0\right)^2}\text{erfi}(u_j^0) \tag{36}$$

The profile of $\left(u_j \mid_{average} - u_j^0\right)$ in Fig. 11 can be understood if we decompose the profile into two main trends, namely an increasing trend and a decreasing trend. First we note that Maxwell's velocity distribution decays exponentially, which means that the population of fast particles is quite small.

By Eq.23 and Fig. 9, the number of collisions provided by a background particle (with position distribution having been averaged by $\frac{1}{L}\int_0^L dx_k^0$) can be written as

$$1 \text{ forward collision} + n \;\; (\text{forward collision}, \text{backward collision}) \;\; \text{pair} \tag{37}$$

where $n = \frac{1}{L}\int_0^L dx_k^0 \#_L\left(v_j^0, v_k^0, x_k^0\right)$. For any v_k^0, there is always one forward collision, but the number of (forward collision, backward collision) pairs depends on the value of v_k^0.

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For a background particle with a high speed, there are many (forward collision, backward collision) pairs. What is the effect of a (forward collision, backward collision) pair? Increasing the velocity of the main particle or decreasing the velocity of the main particle? The effect of particle-particle interaction is significant when the relative velocity of two particles is small. If the relative velocity is large, the two particles almost neglect the potential and behave as two free particles. For a background particle, compared with its forward collision, the relative velocity of the background particle (v_k) and the main particle (v_j^0) is smaller in its backward collision. Therefore, for a background particle, the effect of its backward collision (velocity decreasing) is stronger than its forward collision (velocity increasing), and so the effect of a (forward collision, backward collision) pair is decreasing the velocity of the main particle. For a background particle having slow speed of $-v_j^0 < v_k^0 < 2v_j^0$, there is no (forward collision, backward collision) pair and just one forward collision, and the effect provided by such background particle is velocity increasing. As the background particle moves faster, the number of (forward collision, backward collision) pairs increases, and this brings velocity decreasing.

When the velocity of the main particle (v_j^0) increases, the domain of $-v_j^0 < v_k^0 < 2v_j^0$ also increases. Population of background particles that have one forward collision plus zero backward collision increases; population of background particles that have nonzero (forward collision, backward collision) pairs decreases. The increasing trend in Fig. 11 is due to population decreasing for (forward collision, backward collision) pair.

Since the effect of particle-particle interaction is significant when the relative velocity is small, the velocity domain of background particles that has significant contribution is a small neighborhood around the velocity of the main particle. When the velocity of the main particle increases, the velocity of this small neighborhood also increases, and hence the population in this domain decreases, due to the exponential decay of Maxwell's velocity distribution. This is the reason for the decreasing trend.

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In conclusion, the profile of the correction of average velocity due to particle-particle attraction shown in Fig. 11 can be understood by the product of two trends, an increasing trend and a decreasing trend. The increasing trend comes from the population increasing of $\{(1 \text{ forward collision}, 0 \text{ backward collision})\}$ and the population decreasing of $(\text{forward collision}, \text{backward collision})$ pairs. The decreasing trend comes from the suppression of exponential decay from Maxwell's velocity distribution.

In the traditional picture of an interacting gas, particle-particle interaction disappears for the bulk part under mean field approximation [18]. With our mechanical approach, now we know that such mean field approximation is not quite correct. Background particles are uniform, but the effect is not zero, since the main particle flies to a certain direction and thus breaks left-right symmetry. The effect of forward collisions and the effect of backward collisions don't cancel out. A particle is sped up when particle-particle attraction is turned on.

3.2.4 Correction of flying time period in equation of state

In the last part of this chapter dealing with flying time period, we calculate the effect of this flying time correction in the equation of state. The effect of ΔT_j^0 appears in the

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equation of state with the form of $-\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}$. By Eq.33, we have

$$
\begin{aligned}
&-\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} \\
&=-\sum_j \frac{m}{L^2}\left(v_j^0\right)^3\frac{\Delta T_j^0}{2} \\
&=-\frac{2N}{\sqrt{a\pi}}\int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}}\left[\frac{m}{L^2}\left(v_j^0\right)^3\right]\left[-\frac{Nd_1}{v_j^0}-\frac{N\left(d_2-d_1\right)\sqrt{a\pi}}{\left(v_j^0\right)^2}e^{-\frac{\left(v_j^0\right)^2}{a}}\mathrm{erfi}(\frac{v_j^0}{\sqrt{a}})\frac{\epsilon}{k_BT}\right] \\
&=\frac{2\rho^2 md_1}{\sqrt{a\pi}}\int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}}\left(v_j^0\right)^2+2\rho^2 m\left(d_2-d_1\right)\frac{\epsilon}{k_BT}\int_0^\infty dv_j^0 e^{-2\frac{\left(v_j^0\right)^2}{a}}\mathrm{erfi}(\frac{v_j^0}{\sqrt{a}})v_j^0 \\
&=\frac{2\rho^2 md_1 a}{\sqrt{\pi}}\int_0^\infty du_j^0 e^{-\left(u_j^0\right)^2}\left(u_j^0\right)^2+2\rho^2 m\left(d_2-d_1\right)\frac{\epsilon}{k_BT}a\int_0^\infty du_j^0 e^{-2\left(u_j^0\right)^2}\mathrm{erfi}(u_j^0)u_j^0 \\
&=\frac{1}{2}\rho^2 md_1 a+\frac{1}{2}\rho^2 m\left(d_2-d_1\right)\frac{\epsilon}{k_BT}a \\
&=\rho^2\left(k_BT\right)d_1+\rho^2\left(d_2-d_1\right)\epsilon
\end{aligned}
\tag{38}
$$

The equation of state is

$$
\begin{aligned}
F&=\sum_j \frac{2mv_j^0}{T_j^0}-\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}+\sum_j \frac{2m\Delta v_j^0}{T_j^0} \\
&=\rho k_BT+\rho^2\left(k_BT\right)d_1+\rho^2\left(d_2-d_1\right)\epsilon+\sum_j \frac{2m\Delta v_j^0}{T_j^0}
\end{aligned}
\tag{39}
$$

3.3 Temperature modification

In Section 3.2, we see that when particle-particle attraction is turned on, the average velocity of each particle in the box increases due to the attraction tail in the square well potential. An increase in velocity implies an increase in kinetic energy, and so the temperature of the box of gas should also increase. For example, for v_j^0 described by Maxwell's velocity distribution of 300K, the real temperature of the box of interacting gas may be 305K. In our previous calculations, we introduced T via Maxwell's velocity distribution on free particle velocity v_j^0. It turns out that T is *not* the real temperature

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of the system, since we now know that the temperature is affected by particle-particle interaction. The real temperature of the system should not be decided before considering particle-particle interaction. The real temperature should be a function of particle-particle interaction. So how do we fix this "mistake?"

This goes back to the same old question: How do we introduce the idea of temperature, which is a thermodynamic concept but not a mechanical concept? We introduce temperature as a parameter in the velocity distribution of a system at thermal equilibrium. When dealing with equation of state, what we actually need to calculate is

$$\sum_j \frac{2mv_j^0}{T_j^0} = \frac{2}{L} \sum_j \frac{1}{2} m \left(v_j^0\right)^2 = \frac{2N}{L} \langle K.E. \rangle \tag{40}$$

where $\langle K.E. \rangle$ stands for average kinetic energy. We require $\langle K.E. \rangle = \frac{1}{2} k_B T$ and obtain

$$\sum_j \frac{2mv_j^0}{T_j^0} = \rho k_B T \tag{41}$$

To modify the temperature of the system due to particle-particle interaction, we use the notion of average kinetic energy. The idea is, when replacing v_j^0 with $v_j \mid_{average}$ and calculating the kinetic energy, we should get $N \langle K.E. \rangle = \frac{N}{2} k_B T_{real}$. Here we denoted the modified temperature by T_{real}. The real temperature of the box of interacting gas should be introduced by

$$\sum_j \frac{1}{2} m \left(v_j \mid_{average}\right)^2 = \frac{N}{2} k_B T_{real} \tag{42}$$

Now we want to figure out the relation between T_{real} and T. Before we calculate, we should mention that the effect of particle-particle interaction will only be kept to first order in the following calculations. We will no longer stress this point. As particle-

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particle interaction is considered, the average velocity is

$$v_j\mid_{average}=\frac{L-Nd_1}{\frac{1}{2}\left(T_j^0+\Delta T_j^0\right)}=v_j^0\left(1-\rho d_1\right)\left(1-\frac{\Delta T_j^0}{T_j^0}\right)=v_j^0\left(1-\rho d_1-\frac{\Delta T_j^0}{T_j^0}\right) \tag{43}$$

By Eq.42, the total kinetic energy is given by

$$\begin{aligned}\frac{N}{2}k_BT_{real}&=\sum_j\frac{1}{2}m\left(v_j\mid_{average}\right)^2\\&=\sum_j\frac{1}{2}m\left(v_j^0\left(1-\rho d_1-\frac{\Delta T_j^0}{T_j^0}\right)\right)^2\\&=\sum_j\frac{1}{2}m\left(v_j^0\right)^2\left(1-2\rho d_1-\frac{2\Delta T_j^0}{T_j^0}\right)\\&=\frac{N}{2}k_BT\left(1-2\rho d_1\right)-\sum_j m\left(v_j^0\right)^2\frac{\Delta T_j^0}{T_j^0}\end{aligned} \tag{44}$$

Rearrange Eq.44, and we have

$$\begin{aligned}k_BT&=\frac{2}{N}\left(1+2\rho d_1\right)\left(\frac{N}{2}k_BT_{real}+\sum_j m\left(v_j^0\right)^2\frac{\Delta T_j^0}{T_j^0}\right)\\&=k_BT_{real}\left(1+2\rho d_1\right)+\frac{2}{N}\sum_j m\left(v_j^0\right)^2\frac{\Delta T_j^0}{T_j^0}\end{aligned} \tag{45}$$

And ρk_BT is given by

$$\begin{aligned}\rho k_BT&=\rho k_BT_{real}+2\rho^2\left(k_BT_{real}\right)d_1+\frac{2}{L}\sum_j m\left(v_j^0\right)^2\frac{\Delta T_j^0}{T_j^0}\\&=\rho k_BT_{real}+2\rho^2\left(k_BT_{real}\right)d_1+2\sum_j\frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}\end{aligned} \tag{46}$$

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By Eq.46, the equation of state is modified to

$$\begin{aligned}F &= \sum_j \frac{2mv_j^0}{T_j^0} - \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0} \\ &= \left(\rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 + 2\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}\right) - \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0} \\ &= \rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 + \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0} \end{aligned} \tag{47}$$

In summary, the equation of state is given by

$$\begin{aligned}F &= \sum_j \frac{2m(v_j^0 + \Delta v_j^0)}{T_j^0 + \Delta T_j^0} \\ &= \sum_j \frac{2mv_j^0}{T_j^0} - \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0} \\ &= \rho k_B T - \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0} \\ &= \rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 + \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0} \end{aligned} \tag{48}$$

Since the temperature is modified, we may worry about the validity of previous calculations based on Maxwell's velocity distribution with T, but not the real temperature T_{real}. Fortunately, our previous calculations are still correct even if T is not the real temperature of the system. This is, again, because we were already dealing with the first order corrections when computing $\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}$ and $\sum_j \frac{2m\Delta v_j^0}{T_j^0}$.

In the above we had argued that the actual temperature should be slightly higher than that of its ideal gas part because of the attraction in the particle-particle attraction. Here we provide yet another point of view without concerning ourselves with the detail of the particle-particle interaction. In this point of view, the idea of temperature correction is discussed with the idea of total energy of the box of gas.

So, what is the total energy of the box of an interacting gas? On the one hand,

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the total energy is given by total kinetic energy when all particles fly with their free particle velocities, since potential energy plays no role in the situation of "free particle" by construction. In other words, by our construction of the mechanical model, the total energy is given by

$$\text{total energy} = \sum_j \frac{1}{2} m \left(v_j^0\right)^2 = \frac{N}{2} k_B T \tag{49}$$

On the other hand, when a particle flies in the box, it does experience interactions occasionally, and not always as a free particle. The total energy is the summation of average kinetic energy and average potential energy, and is given by

$$\text{total energy} = N \left(\langle K.E.\rangle + \langle U\rangle\right) = \frac{N}{2} k_B T_{real} + N \langle U\rangle \tag{50}$$

Compare the two forms of total energy, and we have

$$k_B T_{real} = k_B T - 2 \langle U\rangle \tag{51}$$

Therefore, for particle-particle attraction, which corresponds to negative potential energy, the real temperature T_{real} is higher than the unperturbed temperature T. Furthermore, we can see that their difference is average potential energy, which is of the same order of accuracy that is required in our calculations. In other words, the effect of temperature correction is not negligible.

We want to point out that, temperature correction from the point of view of total energy of the system presented here doesn't require any consideration of the detailed dynamics. In Section 3.2, we counted the number of collisions and dealt with the effect of each collision, and finally summed over all the effects to get the correction of the flying time period. But here we just considered the energy of the system, and it is enough to allow us to see the increase of the temperature.

Note that we can see that traditional interpretation of the van der Waals equation

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adopting mean field approximation is incorrect simply by $\sum_j \frac{1}{2}m\left(v_j\mid_{average}\right)^2 + N\langle U\rangle = \sum_j \frac{1}{2}m\left(v_j^0\right)^2$, without doing detailed calculations. When particle-particle attraction is turned on, potential energy is negative and hence particles move faster.

So here we are facing the ambiguous notations of T and T_{real}. When taking standard statistical mechanics, we always work with the real temperature of the system, so T in Eq.1 to Eq.4 and Eq.12 should always be treated as meaning T_{real}.

3.4 Momentum transferred

During its entire trip, the main particle experiences lots of collisions with the $N-1$ background particles, and the consequences are the correction of the flying time period and the correction of the temperature. But to compute the force experienced by the wall, only the state of the main particle at the end of its trip is relevant, but not what it experiences en route.

When the main particle hits the wall with velocity v, the wall absorbs a momentum of $2mv$. When particle-particle interaction is considered, the main particle may hit the wall when it is still coupled with another particle. In this case, the main particle hits the wall with a velocity different from its free particle velocity v_j^0, and the corresponding momentum collected by the wall is different from $2mv_j^0$. For the main particle with free particle velocity of v_j^0, the collision velocity can be equal to, bigger than or smaller than v_j^0, depending on its behavior around the wall. If the main particle hits the wall as a free particle, the collision velocity is equal to v_j^0. If the main particle hits the wall during a forward collision, the collision velocity is bigger than v_j^0, since forward collision increases its velocity. If the main particle hits the wall during a backward collision, the collision velocity is smaller than v_j^0, since backward collision decreases its velocity. Hitting the wall as a free particle gives no correction to collision velocity. To have a non-trivial collision velocity, namely nonvanishing Δv_j^0, the main particle must hit the wall while still coupled to another particle (still in interaction).

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Actually, the above consideration is not complete. If particle-wall collision is simultaneously happening when two particles are interacting, nonvanishing Δv_j^0 appears, no matter which particle is hitting the wall. That is, nonvanishing Δv_j^0 appears once the wall comes into play during the interaction of the main particle and the background particle, and thus interrupts their otherwise "normal" interaction. This complication can cause non-trivial effect. Things will become clear in the following when we analyze this situation (Classes 2 and 3 in Section 3.4.3 when dealing with the backward collision).

In order to investigate the effect of Δv_j^0 arising from particle-particle interaction, we collect the cases having nonvanishing Δv_j^0. The basic idea is that Δv_j^0 is determined by the situation at $t = \frac{L}{v_j^0} = \frac{1}{2}T_j^0$. (The reason that we can use $\frac{1}{2}T_j^0$ instead of $\frac{1}{2}\left(T_j^0 + \Delta T_j^0\right)$ is that free particle model is sufficient.) Let's focus on the last particle-particle collision in the whole trip of the main particle. The namesake of "the last collision of the main particle" implies that nothing can happen between "the last collision" and "hitting the wall," that is, the last collision is the last event of the main particle before hitting the right wall and ending its trip. Therefore, with the information of the last particle-particle interaction of the main particle, the situation of the main particle at the moment hitting the wall ($t = \frac{L}{v_j^0} = \frac{1}{2}T_j^0$) can be determined, by the very idea of "the last collision."

In dealing with flying time period, the total effect can be decomposed into the number of collisions and the effect of each collision. Here we have a similar strategy. To understand the effect of Δv_j^0, we may decompose it into two parts. The first part is about the probability of a given situation of the last collision (Section 3.4.2). The second part is about the effect associated with the last collision (Section 3.4.3). The total effect is the product of the two parts (Section 3.4.4). This is what we are going to do.

Before studying Δv_j^0 for the interacting gas, we first describe a toy model in Section

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3.4.1. This is because, though the calculations for Δv_j^0 will be complicated, the picture one uses is basically the same as that in the much simpler toy model. It is a good thing having a clear picture for what we are calculating, especially when we have a lot of calculations to do.

3.4.1 Toy bean model

Before attacking interacting gases, here we study a toy model which involves putting some beans in a one-dimensional box. The toy bean model is as follows.

Consider a one-dimensional box of length L and some beans having no size. We put N beans in the box in a totally random manner. That is, the position distribution is homogeneous inside the box for each bean. A bean is labeled by its position. Now we are interested in the question, what is the probability that the right-most bean is sitting inside $(x, x + \Delta x)$? Here Δx is an infinitesimal spacing.

If the right-most bean is at x, it means that all the other $N - 1$ beans are in the region $(0, x)$. Since the beans are put randomly, the probability of a bean sitting in $(0, x)$ is just $\frac{x}{L}$. The probability that the right-most bean sits inside $(x, x + \Delta x)$ is given by

$$P(x) = N\left(\frac{\Delta x}{L}\right)\left(\frac{x}{L}\right)^{N-1} = \rho\Delta x\left(\frac{x}{L}\right)^{N-1} \tag{52}$$

where $\rho \equiv \frac{N}{L}$ is the number density. The factor of N is from the permutation of the N beans. The reasoning leading to the above formula is simple: The probability for the right-most bean to be in that small region is simply $\frac{\Delta x}{L}$, and then one has to place all the remaining $N - 1$ beans to its left (these beans can only sit in $(0, x)$). This then gives rise to the above formula. As a check, we find

$$\sum_{x=0}^{L} P(x) = \sum_{x=0}^{L} \rho\Delta x\left(\frac{x}{L}\right)^{N-1} = \int_0^L \rho dx\left(\frac{x}{L}\right)^{N-1} = 1. \tag{53}$$

From Eq.52, we can see that $P(x)$ is quite small if $\frac{x}{L} \nsim 1$. This is intuitively obvious.

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If the right-most bean is far from the right wall, the remaining $N-1$ beans simply don't have enough "leg room." When there are many beans in the box, the probability of finding all beans concentrating in the left side is extremely small. We are quite sure we can find at least one bean near the right wall. Therefore, when N is large, we only need to consider the cases of $x \approx L$ for nonvanishing probability.

Now let's consider the limits that $N \to \infty$, $L \to \infty$, while $\rho \equiv \frac{N}{L}$ is fixed. We consider such limit because it is the thermodynamic limit that is usually of interest. Consider a point at $x = L - \xi\frac{L}{N}$, where ξ is fixed when we take the limit. It means a point standing from the right wall with spacing $\xi\frac{L}{N}$. In this case, $\Delta x = -(\Delta\xi)\frac{L}{N}$ and is fixed when we take the limit. Notice that $\frac{L}{N}$ is the average spacing for each bean in the box, and it is fixed when the limit is considered. Taking the limit for such x, by Eq.52, we have

$$\begin{aligned}
\lim_{N\to\infty} P(x = L - \xi\frac{L}{N}) &= \lim_{N\to\infty} \rho\Delta x \left(\frac{L - \xi\frac{L}{N}}{L}\right)^{N-1} \\
&= (\rho\Delta x)\lim_{N\to\infty}\left(1 - \frac{\xi}{N}\right)^{N} \\
&= (\rho\Delta x)\, e^{-\xi} \\
&= (\rho\Delta x)\, e^{-\rho(L-x)}
\end{aligned} \tag{54}$$

which decays exponentially as x departs from $x = L$.

At this stage, we only put in the beans and find the corresponding probabilities specified by the position of the right-most bean. Now let's go one step further. First we consider some function $g(x)$ of the position of the right-most bean. The function is nonvanishing only for $x \in (L-d, L)$. We consider d to be small in the sense that $d \ll \frac{L}{N}$, namely $\rho d \ll 1$. That is, d is much smaller than the average spacing between two nearby beans. The average value of $g(x)$ weighted by the probability given by Eq.54

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is

$$\begin{aligned}\int_0^L dx\rho e^{-\rho(L-x)}g(x) &= \rho\int_{L-d}^L dx e^{-\rho(L-x)}g(x)\\ &= \rho\int_{L-d}^L dx g(x)\left(1-\rho\left(L-x\right)+\mathcal{O}\left((\rho d)^2\right)\right) \quad (55)\end{aligned}$$

The average value of $g(x)$, correct to first order of ρ, is

$$\rho\int_{L-d}^L dx g(x) = \int_{L-d}^L \left(\rho\left[e^{-\rho(L-x)}\mid_{x=L}\right]dx\right)g(x), \quad (56)$$

which means that we can just replace the exponential decay probability with a constant equal to the value at $x = L$. Around $x = L$, the probability decays exponentially in the form $e^{-\rho(L-x)}$. For x having a change of $\mathcal{O}(d)$, the probability changes by a factor of $e^{-\rho d} \approx (1-\rho d) \approx 1$. In other words, since $g(x)$ is nonvanishing only for $x \in (L-d, L)$, and d is much smaller than the decay rate of the probability, the probability is almost a constant in the domain when $g(x)$ is nonvanishing.

Here we summarize what we have learned in this toy bean model. Firstly, for putting N beans in the box, we may put the right-most bean first and then put the remaining $N-1$ beans with the constraint established by the right-most bean we just put in. Secondly, if thermodynamic limit is considered, the probability associated with the position of the right-most bean decays exponentially as the position of the right-most bean goes away from the right wall at $x = L$. Thirdly, if there is a function of the position of the right-most bean that has nonvanishing value only for $x \in (L-d, L)$, and d is small in the sense that $\rho d \ll 1$, then the average value of the function weighted by the probability is necessarily of first order in ρ, and the probability distribution can be approximated as being essentially the same as that right at $x = L$.

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3.4.2 Probability of the last collision

Equipped with lessons learned from the toy bean model, now let's deal with our interacting gas system.

The setting of the start of the last collision is that the main particle is at $L - d_3$ and the background particle that causes the last collision hits the main particle with v_k^0. We now put the N particles in the one-dimensional box one by one, like what we did in the toy bean model. The first step is putting the main particle, which is trivial. By construction, the main particle starts with $(x, t) = (0, 0)$ and ends with $(x, t) = (L, \frac{L}{v_j^0})$. Now let's put in the first background particle. The main particle has its last particle-particle interaction with a background particle, and we may call it the first background particle, since we put it in the box before all the other $N-2$ background particles. This first background particle plays the role of being the provider of the last particle-particle interaction of the main particle before it hits the right wall. To have non-trivial collision velocity (nonvanishing Δv_j^0), the position of the last collision needs to be close to the right wall so that the right wall can come into play during the last particle-particle interaction of the main particle. As the first background particle is put in, it establishes a constraint for the remaining $N - 2$ background particles. The constraint is that, the remaining $N - 2$ background particles should be put in the box in the manner that their collisions with the main particle are forbidden if the collision occurs after the main particle has its last collision with the first background particle, or else the collision with the first background particle is not "the last collision" of the main particle. In other words, the existence of the last collision provided by the first background particle establishes a constraint on the admissible way of putting the remaining $N - 2$ background particles. Notice that the information of the last collision is equivalent to the information of (x_k^0, v_k^0) of the first background particle.

Firstly, probability is associated with the last collision, which is equivalent to the state of the first background particle. Secondly, we have a function of the state of the

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first background particle, that is, the value of Δv_j^0 is determined by the state of the first background particle. Thirdly, the state of the first background particle determines the room for the remaining $N-2$ background particles. It is clear that the first background particle here is the counterpart of the right-most bean in the toy bean model.

In the toy bean model, as the right-most bean is put in the box at x, the admissible zone for the remaining $N-1$ beans is $(0, x)$, and the corresponding probability for each left bean is thus $\frac{x}{L}$. For the interacting gas, what is the admissible zone for the remaining $N-2$ background particles and the corresponding probability? The answer is shown in Fig. 12. In Fig. 12, the lower half part is the mirror image of the upper half part.

The remaining $N-2$ background particles are put in at the moment that the main particle starts its last collision with the first background particle, namely $t = \frac{L}{v_j^0} - \frac{d_3}{v_j^0}$. The position of one of the remaining $N-2$ background particles with free particle velocity v_l^0 at this moment ($t = \frac{L}{v_j^0} - \frac{d_3}{v_j^0}$) is defined as $\widetilde{x}_l$. In order to avoid the collisions between the remaining $N-2$ background particles and the main particle in $\frac{L-d_3}{v_j^0} < t < \frac{L}{v_j^0}$, there are some constraints for the position and the velocity of the remaining $N-2$ background particles. The requirement for $\widetilde{x}_l$ is that

$$0 < \widetilde{x}_l < L - d_3 \tag{57}$$

The admissible velocity is a function of $\widetilde{x}_l$, as shown in Fig. 12. With the help of Fig. 12, we can see that the admissible velocity has the range of

$$-\frac{L + \widetilde{x}_l}{d_3} v_j^0 < v_l^0 < \frac{L - \widetilde{x}_l}{d_3} v_j^0 \tag{58}$$

In order to get the probability, we introduce the assumptions that spatial distribution is homogeneous and velocity distribution is Maxwell velocity distribution. The probability of one of the remaining $N-2$ background particles with free particle velocity

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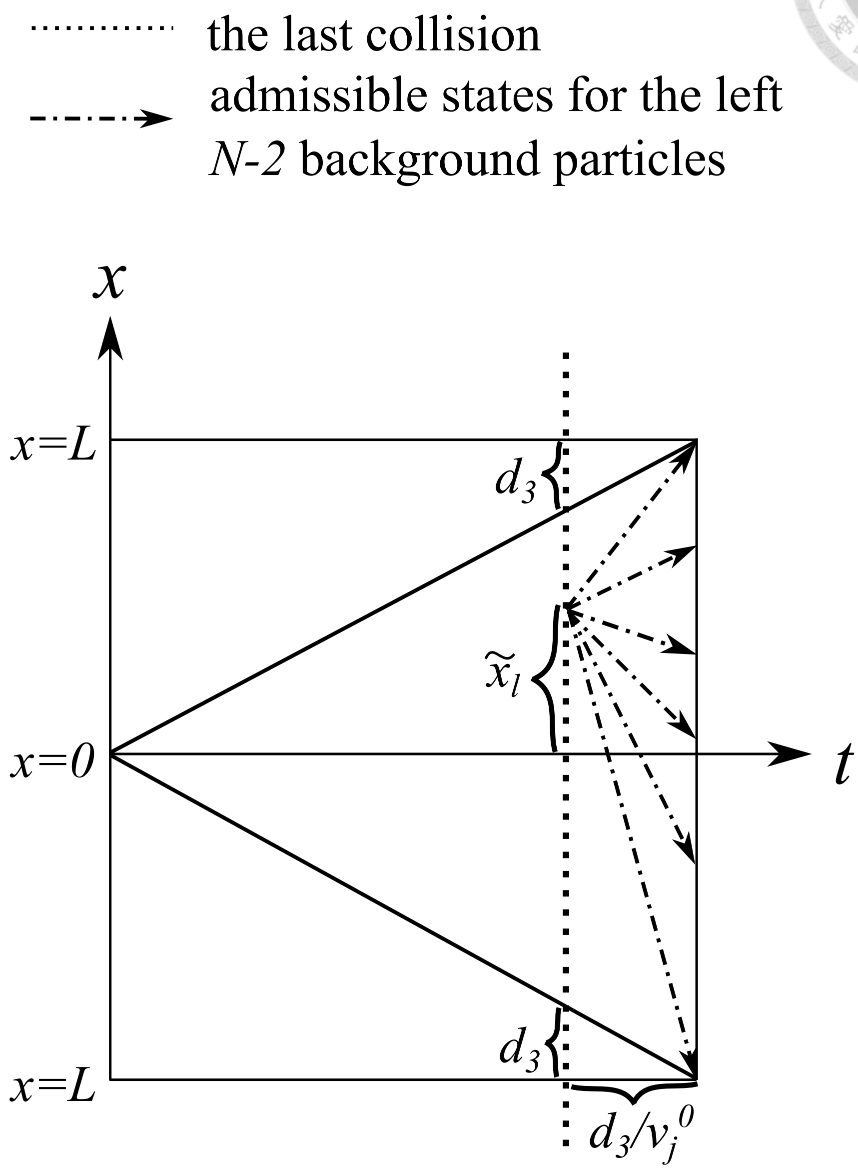

Figure 12: Admissible zone for the remaining $N-2$ background particles under the constraint established by the last collision provided by the first background particle. The idea is that the remaining $N-2$ background particles cannot touch the main particle (solid line) for $t \geq \frac{L}{v_j^0} - \frac{d_3}{v_j^0}$, where $L - d_3$ is the position of the main particle at the beginning of the last collision. The position of one of the remaining $N-2$ background particles with free particle velocity v_l^0 at $t = \frac{L}{v_j^0} - \frac{d_3}{v_j^0}$ is denoted as $\widetilde{x}_l$. The lower half part is the mirror image of the upper half part.

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v_l^0 in the admissible zone is given by

$$\begin{aligned}
&\text{probability of a single background particle} \\
&= \int_0^{L-d_3} \frac{d\widetilde{x}_l}{L} \int_{-\frac{L+\widetilde{x}_l}{d_3}v_j^0}^{\frac{L-\widetilde{x}_l}{d_3}v_j^0} dv_l^0 \frac{1}{\sqrt{a\pi}} e^{-\frac{\left(v_l^0\right)^2}{a}} \\
&= \frac{1}{2L}\int_0^{L-d_3} d\widetilde{x}_l \left(\mathrm{erf}\left(\frac{1}{\sqrt{a}}\frac{L-\widetilde{x}_l}{d_3}v_j^0\right) - \mathrm{erf}\left(\frac{1}{\sqrt{a}}\frac{L+\widetilde{x}_l}{d_3}v_j^0\right)\right) \\
&= \frac{1}{2L}\left([2L-d_3]\,\mathrm{erf}\left(\frac{v_j^0}{\sqrt{a}}\left[\frac{2L}{d_3}-1\right]\right) - d_3\mathrm{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)\right) \\
&+ \frac{1}{2L}\left(\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}d_3\left(e^{-\frac{\left(v_j^0\right)^2}{a}\left[\frac{2L}{d_3}-1\right]^2} - e^{-\frac{\left(v_j^0\right)^2}{a}}\right)\right)
\end{aligned} \tag{59}$$

Since the increasing of d_3 means that the admissible zone of the remaining $N-2$ background particles becomes smaller, we expect that the probability of a single background particle will decrease as d_3 increases. In the toy bean model, when considering N beans and taking thermodynamic limit, the probability associated with the position of the right-most bean decays exponentially. Do we have similar feature here? The answer is yes and the derivation is in Appendix B. The result is

$$\text{probability of } (N-2) \text{ background particles} = e^{-\left(\frac{1}{2}\left[1+\mathrm{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\right)\rho d_3} \tag{60}$$

Compare Eq.60 with Eq.54. When thermodynamic limit is implemented, the probability decays exponentially with the distance from the right wall ($x = L$) for both the toy bean model and the interacting gas system. In the toy bean model, a bean is labeled by one single parameter, the position. For the gas system, a gas particle is labeled by two parameters, the position and the velocity. In putting the remaining $N-2$ background particles, the admissible velocity couples to the admissible position (Eq.58), due to the constraint established by the first background particle. This is the reason that the gas system is more complicated than the toy bean model and why there

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is a coefficient consists of $\frac{v_j^0}{\sqrt{a}}$ in the exponential function.

Eq.60 corresponds to $\left(\frac{x}{L}\right)^{N-1}$ in Eq.52. To get the complete probability, we need to put in the part of the first background particle, which corresponds to $\frac{\Delta x}{L}$ in Eq.52. A particle with initial condition $\{\text{position} \in \left(x_k^0, x_k^0 + \Delta x_k^0\right), \text{velocity} \in \left(v_k^0, v_k^0 + \Delta v_k^0\right)\}$ has the probability of $\left(\frac{\Delta x_k^0}{L}\right)\left(f\left(v_k^0\right)\Delta v_k^0\right)$. For the probability of the first background particle, is it given by $\left(\frac{\Delta d_3}{L}\right)\left(f\left(v_k^0\right)\Delta v_k^0\right)$? The answer is no. There is an additional factor, which can be seen by Fig. 13.

In Fig. 13, L_1 is the main particle, L_2 is the first background particle with $x_k^0 = 0$, and L_3 is the first background particle with $x_k^0 = \Delta x_k^0$. So the equations are

$$
\begin{aligned}
&L_1 : x = v_j^0 t \\
&L_2 : x = v_k^0 t \\
&L_3 : x = v_k^0 t + \Delta x_k^0
\end{aligned}
\tag{61}
$$

And we have

$$L_1 \cap L_2 = (0, 0) \tag{62}$$

$$L_1 \cap L_3 = \left(\frac{\Delta x_k^0}{v_j^0 - v_k^0}, v_j^0 \frac{\Delta x_k^0}{v_j^0 - v_k^0}\right) \tag{63}$$

So Δd_3 corresponding to Δx_k^0 is

$$\Delta d_3 = v_j^0 \frac{\Delta x_k^0}{v_j^0 - v_k^0} - 0 = \frac{v_j^0}{v_j^0 - v_k^0} \Delta x_k^0 \tag{64}$$

And hence

$$\frac{\Delta x_k^0}{L} = \left(1 - \frac{v_k^0}{v_j^0}\right) \frac{\Delta d_3}{L} \tag{65}$$

Here we draw Fig. 13 with $0 < v_k^0 < v_j^0$. A careful analysis for all v_k^0 (just draw more

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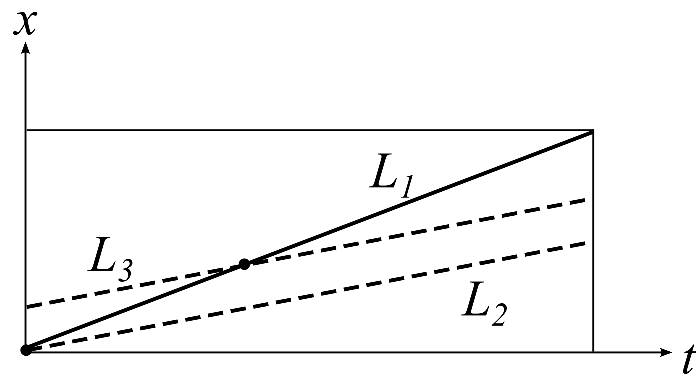

Figure 13: $x-t$ diagram for the main particle and the first background particle. L_1 is the main particle, L_2 and L_3 are the first background particle with different initial positions.

diagrams like Fig. 13), namely considering the cases for $v_k^0<0$ and $v_k^0>v_j^0$, shows

$$\frac{\Delta x_k^0}{L}=\mid 1-\frac{v_k^0}{v_j^0}\mid\frac{\Delta d_3}{L} \tag{66}$$

The probability of the first background particle is given by

$$\left(\mid 1-\frac{v_k^0}{v_j^0}\mid\frac{\Delta d_3}{L}\right)\left(f\left(v_k^0\right)\Delta v_k^0\right) \tag{67}$$

Finally, the complete probability of the last collision is the product of Eq.60 and Eq.67 and the permutation factor N

$$N\left(\mid 1-\frac{v_k^0}{v_j^0}\mid\frac{\Delta d_3}{L}\right)\left(f\left(v_k^0\right)\Delta v_k^0\right)e^{-\left(\frac{1}{2}\left[1+\mathrm{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\right)\rho d_3} \tag{68}$$

It is the counterpart of Eq.54 for the toy bean model.

This is how we construct the probability for a given situation of the main particle colliding with the first background particle around the right wall. Having probability in hand, now it's time to analyze possible situations around the wall and their corresponding effects (nonvanishing Δv_j^0), which plays the role of the counterpart of the

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function $g(x)$ in Eq.55 in the toy bean model.

3.4.3 Situation around the wall

Let's consider non-trivial situations (nonvanishing Δv_j^0) of the main particle around the wall. For square well potential, the force between two interacting particles exists only at $r = d_2$ and $r = d_1$. In other words, when two particles interact, they are actually two free particles inside the potential for $d_1 < r < d_2$. This feature of square well potential simplifies our analysis that follows. Fig. 14 shows the motions of two particles interacting via square well potential, as viewed in the center-of-mass frame. The relation between v_{in} and v_{out} (v_{in} and v_{out} are defined in the center-of-mass frame) is

$$v_{in} = \sqrt{(v_{out})^2 + \frac{\epsilon}{m}}$$
$$v_{out} = \sqrt{(v_{in})^2 - \frac{\epsilon}{m}} \tag{69}$$

Particle-particle interaction is easy to analyze in the center-of-mass frame. However, to investigate the role played by the wall, lab frame is a better choice. Therefore, in the following analysis, we will switch between center-of-mass frame and lab frame. Note that collision velocity is defined in the lab frame. In the following analysis, we separate the situations of the last collision into forward collision part and backward collision part.

Forward collision part

The situation for the beginning of the forward collision is shown in Fig. 15. The velocity of the first background particle is not arbitrary, though. Firstly, the occurrence of forward collision implies $v_k^0 < v_j^0$. Secondly, from Fig. 14, we see that, in the center-of-mass frame, when compared with the beginning of the interaction, the two arrows of momentum just exchange their positions when the interaction ends. Switching to the

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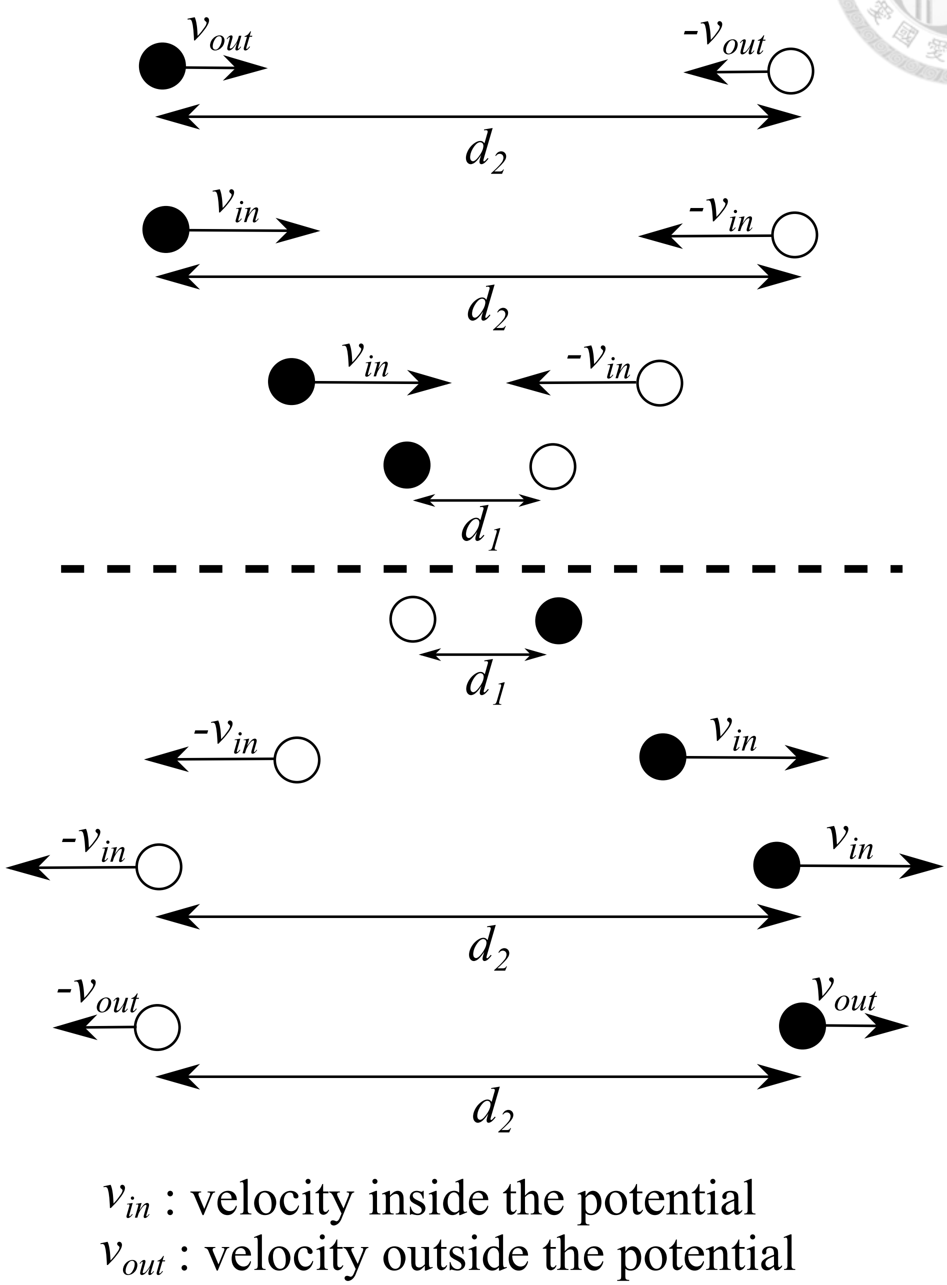

Figure 14: The motions of two particles interacting via square well potential, in center-of-mass frame. Velocity changes only at the beginning ($r = d_2$) and the ending ($r = d_2$) of the interaction.

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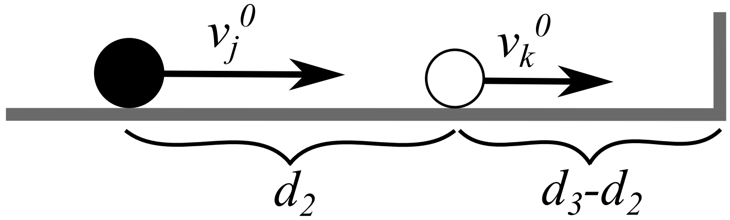

Figure 15: The initial state of the last collision being a forward collision.

lab frame, we can see that, if the center-of-mass velocity $v_{CM} = \frac{v_j^0 + v_k^0}{2}$ is not positive, then the two particles don't hit the wall until their interaction is over. Combining the two considerations, the condition for v_k^0 is

$$-v_j^0 < v_k^0 < v_j^0. \tag{70}$$

If there is no wall, the main particle will have a displacement to the right, as shown in Eq.13, when the forward collision ends. For the main particle to hit the wall when it is still in the potential well, d_3 should be shorter than the displacement of the main particle in the whole interaction process. That is, by Eq.13, the condition for d_3 is

$$d_2 < d_3 < d_2 + v_{CM}\Delta t_{interaction} = d_2 + v_{CM}\frac{d_2 - d_1}{v_{in}} = d_2 + (d_2 - d_1)\frac{\frac{v_j^0 + v_k^0}{2}}{\sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}}. \tag{71}$$

Here we have used $v_{out} = \frac{v_j^0 - v_k^0}{2}$ and Eq.69. If the main particle hits the wall when it is in the potential well, by Eq.69, the collision velocity is

$$v_j^0 + \Delta v_j^0 = v_{CM} + v_{in} = \frac{v_j^0 + v_k^0}{2} + \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}. \tag{72}$$

But is this the whole story to the forward collision part? Actually, we need to check one more thing. The idea is as follows. During the process of an interaction, if there is a particle-wall collision and hence the particle hitting the wall reverses its velocity (in the lab frame), the relative velocity of the two particles will change abruptly, and

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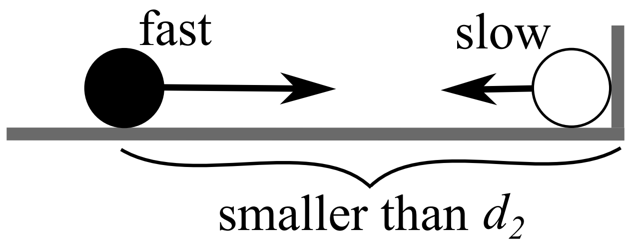

Figure 16: The first background particle hits the wall and reverses its velocity, while the main particle is moving to the right wall. The two particles are still in interaction and their separation is smaller than d_2. The speed of the main particle is larger than the speed of the first background particle.

so the effect of particle-particle interaction on the two particles also changes. This is how the wall interrupts the otherwise smooth particle-particle interaction. The result is, after the interaction is over and the two particles become two free particles again, their velocities differ from their original free particle velocities before they interact. In the presence of the wall, we can have nonvanishing Δv_j^0 even if the main particle hits the wall as a free particle. This is the non-trivial effect provided by the wall.

Let's check whether there is such situation in the forward collision part. For such situation to happen, the first background particle hits the wall before the main particle passes it. In other words, the first background particle hits the wall in the upper half part in Fig. 14. As the first background particle hits the wall, its velocity (in the lab frame) is reversed, and starts flying to the left. The thing to be checked is if there is any chance that the two particles will decouple before the main particle hits the wall. The answer is no, and here is the argument.

By Eq.70, the speed of the first background particle is smaller than the speed of the main particle. Since it is the forward collision that is being considered and particle-particle interaction is attractive, the speed of the first background particle is still smaller than the speed of the main particle inside the potential. The reflection provided by the wall only changes the sign of the velocity of the first background particle, but not its speed. At the moment when the first background particle hits the wall, the distance

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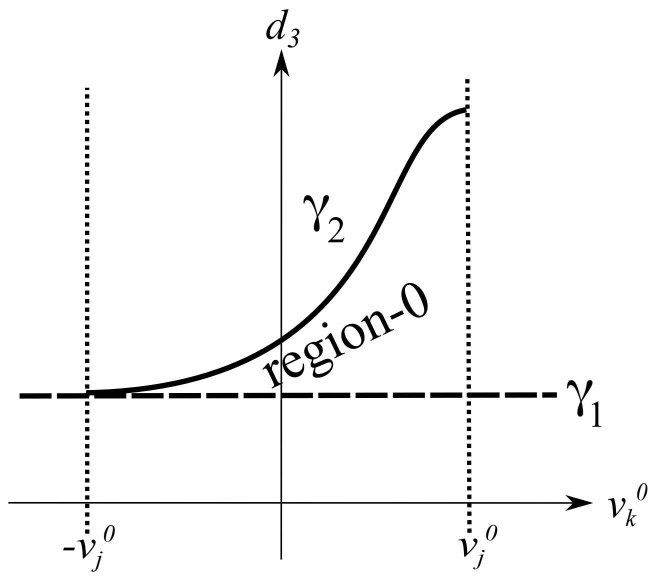

Figure 17: Nonvanishing Δv_j^0 in forward collision part. Nonvanishing Δv_j^0 appears in region-0. Detailed information is given by Eq.73 and Eq.74.

between the main particle and the wall, namely the distance between the main particle and the first background particle, is smaller than d_2. The situation is shown in Fig. 16. In Fig. 16, since the speed of the first background particle is smaller than the speed of the main particle, and their separation is smaller than d_2, as the main particle hits the wall, their separation is still smaller than d_2 and hence the two particles are still coupled when the main particle hits the wall. Therefore, the possibility that the main particle hits the wall as a free particle while the collision velocity is not v_j^0 doesn't exist.

Finally, by Eq.70, Eq.71 and Eq.72, the nonvanishing Δv_j^0 in forward collision part is summarized in Fig. 17. With

$$\begin{aligned} &\gamma_1 : d_3 = d_2 \\ &\gamma_2 : d_3 = d_2 + (d_2 - d_1)\frac{\frac{v_j^0 + v_k^0}{2}}{\sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} \end{aligned} \tag{73}$$

$$\Delta v_j^0 \,|_{region-0} = \frac{-v_j^0 + v_k^0}{2} + \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}} \tag{74}$$

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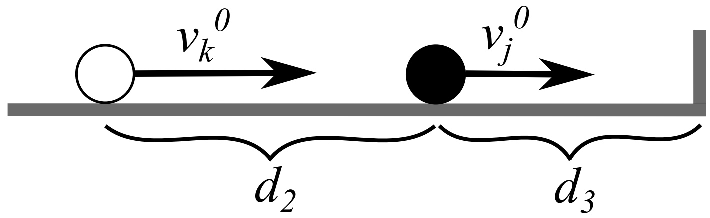

Figure 18: The initial state of the last collision being a backward collision.

Backward collision part

The situation for the beginning of the backward collision is shown in Fig. 18. The occurrence of backward collision implies

$$v_k^0 > v_j^0 \tag{75}$$

In order to have non-trivial situations, at least one particle hits the wall before the particle-particle interaction ends. That is, d_3 should be short enough. By Eq.13, the necessary condition for d_3 that guarantees the above situations is

$$(d_2 + d_3) < d_2 + v_{CM}\Delta t_{interaction} = d_2 + v_{CM}\frac{d_2 - d_1}{v_{in}} = d_2 + (d_2 - d_1)\frac{\frac{v_j^0 + v_k^0}{2}}{\sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}}. \tag{76}$$

So the basic constraint for d_3 is

$$0 < d_3 < (d_2 - d_1)\frac{\frac{v_j^0 + v_k^0}{2}}{\sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}}. \tag{77}$$

Eq.75 and Eq.77 are necessary conditions to have nonvanishing Δv_j^0. Under the two necessary conditions, what is the situation of the main particle hitting the wall? As we are going to see in the following analysis, the situations can be classified into three classes (Class 1, Class 2 and Class 3) by different forms of collision velocities. Note that we have only one class for forward collision part (one form of collision velocity, as

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shown in Eq.74). Backward collision part is more complicated than forward collision part, in the sense that there are three classes instead of just one.

The critical situation separating the three classes is shown in Fig. 19. In Fig. 19 (in the lab frame), step-1 starts with the beginning of backward collision and ends with the event that the first background particle hits the wall; step-2 starts with the end of step-1 and ends at the moment when the two particles are going to decouple. In the whole process of step-1 and step-2, the speed of the first background particle is always larger than the main particle.

In Fig. 19, we can see that

$$\begin{aligned} &\text{total time spent by the main particle} \\ &= \text{time for step} - 1 \text{ spent by the first background particle} \\ &+ \text{time for step} - 2 \text{ spent by the first background particle} \end{aligned} \tag{78}$$

and so we have

$$\frac{d_3 \mid_{critical}}{v_{CM} - v_{in}} = \frac{d_2 + d_3 \mid_{critical} - d_1}{v_{CM} + v_{in}} + \frac{d_2 - d_1}{v_{CM} + v_{in}} = \frac{d_3 \mid_{critical}}{v_{CM} + v_{in}} + 2\frac{d_2 - d_1}{v_{CM} + v_{in}} \tag{79}$$

The critical value of d_3 in Fig. 19 is given by

$$d_3 \mid_{critical} = (d_2 - d_1)\,\frac{v_{CM} - v_{in}}{v_{in}} = (d_2 - d_1)\left(\frac{\frac{v_j^0 + v_k^0}{2}}{\sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} - 1\right) \tag{80}$$

Class 1:

In Class 1, $d_3 < d_3 \mid_{critical}$. In this class, the main particle hits the wall when it is in the potential well. The situation is the same as that in the forward collision part. The only difference is that the main particle is the right particle but not the left one. The

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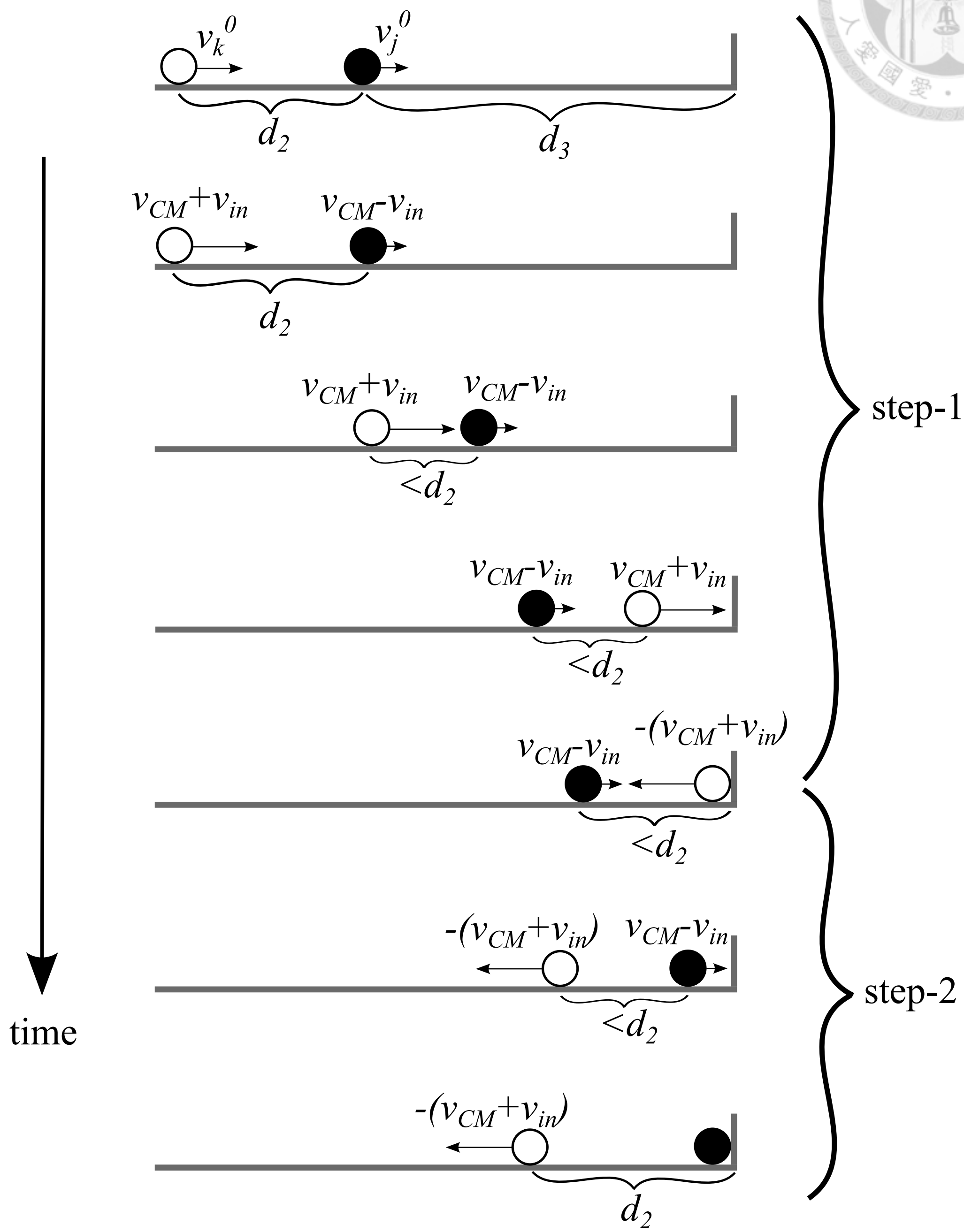

Figure 19: Critical situation that separates the three classes (Class 1, Class 2 and Class 3) for the last collision being a backward collision. The figure shows the motion of the main particle and the first background particle in the lab frame. The value of d_3 in this critical situation is denoted as $d_3\,|_{critical}$.

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collision velocity is

$$v_j^0 + \Delta v_j^0 = v_{CM} - v_{in} = \frac{v_j^0 + v_k^0}{2} - \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}} \tag{81}$$

Class 2:

In Class 2, $d_3 > d_3 \mid_{critical}$. In this class, the main particle hits the wall after it decouples with the first background particle and becomes a free particle again. However, the velocity of the main particle being a free particle is no longer v_j^0, since the wall comes into play and alters particle-particle interaction due to particle-wall collision of the first background particle at the end of step-1. To calculate the new free particle velocity of the main particle, we use Eq.69. Before the two particles decouple and become two free particles again, their velocities are $v_{CM} - v_{in}$ and $-(v_{CM} + v_{in})$. The center-of-mass velocity now is

$$\overline{v_{CM}} = \frac{(v_{CM} - v_{in}) + (-(v_{CM} + v_{in}))}{2} = -v_{in} \tag{82}$$

And v_{in} now becomes

$$\overline{v_{in}} = \frac{(v_{CM} - v_{in}) - (-(v_{CM} + v_{in}))}{2} = v_{CM} \tag{83}$$

By Eq.69 and Eq.83, v_{out} now is

$$\overline{v_{out}} = \sqrt{(\overline{v_{in}})^2 - \frac{\epsilon}{m}} = \sqrt{(v_{CM})^2 - \frac{\epsilon}{m}} \tag{84}$$

By Eq.82 and Eq.84, the collision velocity (in the lab frame), namely the free particle

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velocity of the main particle in such situation, is given by

$$\begin{aligned} v_j^0 + \Delta v_j^0 &= \overline{v_{CM}} + \overline{v_{out}} \\ &= -v_{in} + \sqrt{(v_{CM})^2 - \frac{\epsilon}{m}} \\ &= \sqrt{\left(\frac{v_j^0 + v_k^0}{2}\right)^2 - \frac{\epsilon}{m}} - \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}} \end{aligned} \tag{85}$$

Class 3:

Class 1 and Class 2 do not exhaust all the possibilities, as explained below. In Fig. 19, we actually already assume that the main particle always has a positive velocity. But this is not always guaranteed. When the relative velocity of two particles is small, the effect of particle-particle interaction ϵ is relatively strong, so much so that it might change the direction of the velocities. If the main particle has a negative velocity, it cannot hit the wall, and the collision velocity in such case is zero. There are two situations when no collision happens between the main particle and the wall.

The first situation is that the velocity of the main particle is negative at the moment right after the collision starts. That is,

$$v_{CM} - v_{in} < 0, \tag{86}$$

and it means

$$\frac{v_j^0 + v_k^0}{2} < \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}. \tag{87}$$

In this case, v_k^0 is given by

$$v_k^0 < \frac{\frac{\epsilon}{m}}{v_j^0}. \tag{88}$$

The second situation is that the velocity of the main particle is negative after they

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decouple. That is, the new free particle velocity in Eq.85 is negative. The condition is

$$\sqrt{\left(\frac{v_j^0+v_k^0}{2}\right)^2-\frac{\epsilon}{m}}-\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}<0. \tag{89}$$

In this case, v_k^0 is given by

$$v_k^0<\frac{2\frac{\epsilon}{m}}{v_j^0}. \tag{90}$$

Notice that for $\frac{\frac{\epsilon}{m}}{v_j^0}<v_k^0<\frac{2\frac{\epsilon}{m}}{v_j^0}$, the velocity of the main particle is always positive in step-1 and step-2 in Fig. 19. In the second situation and for in Class 3 to happen, $d_3>d_3\mid_{critical}$ is required.

In Class 1, the main particle hits the wall during its interaction with the first background particle. In Class 2, the main particle hits the wall when it becomes a free particle after it decouples with the first background particle. In Class 3, the main particle simply cannot hit the wall.

The nonvanishing Δv_j^0 in the backward collision part is summarized in Fig. 20. With

$$\begin{aligned}\gamma_3 &: (d_2-d_1)\left(\frac{\frac{v_j^0+v_k^0}{2}}{\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}}-1\right)\\ \gamma_4 &: (d_2-d_1)\frac{\frac{v_j^0+v_k^0}{2}}{\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}}\end{aligned} \tag{91}$$

$$\begin{aligned}\text{Class 1} &: \Delta v_j^0\mid_{region-1}=\frac{-v_j^0+v_k^0}{2}-\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}\\ \text{Class 2} &: \Delta v_j^0\mid_{region-2}=-v_j^0+\left(\sqrt{\left(\frac{v_j^0+v_k^0}{2}\right)^2-\frac{\epsilon}{m}}-\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}\right)\\ \text{Class 3} &: \Delta v_j^0\mid_{region-3}=-v_j^0\end{aligned} \tag{92}$$

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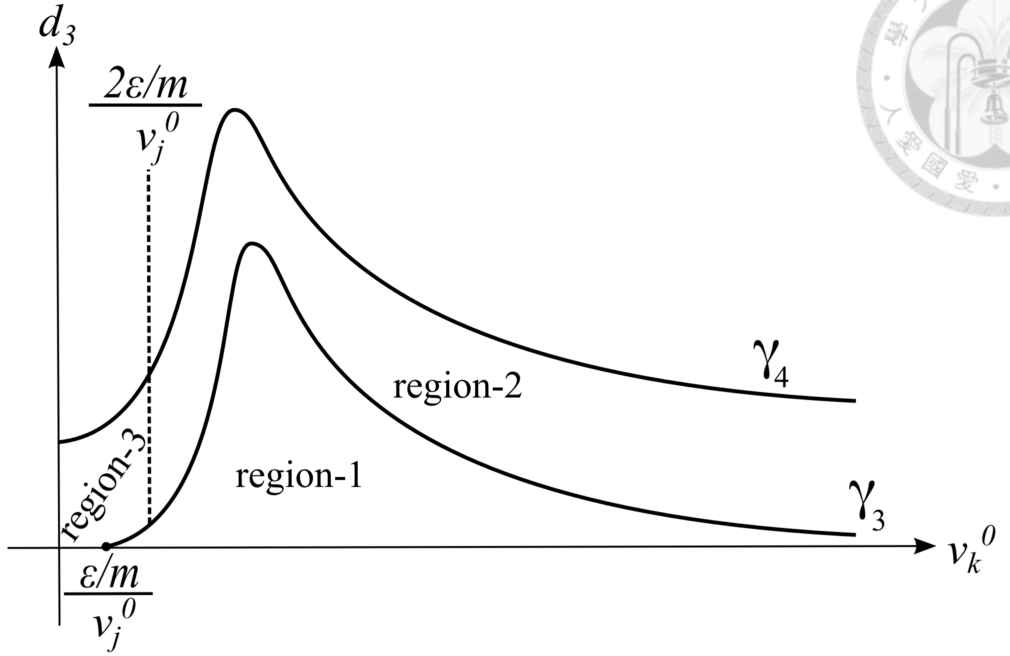

Figure 20: Nonvanishing Δv_j^0 in backward collision part. Region-1,2,3 correspond to Class 1,2,3, respectively. In addition, region for $v_k^0 < v_j^0$ is forbidden. Detailed information is given by Eq.91 and Eq.92.

Note that γ_4 comes from Eq.77. Of course, we also have the condition

$$v_k^0 > v_j^0 \tag{93}$$

and hence the region that $v_k^0 < v_j^0$ is forbidden.

By Eq.93 and Fig. 20, since $v_k^0 > v_j^0$, Class 3 vanishes for $v_j^0 > \frac{2\frac{\epsilon}{m}}{v_j^0}$. That is, there is no chance for Class 3 to happen if

$$v_j^0 > \sqrt{\frac{2\epsilon}{m}}. \tag{94}$$

3.4.4 Correction to the collision velocity

Having considered all the factors, we are now in a position to actually calculate the combined result for Δv_j^0. What we need to do now is quite straightforward. The task

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we are going to do is putting Eq.68 (probability), Eq.74 (Δv_j^0 for forward collision part) and Eq.92 (Δv_j^0 for backward collision part) together and then integrate over the four regions shown in Fig. 17 and Fig. 20. That is, we are going to deal with the integral

$$\begin{aligned}
&\Delta v_j^0 \\
&= \left(\int \Delta v_j^0 \mid_{region-0} + \int \Delta v_j^0 \mid_{region-1} + \int \Delta v_j^0 \mid_{region-2} + \int \Delta v_j^0 \mid_{region-3} \right) \\
&\left(N \left(\mid 1 - \frac{v_k^0}{v_j^0} \mid \frac{\Delta d_3}{L} \right) \left(f\left(v_k^0\right) \Delta v_k^0 \right) e^{-\left(\frac{1}{2} \left[1 + \operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}} \right) + \frac{\sqrt{a}}{\sqrt{\pi} v_j^0} e^{-\frac{\left(v_j^0\right)^2}{a}} \right] \right) \rho d_3} \right) \\
&= \rho \int d(d_3) \int dv_k^0 f\left(v_k^0\right) \mid 1 - \frac{v_k^0}{v_j^0} \mid e^{-\left(\frac{1}{2} \left[1 + \operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}} \right) + \frac{\sqrt{a}}{\sqrt{\pi} v_j^0} e^{-\frac{\left(v_j^0\right)^2}{a}} \right] \right) \rho d_3} \\
&\left(\Delta v_j^0 \mid_{region-0} + \Delta v_j^0 \mid_{region-1} + \Delta v_j^0 \mid_{region-2} + \Delta v_j^0 \mid_{region-3} \right)
\end{aligned} \tag{95}$$

Although we have used some arguments to simplify our calculations (Appendix B), evaluating Eq.95 is still quite a formidable task. Therefore, let's stop and think whether it can be simplified further.

Recall that in the toy bean model, in Eq.55, we introduced a function $g(x)$ of the position x of the right-most bean. In Eq.56, we see that if the accuracy of the average value of $g(x)$ is kept to the first order of ρ, $g(x)$ in the integral can be replaced by a constant of $g\left(x = L\right)$. The reason is that the nonvanishing domain of $g(x)$ is much shorter than the decay rate of the exponential function in probability distribution. The function $g(x)$ in the toy bean model is the counterpart of $\Delta v_j^0 \mid_{region-0}, \Delta v_j^0 \mid_{region-1}, \Delta v_j^0 \mid_{region-2}, \Delta v_j^0 \mid_{region-3}$. Inspired by the toy bean model, we might make the guess that maybe it is all right to replace the exponential decay part in the probability distribution by unity. As it turns out, this is indeed the case, due to the feature that the probability decays slowly. The argument is presented in Appendix C. So, Eq.95 can be simplified to

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$$\Delta v_j^0 = \rho \int d(d_3) \int dv_k^0 f\left(v_k^0\right) \mid 1 - \frac{v_k^0}{v_j^0} \mid \times \left(\Delta v_j^0 \mid_{region-0} + \Delta v_j^0 \mid_{region-1} + \Delta v_j^0 \mid_{region-2} + \Delta v_j^0 \mid_{region-3}\right). \quad (96)$$

Now let's take a look at $\Delta v_j^0 \mid_{region-3}$. By Eq.94, Class 3 in backward collision part occurs only for small u_j^0 satisfying

$$u_j^0 < \sqrt{\frac{\epsilon}{k_B T}}. \quad (97)$$

Since $\Delta v_j^0 \mid_{region-3}$ occurs only for small velocity, its contribution is negligible when we sum over all velocities to get the particle-particle interaction correction in momentum transferred. The argument is presented in Appendix D. And so Eq.96 is now simplified to

$$\Delta v_j^0 = \rho \int d(d_3) \int dv_k^0 f\left(v_k^0\right) \mid 1 - \frac{v_k^0}{v_j^0} \mid \left(\Delta v_j^0 \mid_{region-0} + \Delta v_j^0 \mid_{region-1} + \Delta v_j^0 \mid_{region-2}\right). \quad (98)$$

We would like to point out that, despite our arguing that the effect of Class 3 in backward collision gives negligible contribution to the equation of state, in no way does it immediately imply that we can just throw away the effect of Class 3 in the backward collision when dealing with Δv_j^0. If the effect of Class 3 in the backward collision were thrown away in Eq.98, we would lose the information for $u_j^0 < \sqrt{\frac{\epsilon}{k_B T}}$ altogether. That is, the result of Δv_j^0 we are going to calculate is valid only for $u_j^0 > \sqrt{\frac{\epsilon}{k_B T}}$. Fortunately, we do not have to worry about including $u_j^0 < \sqrt{\frac{\epsilon}{k_B T}}$, since $\frac{\epsilon}{k_B T}$ is extremely small by our construction. In other words, though we do lose the contribution to Δv_j^0 for particles with extremely slow velocity, the final correction to the equation of state is still correct up to the accuracy we want to preserve.

Time for calculating Δv_j^0 via Eq.98.

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Contribution from $\Delta v_j^0 \mid_{region-0}$:

$$
\begin{aligned}
& \Delta v_j^0 \mid_{from-region-0} \\
= \; & \rho \int_{-v_j^0}^{v_j^0} dv_k^0 f\left(v_k^0\right)\left(1-\frac{v_k^0}{v_j^0}\right)\left(\frac{-v_j^0+v_k^0}{2}+\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}\right) \\
& \times\left[\left(d_2-d_1\right) \frac{\frac{v_j^0+v_k^0}{2}}{\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}}\right] \\
= \; & \frac{\rho\left(d_2-d_1\right)}{v_j^0} \int_{-v_j^0}^{v_j^0} dv_k^0 f\left(v_k^0\right)\left(v_j^0-v_k^0\right)\left(\frac{v_j^0+v_k^0}{2}-\frac{\frac{v_j^0+v_k^0}{2} \frac{v_j^0-v_k^0}{2}}{\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}}\right) \\
= \; & \frac{\rho\left(d_2-d_1\right) \sqrt{a}}{\sqrt{\pi} u_j^0} \int_{-u_j^0}^{u_j^0} du_k^0 e^{-\left(u_k^0\right)^2}\left(u_j^0-u_k^0\right)\left(\frac{u_j^0+u_k^0}{2}-\frac{\frac{u_j^0+u_k^0}{2} \frac{u_j^0-u_k^0}{2}}{\sqrt{\left(\frac{u_j^0-u_k^0}{2}\right)^2+\frac{1}{2} \frac{\epsilon}{k_B T}}}\right)
\end{aligned} \tag{99}
$$

Expand $\Delta v_j^0 \mid_{from-region-0}$ to the first order of $\frac{\epsilon}{k_B T}$, and we have

$$
\Delta v_j^0 \mid_{from-region-0}=\left(\frac{\rho\left(d_2-d_1\right) \sqrt{a}}{2 \sqrt{\pi} u_j^0} \int_{-u_j^0}^{u_j^0} du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0+u_k^0}{u_j^0-u_k^0}\right) \frac{\epsilon}{k_B T}. \tag{100}
$$

Contribution from $\Delta v_j^0 \mid_{region-1}$:

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$$
\begin{aligned}
&\Delta v_j^0 \mid_{from-region-1} \\
= \;& \rho \int_{v_j^0}^{\infty} dv_k^0 f\left(v_k^0\right) \left(\frac{v_k^0}{v_j^0} - 1\right) \left(\frac{-v_j^0 + v_k^0}{2} - \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}\right) \\
&\times \left[\left(d_2 - d_1\right) \left(\frac{\frac{v_j^0 + v_k^0}{2}}{\sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} - 1 \right) \right] \\
= \;& \frac{\rho\left(d_2 - d_1\right)}{v_j^0} \int_{v_j^0}^{\infty} dv_k^0 f\left(v_k^0\right)\left(v_j^0 - v_k^0\right) \left(v_k^0 - \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}} + \frac{\frac{v_j^0 + v_k^0}{2}\frac{v_j^0 - v_k^0}{2}}{\sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} \right) \\
= \;& \frac{\rho\left(d_2 - d_1\right)\sqrt{a}}{\sqrt{\pi} u_j^0} \int_{u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2} \left(u_j^0 - u_k^0\right) \\
&\times \left(u_k^0 - \sqrt{\left(\frac{u_j^0 - u_k^0}{2}\right)^2 + \frac{1}{2}\frac{\epsilon}{k_B T}} + \frac{\frac{u_j^0 + u_k^0}{2}\frac{u_j^0 - u_k^0}{2}}{\sqrt{\left(\frac{u_j^0 - u_k^0}{2}\right)^2 + \frac{1}{2}\frac{\epsilon}{k_B T}}} \right) \qquad (101)
\end{aligned}
$$

Expand $\Delta v_j^0 \mid_{from-region-1}$ to the first order of $\frac{\epsilon}{k_B T}$, and we have

$$
\Delta v_j^0 \mid_{from-region-1} = \left(\frac{\rho\left(d_2 - d_1\right)\sqrt{a}}{2\sqrt{\pi} u_j^0} \int_{u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2} \left(\frac{u_j^0 + u_k^0}{u_j^0 - u_k^0} + 1 \right) \right) \frac{\epsilon}{k_B T}. \qquad (102)
$$

Contribution from $\Delta v_j^0 \mid_{region-2}$:

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$$
\begin{aligned}
& \Delta v_j^0 \mid_{from-region-2} \\
= \ & \rho \int_{v_j^0}^{\infty} dv_k^0 f\left(v_k^0\right)\left(\frac{v_k^0}{v_j^0}-1\right) \\
& \times\left(-v_j^0+\left(\sqrt{\left(\frac{v_j^0+v_k^0}{2}\right)^2-\frac{\epsilon}{m}}-\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}\right)\right)\left[\left(d_2-d_1\right)\right] \\
= \ & \frac{\rho\left(d_2-d_1\right)\sqrt{a}}{\sqrt{\pi} u_j^0} \int_{u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2}\left(u_j^0-u_k^0\right) \\
& \times\left(u_j^0-\sqrt{\left(\frac{u_j^0+u_k^0}{2}\right)^2-\frac{1}{2} \frac{\epsilon}{k_B T}}+\sqrt{\left(\frac{u_j^0-u_k^0}{2}\right)^2+\frac{1}{2} \frac{\epsilon}{k_B T}}\right)
\end{aligned}
\tag{103}
$$

Expand $\Delta v_j^0 \mid_{from-region-2}$ to the first order of $\frac{\epsilon}{k_B T}$, and we have

$$
\Delta v_j^0 \mid_{from-region-2}=\left(\frac{\rho\left(d_2-d_1\right)\sqrt{a}}{2\sqrt{\pi} u_j^0} \int_{u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2}\left(\frac{u_j^0-u_k^0}{u_j^0+u_k^0}-1\right)\right) \frac{\epsilon}{k_B T} \tag{104}
$$

Collecting Eq.100, Eq.102 and Eq.104, we finally have

$$
\Delta v_j^0=\frac{\rho\left(d_2-d_1\right)\sqrt{a}}{2\sqrt{\pi} u_j^0}\left(\int_{-u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0+u_k^0}{u_j^0-u_k^0}+\int_{u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0-u_k^0}{u_j^0+u_k^0}\right) \frac{\epsilon}{k_B T}, \tag{105}
$$

whose dimensionless form is

$$
\Delta u_j^0=\frac{\Delta v_j^0}{\sqrt{a}}=\frac{\rho\left(d_2-d_1\right)}{2\sqrt{\pi} u_j^0}\left(\int_{-u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0+u_k^0}{u_j^0-u_k^0}+\int_{u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0-u_k^0}{u_j^0+u_k^0}\right) \frac{\epsilon}{k_B T}. \tag{106}
$$

This is the final result for Δv_j^0, accurate to the first order of $\frac{\epsilon}{k_B T}$.

The result is shown in Fig. 21. The upper curve is the correction of the average velocity given by Eq.36

$$
\frac{u_j \mid_{average} - u_j^0}{\rho\left(d_2-d_1\right) \frac{\epsilon}{k_B T}}=\sqrt{\pi} e^{-\left(u_j^0\right)^2} \operatorname{erfi}(u_j^0). \tag{107}
$$

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The lower curve is the correction of collision velocity given by

$$\frac{\Delta u_j^0}{\rho\left(d_2-d_1\right)\frac{\epsilon}{k_B T}}=\frac{1}{2\sqrt{\pi}u_j^0}\left(\int_{-u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2}\frac{u_j^0+u_k^0}{u_j^0-u_k^0}+\int_{u_j^0}^{\infty} du_k^0 e^{-\left(u_k^0\right)^2}\frac{u_j^0-u_k^0}{u_j^0+u_k^0}\right). \tag{108}$$

Note that Δu_j^0 changes from negative to positive as u_j^0 increases. The profile of Δu_j^0 in Fig. 21 can be understood as we decompose the profile into two main trends, an increasing trend and a decreasing trend. From Eq.70 and Eq.75, as u_j^0 increases, the probability of forward collision leading to nonvanishing Δu_j^0 increases and the probability of backward collision leading to nonvanishing Δu_j^0 decreases. Since forward collision contributes positive Δu_j^0 and backward collision contributes negative Δu_j^0, it is clear that Δu_j^0 increases as u_j^0 increases. This is the reason for the increasing trend. As for the decreasing trend, the physics is the same as the decreasing trend for $\left(u_j\mid_{average}-u_j^0\right)$. Suppression of the effect of particle-particle interaction by exponential decay in the Maxwellian velocity distribution is responsible for the decreasing trend. The analysis is like what we do for the profile of $\left(u_j\mid_{average}-u_j^0\right)$ in Fig. 11. This is why Δu_j^0 and $\left(u_j\mid_{average}-u_j^0\right)$ have similar profiles in Fig. 21.

We can see that average velocity is always larger than collision velocity, for any u_j^0. We will come back to the physical meaning of this feature later when studying generic particle-particle interaction.

At the end of this section, we would like to discuss a technical detail, namely, the divergences in Eq.100 and Eq.102. Eq.100 has a $\frac{1}{x}$ divergence as $u_k^0\to u_j^0$ from the left, whereas Eq.102 has a $\frac{1}{x}$ divergence as $u_k^0\to u_j^0$ from the right. And the two divergences cancel out exactly so that the final result in Eq.105 has no divergence. Why so?

Let's check the physical meaning of the two divergences. What happens when $u_k^0\to u_j^0$? For the relative velocity of two particles being quite small, the effect of particle-particle interaction reaches its maximum. When expanding the effect related to particle-particle interaction around $u_k^0=u_j^0$, we pick up a divergence. So we have a

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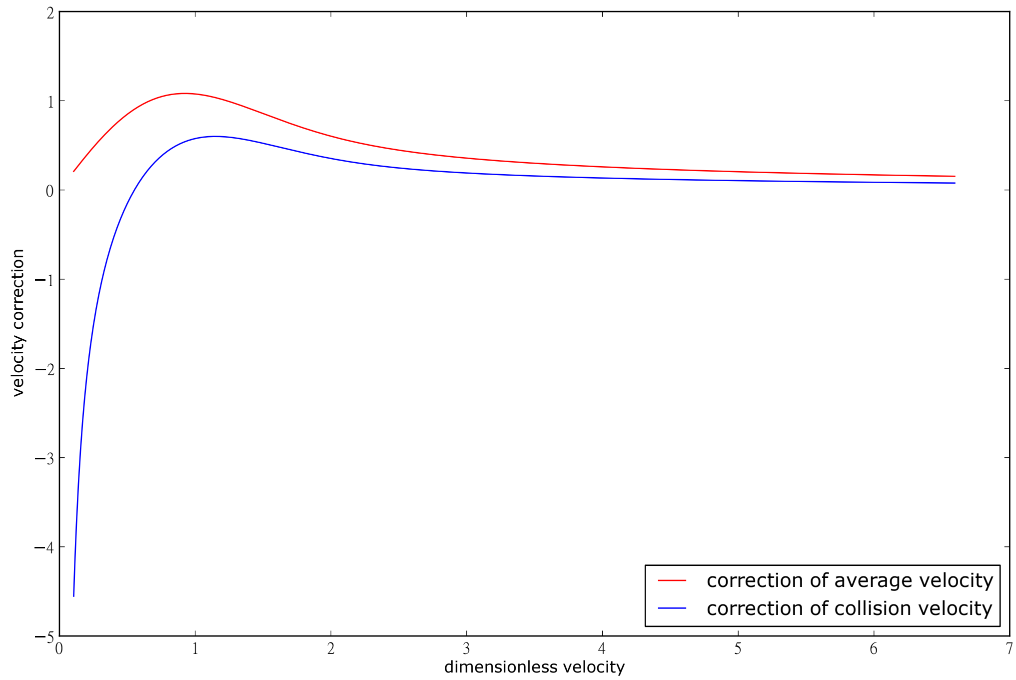

Figure 21: Correction of average velocity and correction of collision velocity due to particle-particle attraction for square well potential. The x-axis is u_j^0. The upper curve is the correction of average velocity given by $\frac{u_j|_{average}-u_j^0}{\rho(d_2-d_1)\frac{\epsilon}{k_BT}}$ in Eq.107. The lower curve is the correction of collision velocity given by $\frac{(u_j^0+\Delta u_j^0)-u_j^0}{\rho(d_2-d_1)\frac{\epsilon}{k_BT}}$ in Eq.108.

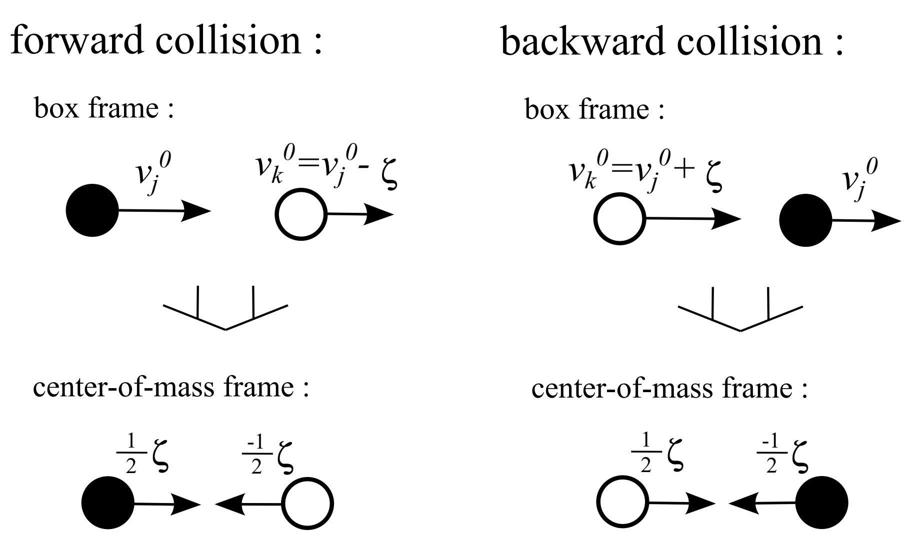

Figure 22: Particle-particle interaction with relative velocity ζ.

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divergence in forward collision and a divergence in Class 1 backward collision. For the main particle hitting the wall when it is still in the potential, from Eq.74 and Eq.92, the particle-particle interaction ϵ appears through the form

$$\frac{-v_j^0 + v_k^0}{2} \pm \sqrt{\left(\frac{v_j^0 - v_k^0}{2}\right)^2 + \frac{\epsilon}{m}} \tag{109}$$

where the plus sign is for Eq.74 (forward collision) and the minus sign is for Eq.92 (Class 1 backward collision). So the effect of ϵ reaches its maximum when $v_j^0 = v_k^0$.

But why do they cancel exactly? Let's check what happens for $v_j^0 \approx v_k^0$. Define ζ to be $\zeta \equiv \mid v_j^0 - v_k^0 \mid$. For $v_j^0 \approx v_k^0$, $\zeta \to 0$, the situation is shown in Fig. 22. In the center-of-mass frame, for both forward collision and backward collision, the situation is the collision between $\frac{1}{2}\zeta$ and $-\frac{1}{2}\zeta$. Therefore, the effects of particle-particle interaction in forward collision and backward collision in Fig. 21 are exactly the same. And for the population, $f\left(v_j^0 - \zeta\right) \approx f\left(v_j^0 + \zeta\right)$ for $\zeta \to 0$. Since the magnitudes of the effect of particle-particle interaction and the population of v_k^0 are all the same, the magnitude of the effect of forward collision for $v_j^0 \approx v_k^0$ is the same as the effect of backward collision for $v_j^0 \approx v_k^0$, and hence the two divergences cancel out.

3.4.5 Correction of momentum transferred in equation of state

Now the last mile to a full description of the correction to the equation of state: the computation of the corrected momentum transferred to the wall. The effect of Δv_j^0

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appears in the equation of state with the form of $\sum_j \frac{2m\Delta v_j^0}{T_j^0}$ and is given by

$$
\begin{aligned}
&\sum_j \frac{2m\Delta v_j^0}{T_j^0} \\
&= \frac{2N}{\sqrt{a\pi}} \int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}} \frac{2m}{\frac{2L}{v_j^0}} \Delta v_j^0 \\
&= \frac{2\rho m}{\sqrt{a\pi}} \int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}} v_j^0 \Delta v_j^0 \\
&= \frac{2\rho m a}{\sqrt{\pi}} \int_0^\infty du_j^0 e^{-(u_j^0)^2} u_j^0 \Delta u_j^0.
\end{aligned}
\tag{110}
$$

Plugging Eq.106 into Eq.110, we have

$$
\begin{aligned}
&\sum_j \frac{2m\Delta v_j^0}{T_j^0} \\
= \; & \frac{2\rho m a}{\sqrt{\pi}} \int_0^\infty du_j^0 e^{-(u_j^0)^2} u_j^0 \frac{\rho\left(d_2 - d_1\right)}{2\sqrt{\pi} u_j^0} \\
& \times \left(\int_{-u_j^0}^\infty du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0 + u_k^0}{u_j^0 - u_k^0} + \int_{u_j^0}^\infty du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0 - u_k^0}{u_j^0 + u_k^0} \right) \frac{\epsilon}{k_B T} \\
= \; & \frac{2\rho^2\left(d_2 - d_1\right)\epsilon}{\pi} \left(\int_0^\infty du_j^0 e^{-(u_j^0)^2} \int_{-u_j^0}^\infty du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0 + u_k^0}{u_j^0 - u_k^0} \right. \\
& \left. + \int_0^\infty du_j^0 e^{-(u_j^0)^2} \int_{u_j^0}^\infty du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0 - u_k^0}{u_j^0 + u_k^0} \right).
\end{aligned}
\tag{111}
$$

Introducing a change of variables by

$$
\begin{aligned}
x &\equiv \frac{u_j^0 + u_k^0}{\sqrt{2}}, \\
y &\equiv \frac{-u_j^0 + u_k^0}{\sqrt{2}},
\end{aligned}
\tag{112}
$$

we have

$$
\int_0^\infty du_j^0 e^{-(u_j^0)^2} \int_{-u_j^0}^\infty du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0 + u_k^0}{u_j^0 - u_k^0} = -\int_0^\infty dx e^{-x^2} x \int_{-\infty}^x dy \frac{e^{-y^2}}{y} = \frac{\ln 2}{4}, \tag{113}
$$

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$$\int_0^\infty du_j^0 e^{-(u_j^0)^2} \int_{u_j^0}^\infty du_k^0 e^{-\left(u_k^0\right)^2} \frac{u_j^0 - u_k^0}{u_j^0 + u_k^0} = -\int_0^\infty dx \frac{e^{-x^2}}{x} \int_0^x dy e^{-y^2} y = -\frac{\ln 2}{4}. \tag{114}$$

Putting Eq.113 and Eq.114 into Eq.111, we get

$$\sum_j \frac{2m\Delta v_j^0}{T_j^0} = 0. \tag{115}$$

In order to obtain $\sum_j \frac{2m\Delta v_j^0}{T_j^0}$, we built up a mechanical model and went through all the calculations from Eq.52 to Eq.115, and yet the final result is just zero! What's going on?

It will be unsatisfactory regarding Eq.115 as just a coincidence. It is hard to believe that such simple result doesn't have any simple explanation. For obtaining such simple result after a long calculation, we had better give a story. So here is the story.

Note that what we have is $\sum_j \frac{2m\Delta v_j^0}{T_j^0} = 0$ but not $\frac{2m\Delta v_j^0}{T_j^0} = 0$. A summation giving zero often relates to conservation law. This is the first hint for the physics behind Eq.115.

In order to figure out the physics behind $\sum_j \frac{2m\Delta v_j^0}{T_j^0}$, we should ask, what exactly is this Δv_j^0? In our construction, $v_j^0 + \Delta v_j^0$ is the collision velocity that a particle hits the wall. But we can take another point of view. What is the role of the wall? A particle reverses its velocity when hitting the wall due to the reflection provided by the wall. A different point of view is that, the wall provides some momentum to the box of gas every time a particle hits the wall. That is, the wall is a momentum provider. This is the central idea to understanding Eq.115.

With the idea of the wall being the momentum provider, a natural step is checking the momentum of the box of gas. By our very assumption, the total momentum of the system is zero, so that the box of gas just sits there without "drifting" away. Since total momentum gives us nothing, let's check the positive momentum of the system, that is, the total momentum of particles with positive velocity. When the box of gas

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is at thermal equilibrium, it is a steady state. For steady state, the total positive momentum is time-independent. We are going to utilize the basic assumption from steady state.

$$\text{total positive momentum is time} - \text{independent} \tag{116}$$

After the system evolves for Δt, what is the total positive momentum now? A particle with free particle velocity $v_j^0 > 0$ may hit the right wall and reverse its velocity, if it starts with a position near the right wall. To be more precise, for a particle with free particle velocity $v_j^0 > 0$ having initial position in $\left(L - v_j^0 \Delta t, L\right)$, its velocity will be negative at $t = \Delta t$. When counting the total positive momentum at $t = \Delta t$, such particle has no contribution since it has a negative velocity at $t = \Delta t$ and hence no longer belongs to the class of particles having positive momentum. The particle disappears from the class of particles having positive momentum. Due to the basic assumption that position distribution is homogeneous, such particles have the population of

$$\frac{v_j^0 \Delta t}{L} = \frac{\Delta t}{\frac{1}{2} T_j^0}. \tag{117}$$

When counting the total positive momentum at $t = \Delta t$, momentum loss due to the effect that a particle can change its direction is given by

$$\text{momentum loss} = \sum_j \frac{\Delta t}{\frac{1}{2} T_j^0} \left(-m v_j^0\right). \tag{118}$$

On the other hand, we also have momentum gain, since a particle with negative velocity at $t = 0$ may have positive velocity at $t = \Delta t$, due to the reflection provided by the left wall. When regarding the wall as the momentum provider, the momentum gain can be seen as provided by the wall, since momentum gain comes from particles that reverse their velocities basing on the mechanism that the wall gives them the momentum. For each collision, the left wall provides a momentum of $m\left(v_j^0 + \Delta v_j^0\right)$ to

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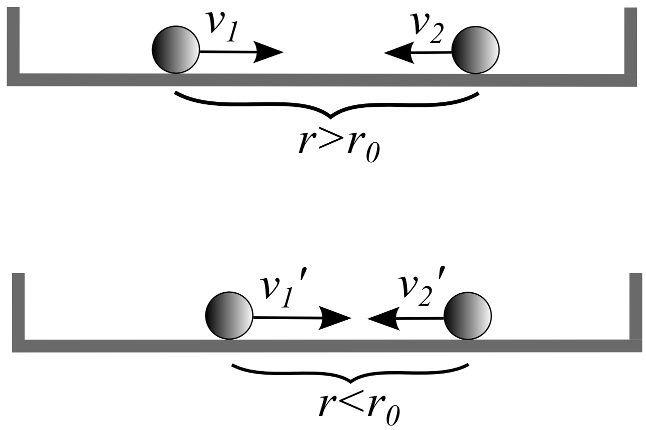

Figure 23: Two particles in the box. The two particles are free particles in the upper situation and are coupled in the lower situation.

the total positive momentum of the system. That is, the momentum gain of the total positive momentum of the system provided by the left wall during time interval of Δt is given by

$$\text{momentum gain} = \sum_j \frac{\Delta t}{\frac{1}{2}T_j^0}\left(m\left(v_j^0 + \Delta v_j^0\right)\right) \tag{119}$$

Since the total positive momentum of the system at $t = \Delta t$ should be the same as the one at $t = 0$, by Eq.118 and Eq.119, we have

$$\sum_j \frac{\Delta t}{\frac{1}{2}T_j^0}\left(-mv_j^0\right) + \sum_j \frac{\Delta t}{\frac{1}{2}T_j^0}\left(m\left(v_j^0 + \Delta v_j^0\right)\right) = 0 \tag{120}$$

and hence we get

$$\sum_j \frac{2m\Delta v_j^0}{T_j^0} = 0 \tag{121}$$

But why should we use $-mv_j^0$ instead of $-mv_j\mid_{average}$ in Eq.118 for the momentum loss? The answer is hidden in what is meant by the total positive momentum of the system, which we did not state clearly in the above argument. Consider the very simple case when there are just two interacting particles in the box, as shown in Fig. 23. What is the total positive momentum of the system, mv_1 or mv_1'? In Fig. 23, compared with the upper situation that the two particles are decoupled, the two particles are coupled

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and hence their momenta (one positive and one negative) are also coupled in the lower situation. For a box of N particles, if total positive momentum couples to total negative momentum, negative momentum gain from the right wall and negative momentum loss should be taken into account when dealing with total positive momentum. In order to have an idea of total positive momentum that is separate from total negative momentum, the appropriate definition should be constructed in the way that all coupled particle pairs are pull apart as free particles. That is, we take a snapshot for the box of gas and pull apart all particle pairs, and then define total positive momentum and total negative momentum by these N decoupled particles. It is in this sense of total positive momentum that we should use $-mv_j^0$ but not $-mv_j\,|_{average}$ in Eq.118, and this is also why the negative momentum gain provided by the right wall and the negative momentum loss play no role when dealing with total positive momentum.

Notice that we don't use any information of particle-particle interaction in the above argument. It is a result of steady state assumption. To be more precise, it is a result of the requirement that the total positive momentum of the system is time-independent. Since it has nothing to do with the form of particle-particle interaction, the result is general and valid for generic particle-particle interactions.

By requiring that the total positive momentum of the system to be time-independent, we can get the correction of momentum transferred in equation of state (namely $\sum_j \frac{2m\Delta v_j^0}{T_j^0}$), which is the total effect of Δv_j^0 for all v_j^0. However, the total effect exhibited in the equation of state cannot tell apart the behavior of Δv_j^0, namely the v_j^0-dependence of Δv_j^0, since we have summed over all v_j^0 and thus lost such information. Such information can be figured out only if we study individual Δv_j^0 instead of $\sum_j \frac{2m\Delta v_j^0}{T_j^0}$. This is one merit of the mechanical model for calculating Δv_j^0 (Eq.105 and Fig. 21).

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3.5 Equation of state

Now we are ready to write down the equation of state for a one-dimensional gas with square well interparticular potential. Putting Eq.121 into Eq.48, we have

$$F = \rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 + \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}. \tag{122}$$

Then putting Eq.38 into Eq.122, we have

$$F = \rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 - \rho^2 \left(k_B T\right) d_1 - \rho^2 \left(d_2 - d_1\right) \epsilon. \tag{123}$$

Keeping up to the lowest order of particle-particle interaction, we see that Eq.123 becomes

$$F = \rho k_B T_{real} + \rho^2 \left(k_B T_{real}\right) d_1 - \rho^2 \left(d_2 - d_1\right) \epsilon. \tag{124}$$

This is the final result of our mechanical approach to the equation of state for one-dimensional interacting gas with square well potential. Equation of state in our mechanical approach (Eq.124) gives the same answer as equation of state by the recipe of standard statistical mechanics (Eq.12). As a reminder, do recall that T in Eq.12 should be T_{real}.

The physical meaning behind Eq.124 is a little subtle. Putting Eq.121 into Eq.39, we have the equation of state of form

$$F = \rho k_B T + \rho^2 \left(k_B T\right) d_1 + \rho^2 \left(d_2 - d_1\right) \epsilon. \tag{125}$$

As a limiting case, let us neglect hard core and consider the effect of particle-particle attraction. By Eq.124 and Eq.125, we have

$$\rho k_B T < F < \rho k_B T_{real}. \tag{126}$$

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Thus, if we ask "When particle-particle attraction is turned on, is the force increased or decreased?", the answer is that the force is increased. "Force is decreased by particle-particle attraction." makes sense if we compare the force with $\rho k_B T_{real}$, namely a box of ideal gas of the actual, modified temperature.

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4 One-dimensional interacting gas with generic particle-particle interaction

With the lessons learnt from one-dimensional interacting gas with square well potential, we can generalize the mechanical model to generic one-dimensional interacting gas. By generic particle-particle interaction, we mean the potential is consisted of a hard core and an interaction tail. In the following, we first study potentials with an attraction tail, and then study potentials with a repulsion tail.

4.1 Particle-particle attraction

In this section, we deal with potentials consisting of a hard core and an attraction tail, as shown in Fig. 1. Starting with Eq.48, we have

$$F = \rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 + \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} + \sum_j \frac{2m\Delta v_j^0}{T_j^0}. \tag{127}$$

By Eq.121, we have

$$F = \rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 + \sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}. \tag{128}$$

On the one hand, the contribution of Δv_j^0 to the equation of state is zero by Eq.121. On the other hand, the idea of T_{real} is introduced by Eq.44. The relation of T and T_{real} and the information of its dependence on particle-particle interaction is hidden in ΔT_j^0. Therefore, in order to get the equation of state, the only thing to be considered is ΔT_j^0, the correction of flying time period due to particle-particle interaction. Notice that by Eq.46 and Eq.47, for equation of state, the effect of replacing T by T_{real} is to double the effect of ΔT_j^0 itself, but with an extra minus sign. For particle-particle attraction, we then have an increased velocity, shortened flying time period, a higher temperature,

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and a negative contribution to F, after we have replaced T with T_{real}, whose net effect is a decreased force.

To deal with ΔT_j^0, we first deal with $\Delta t_{interaction}$. By Eq.16, we have

$$\Delta t_{interaction}\left(0, v_k^0\right) = \int_{d_1}^{r_0} \frac{dr}{\sqrt{\left(\frac{v_k^0}{2}\right)^2 - \frac{U(r)}{m}}}. \tag{129}$$

Putting Eq.129 into Eq.27, we have

$$\begin{aligned}
&\frac{1}{2}\Delta T_j^0 \\
&= -r_0 \frac{N}{v_j^0} + \frac{N}{2} \frac{1}{\sqrt{a\pi}\left(v_j^0\right)^2} \int_0^\infty dv_k^0 \left[e^{-\frac{\left(v_k^0 - v_j^0\right)^2}{a}} - e^{-\frac{\left(v_k^0 + v_j^0\right)^2}{a}}\right] \left(v_k^0\right)^2 \int_{d_1}^{r_0} \frac{dr}{\sqrt{\left(\frac{v_k^0}{2}\right)^2 - \frac{U(r)}{m}}} \\
&= -r_0 \frac{N}{v_j^0} \\
&+ \frac{N}{2} \frac{\sqrt{a}}{\sqrt{\pi}\left(v_j^0\right)^2} \int_0^\infty du_k^0 \left[e^{-(u_k^0 - u_j^0)^2} - e^{-(u_k^0 + u_j^0)^2}\right] \left(u_k^0\right)^2 \int_{d_1}^{r_0} \frac{dr}{\sqrt{\left(\frac{u_k^0}{2}\right)^2 - \frac{1}{2}\frac{U(r)}{k_B T}}}.
\end{aligned} \tag{130}$$

Expanding out to first order in the small parameter $\frac{U(r)}{k_B T}$, we have

$$\int_{d_1}^{r_0} \frac{dr}{\sqrt{\left(\frac{u_k^0}{2}\right)^2 - \frac{1}{2}\frac{U(r)}{k_B T}}} = \frac{2\left(r_0 - d_1\right)}{u_k^0} - \frac{2}{\left(u_k^0\right)^3} \int_{d_1}^{r_0} dr \left[\frac{-U(r)}{k_B T}\right]. \tag{131}$$

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And so we have

$$\int_0^\infty du_k^0 \left[e^{-(u_k^0-u_j^0)^2} - e^{-(u_k^0+u_j^0)^2} \right] \left(u_k^0\right)^2 \int_{d_1}^{r_0} \frac{dr}{\sqrt{\left(\frac{u_k^0}{2}\right)^2 - \frac{1}{2}\frac{U(r)}{k_BT}}}$$
$$= 2\left(r_0 - d_1\right) \int_0^\infty du_k^0 \left[e^{-(u_k^0-u_j^0)^2} - e^{-(u_k^0+u_j^0)^2} \right] u_k^0$$
$$- 2\left(\int_{d_1}^{r_0} dr \left[-\frac{U(r)}{k_BT} \right] \right) \int_0^\infty du_k^0 \left[e^{-(u_k^0-u_j^0)^2} - e^{-(u_k^0+u_j^0)^2} \right] \frac{1}{u_k^0}$$
$$= 2\sqrt{\pi}\left(r_0 - d_1\right) u_j^0 - 2\pi e^{-(u_j^0)^2} \mathrm{erfi}(u_j^0) \left(\int_{d_1}^{r_0} dr \left[-\frac{U(r)}{k_BT} \right] \right). \tag{132}$$

Putting Eq.132 into Eq.130, we then have

$$\frac{1}{2}\Delta T_j^0 = -\frac{N d_1}{v_j^0} - \frac{N\sqrt{a\pi}}{\left(v_j^0\right)^2} e^{-\frac{\left(v_j^0\right)^2}{a}} \mathrm{erfi}\left(\frac{v_j^0}{\sqrt{a}}\right) \left(\int_{d_1}^{r_0} dr \left[-\frac{U(r)}{k_BT} \right] \right). \tag{133}$$

Eq.133 is just Eq.33, with $\left(d_2 - d_1\right) \frac{\epsilon}{k_BT}$ replaced by $\left(\int_{d_1}^{r_0} dr \left[-\frac{U(r)}{k_BT} \right] \right)$. Therefore, the physics is all the same. The analysis and physical picture in Section 3.2 are all valid for the generic potential here.

For $\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}$, we can just take Eq.38 and replace $\left(d_2 - d_1\right) \frac{\epsilon}{k_BT}$ with $\left(\int_{d_1}^{r_0} dr \left[-\frac{U(r)}{k_BT} \right] \right)$. We get

$$\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0} = -\left(\rho^2 \left(k_BT\right) d_1 + \rho^2 \left(\int_{d_1}^{r_0} dr \left[-U(r) \right] \right) \right) \tag{134}$$

Putting Eq.134 into Eq.128, we have

$$F = \rho k_B T_{real} + 2\rho^2 \left(k_B T_{real}\right) d_1 - \rho^2 \left(k_BT\right) d_1 - \rho^2 \left(\int_{d_1}^{r_0} dr \left[-U(r) \right] \right). \tag{135}$$

Equation of state, correct to the first order in the particle-particle interaction is

$$F = \rho k_B T_{real} + \rho^2 \left(k_B T_{real}\right) d_1 - \rho^2 \left(\int_{d_1}^{r_0} dr \left[-U(r) \right] \right). \tag{136}$$

This is exactly the equation of state derived using standard statistical mechanics, as we

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show in Eq.3. The equation of state in our mechanical approach matches traditional result provided by statistical mechanics.

4.2 Meaning and interpretation

As particle-particle attraction is turned on, there are several effects.

On the average, a particle is sped up by its interaction with other particles. Forward collisions increase velocity and backward collisions decrease velocity. For a backward collision to happen, the background particle needs to move fast enough in order to hit the main particle from the back. For a forward collision, there is no such velocity constraint. Forward collisions occur more often than backward collisions. This is why the velocity of particle is enhanced when particle-particle attraction is turned on. The effect associated with velocity enhancement is that the temperature of the system is also enhanced, since temperature is a measurement of kinetic energy.

When a particle hits the wall, due to particle-particle interaction, the collision velocity can differ from its free particle velocity. By our very assumption that the box of gas is a steady state, the total effect of correction of collision velocity to the equation of state is zero. That is, while some particles hit the wall with velocities enhanced and some particles hit the wall with velocities suppressed, the two effects just cancel out.

For the equation of state, the correction to the collision velocity near the wall simply contributes nothing to the force. However, the change in the flying time period does give a positive contribution to the force. As to the contribution due to a modification of the temperature, since the temperature becomes higher when particle-particle attraction is turned on, when the ideal gas part $\rho k_B T$ is (correctly) replaced by the new temperature T_{real} as $\rho k_B T_{real}$, the residual part $\rho k_B \left(T - T_{real}\right)$ gives a negative contribution. The competition between the flying time period correction and temperature correction turns out to be a net negative contribution, and the force felt by the wall decreases. This is the physics behind the equation of state (Eq.136).

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Now we want to analyze the physics from another point of view base on the idea of average velocity. When particle-particle interaction is turned on, the velocity of a particle fluctuates. After averaging, we can come up with the idea of an average velocity $v_j \mid_{average}$, which is different from v_j^0. The average velocity $v_j \mid_{average}$ is the modified velocity for v_j^0, which is the average velocity when there is no particle-particle interaction. If we work with the idea of average velocity directly but not the free particle velocity, there is no "velocity enhancement" or "correction of flying time period" by the very construction of this average velocity, which is defined as $v_j \mid_{average}= \frac{L-Nd_1}{\frac{1}{2}\left(T_j^0+\Delta T_j^0\right)}$, and hence $\frac{1}{2}T_j = \frac{1}{2}\left(T_j^0 + \Delta T_j^0\right) = \frac{L-Nd_1}{v_j|_{average}}$. The issue of "what happens when a particle flies in the middle of the box" doesn't exist in this point of view, or we can say that it is embedded in the idea of average velocity. The issue of temperature modification also disappears, since temperature relates to velocities of the particles. The only effect is what happens when a particle hits the wall. When a particle hits the wall, the collision velocity may be different from its average velocity. Such effect gives correction to the equation of state.

We can rewrite the equation of state using the average velocity $v_j \mid_{average}$ and collision velocity $\left(v_j^0 + \Delta v_j^0\right)$. Again, keeping up to the first order in the particle-particle

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interaction, we have

$$
\begin{aligned}
F &= \sum_j \frac{2m(v_j^0 + \Delta v_j^0)}{T_j^0 + \Delta T_j^0} \\
&= \frac{2}{L - Nd_1} \sum_j \frac{1}{2} m \left(v_j \mid_{average}\right) \left(v_j^0 + \Delta v_j^0\right) \\
&= \frac{2}{L - Nd_1} \sum_j \frac{1}{2} m \left(v_j \mid_{average}\right) \left[v_j \mid_{average} + \left(\left(v_j^0 + \Delta v_j^0\right) - v_j \mid_{average}\right)\right] \\
&= \frac{2}{L - Nd_1} \left\{ \sum_j \frac{1}{2} m \left(v_j \mid_{average}\right)^2 + \sum_j \frac{1}{2} m \left(v_j \mid_{average}\right) \left(\left(v_j^0 + \Delta v_j^0\right) - v_j \mid_{average}\right) \right\} \\
&= \frac{2}{L - Nd_1} \left(\frac{N}{2} k_B T_{real}\right) + \frac{2}{L - Nd_1} \sum_j \frac{1}{2} m \left(v_j \mid_{average}\right) \left(\left(v_j^0 + \Delta v_j^0\right) - v_j \mid_{average}\right) \\
&= \rho k_B T_{real} + \rho^2 \left(k_B T_{real}\right) d_1 + \frac{m}{L} \sum_j \left(v_j \mid_{average}\right) \left(\left(v_j^0 + \Delta v_j^0\right) - v_j \mid_{average}\right) \qquad (137)
\end{aligned}
$$

In Eq.137, the first term is ideal gas part and the second term is hard core effect as usual. The effect of particle-particle interaction appears in the third term. Compared with Eq.136, for particle-particle interaction being attractive, the third term in Eq.137 should be negative. But can we see why?

For $v_j \mid_{average}$, it is positive. So we are going to deal with $\left(v_j^0 + \Delta v_j^0\right) - v_j \mid_{average}$. Compared with $v_j \mid_{average}$, the collision velocity $\left(v_j^0 + \Delta v_j^0\right)$ should be faster or slower? The basic idea is, both $\left(v_j^0 + \Delta v_j^0\right)$ and $v_j \mid_{average}$ are close to v_j^0. Their departures from v_j^0 arise from particle-particle interaction. Therefore, our strategy is comparing $\left[\left(v_j^0 + \Delta v_j^0\right) - v_j^0\right]$ and $\left[v_j \mid_{average} - v_j^0\right]$.

Let's consider comparing the average velocity and collision velocity with v_j^0. For $v_j \mid_{average}$, particle-particle interaction enters in the trip of a particle flying from one side to another side. We have forward collisions and backward collisions. For $\left(v_j^0 + \Delta v_j^0\right)$, particle-particle interaction enters when a particle hits the wall. Here we also have forward collisions and backward collisions. However, for a forward collision around the wall, if $v_{CM} = \frac{v_j^0 + v_k^0}{2}$ is not positive, the forward collision loses its effect before the

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main particle hits the wall. The velocity domain of forward collisions for $v_j\mid_{average}$ is $v_k^0 < v_j^0$. The velocity domain of forward collisions for $\left(v_j^0 + \Delta v_j^0\right)$ is $-v_j^0 < v_k^0 < v_j^0$. In other words, compared with collision velocity, average velocity has more forward collisions. Since forward collisions increase the velocity, we have $\left[v_j\mid_{average} - v_j^0\right] > \left[\left(v_j^0 + \Delta v_j^0\right) - v_j^0\right]$, and hence

$$\left(v_j^0 + \Delta v_j^0\right) - v_j\mid_{average} < 0 \tag{138}$$

And so we have

$$\frac{m}{L}\sum_j \left(v_j\mid_{average}\right)\left(\left(v_j^0 + \Delta v_j^0\right) - v_j\mid_{average}\right) < 0 \tag{139}$$

The feature that $\left(v_j^0 + \Delta v_j^0\right) - v_j\mid_{average} < 0$ can be seen in Fig. 21. So now we understand that it is caused by the fact that the two kinds of velocities have different numbers of forward collisions.

In summary, when analyzing the physics with average velocity $v_j\mid_{average}$ and collision velocity $\left(v_j^0 + \Delta v_j^0\right)$, the only effect to be considered in this approach is the relation between average velocity $v_j\mid_{average}$ and collision velocity $\left(v_j^0 + \Delta v_j^0\right)$. Collision velocities has less forward collisions than average velocity has, and so collision velocity is slower than average velocity. Due to such effect, the force is decreased.

In a naive description trying to explain the form of the van der Waals equation [18], one is tempted to claim that a particle hitting the wall is slowed down due to the attraction of other gas particles from the back, and hence the force felt by the wall is decreased. Put differently, this seemingly plausible theory claims that the velocity hitting the wall (collision velocity) is smaller than the velocity in the bulk (average velocity), which also holds true in our detailed mechanical approach.

However, we must quickly point out that, as particle-particle attraction is turned on, velocity in the bulk is different from the free particle velocity and particles in the

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box do fly faster. Positive contribution from forward collisions (velocity increasing) and negative contribution from backward collisions (velocity decreasing) don't cancel out. Furthermore, compared with v_j^0, which is the collision velocity when there is no particle-particle attraction, the collision velocity in the presence of particle-particle attraction is not always smaller. For a slow particle, the collision velocity is smaller than its free particle velocity ($\Delta v_j^0 < 0$). For a fast particle, the collision velocity is larger than its free particle velocity ($\Delta v_j^0 > 0$).

The reason that we don't need to consider average velocity correction (which is equivalent to flying time correction and leads to temperature correction) in the conventional description of the van der Waals equation is not because forward collisions and backward collisions cancel out exactly (they don't), but lies in the fact that they are all lumped into the idea of $v_j \mid_{average}$. When taking $v_j \mid_{average}$ but not v_j^0, the issue of "what happens when a particle flies in the middle of the box" disappears, by the very construction of $v_j \mid_{average}$. Now it is clear that traditional picture of van der Waals equation actually uses $v_j \mid_{average}$ but not v_j^0 in the argument. For physics of the bulk, it just takes the net result ($v_j \mid_{average}$) and then bypasses all the issues related to "what happens when a particle flies in the middle of the box", including temperature modification. It is in this sense that traditional picture makes sense.

4.3 Particle-particle repulsion

We haven't deal with particle-particle repulsion yet, except for the hard core at $r = d_1$, which stands for the nonzero size of a particle. For a potential consisting of a hard core and a repulsion tail, the physics is just the same as we do for attraction tail, except that particle-particle attraction is now replaced by particle-particle repulsion and hence many effects pick up minus signs. For particle-particle repulsion, we have a decreased velocity, lengthened flying time period, lower temperature, which causes a positive contribution to F if we replace T by T_{real}. The net effect is that we have an

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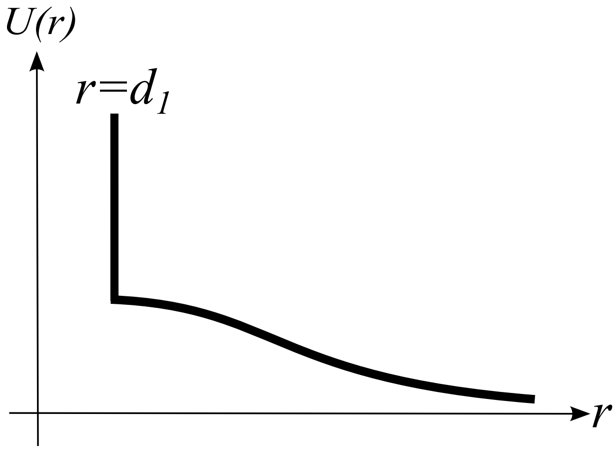

Figure 24: Particle-particle interaction consisting of a hard core and a repulsion tail.

increased force.

However, one feature does stand out that is characteristic to particle-particle repulsion alone. Consider a potential consisting of a hard core and a repulsion tail, as shown in Fig. 24. When the relative velocity of two interacting particles is small, they don't have enough kinetic energy to overcome the potential barrier and reach $r = d_1$. In the center-of-mass frame, their speeds are decreased by repulsion and they will stop before reaching $r = d_1$. Suppose the minimum distance between the two particles is $d_{min}(\Delta v)$, with $d_1 \leq d_{min}(\Delta v) \leq r_0$, where $\Delta v > 0$ is the relative velocity of the two particles when they are free particles. In what situation do we have $d_{min}(\Delta v) > d_1$, which means that the particle pair cannot probe the whole potential? The critical relative velocity is determined by energy conservation

$$\frac{1}{2}m\left(\frac{\Delta v\mid_{critical}}{2}\right)^2 + \frac{1}{2}m\left(\frac{\Delta v\mid_{critical}}{2}\right)^2 = U_{max} \tag{140}$$

where U_{max} is the maximum of the potential energy for $r > d_1$. So $\Delta v\mid_{critical}$ is given by

$$\Delta v\mid_{critical} = 2\sqrt{\frac{U_{max}}{m}} \tag{141}$$

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and the dimensionless form is

$$\Delta u \mid_{critical} = \frac{\Delta v \mid_{critical}}{\sqrt{a}} = \sqrt{\frac{2U_{max}}{k_B T}}. \tag{142}$$

With Eq.142, we can see that in order to have $d_{min}(\Delta v) > d_1$, the dimensionless relative velocity should be smaller than $\sqrt{\frac{2U_{max}}{k_B T}}$, which is quite small by our construction. In most situations, $\Delta u > \Delta u \mid_{critical} = \sqrt{\frac{2U_{max}}{k_B T}}$ and hence $d_{min}(\Delta v) = d_1$. In other words, there are particle pairs that their separations cannot reach $r = d_1$ due to the potential barrier. But since particle-particle interaction is weak by our construction, the population of such particle pairs is quite small. In most situations, particle pairs have enough kinetic energy to overcome the potential barrier and reach $r = d_1$, just like the case of particle-particle attraction.

Is the equation of state modified by the presence of the cases having $d_{min}(\Delta v) > d_1$? That is, since there is a small population having $d_{min}(\Delta v) > d_1$ for particle-particle repulsion, we may worry whether Eq.136 is valid or not. The answer is that Eq.136 holds for both particle-particle attraction and particle-particle repulsion, provided that particle-particle interaction is weak. The argument is left for Appendix E.

Another issue related to particle-particle repulsion is soft core, which we haven't discussed yet. For a soft core, discontinuous infinite repulsion at $r = d_1$ (hard core) is replaced by continuous repulsion that is strong enough to stop particle pairs with any relative velocity. An example for such a soft core is Lennard-Jones potential, which has a r^{-12} repulsive term. Can we capture the physics of soft core in our mechanical model? The answer is a sadly no. The physics of soft core is beyond the scope of our weakly interacting model. Soft core aims to stop two colliding particles, and this goal needs particle-particle interaction that is strong enough. As attempting to expand with $\frac{U(r)}{k_B T}$, $\frac{U(r)}{k_B T}$ needs to be small. For potential having a hard core, gas particles probe the region of $r > d_1$, where the interaction is weak, and hence perturbation scheme can be implemented. For potential having a soft core, gas particles are stopped by a very

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strong repulsion and hence probe the region with strong particle-particle interaction that cannot be treated as a perturbation. Nonperturbative approach is needed for studying soft cores.

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5 Conclusion

In this work, we have taken a mechanical approach to a one-dimensional interacting gas with particle-particle interaction made up of a hard core and an interaction tail. Perturbations around ideal gas are considered and the physics is computed correct up to $\mathcal{O}\left(\frac{U}{k_B T}\right)$. Equation of state given by our mechanical approach matches the result given by statistical mechanics. Assumptions and conditions we put in by hand include (1) the homogeneity assumption on the spatial distribution, (2) velocity distribution being Maxwellian, (3) the system being in steady state, (4) short range and weak interparticular interaction, (5) low density, and (6) high temperature, all of which are common assumed in traditional statistical mechanics.

5.1 Summary

Besides having been able to reproduce the equation of state, we do obtain some physics insight that traditional statistical mechanics doesn't readily tell us. In the following, we take particle-particle attraction as an example. The effect of particle-particle repulsion just reverses the effect of particle-particle attraction. We list six points for the effects of particle-particle attraction. Almost all the physics in the mechanical model is hidden in Fig. 21.

The first point is about the sign of the correction to the average velocity. Due to the fact that the number of forward collisions is larger than the number of backward collisions, on the average, all particles move faster in the presence of particle-particle attraction (Eq.35).

The second point is about the temperature. Since particles move faster as particle-particle attraction is turned on, the temperature of the system increases (Eq.44). Another point of view without concerning mechanics is considering total energy of the system (Eq.51).

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The third point is about the correction to the collision velocity. For a slow particle, $\Delta v_j^0 < 0$. For a fast particle, $\Delta v_j^0 > 0$. The increase and decrease of collision velocity necessarily cancel out due to our very assumption that the system is a steady state.

The fourth point is about the trends for average velocity correction and collision velocity correction. They have similar trends since the physics are similar. When the main particle moves fast, the effect of forward collisions dominates. Velocity increasing due to forward collision is responsible for the increasing trend. The velocity domain of background particles that have significant contributions is a small neighborhood around the velocity of the main particle. Suppression of the effect of particle-particle interaction by the exponential decay in the Maxwellian velocity distribution is responsible for the decreasing trend.

The fifth point is about the difference between average velocity correction and collision velocity correction. Compared with collision velocity, average velocity has more forward collisions. Since forward collisions increase velocity, average velocity is bigger than collision velocity (Eq.138).

The sixth point is about the force. Compared with $\rho k_B T$, the force is increased. But compared with $\rho k_B T_{real}$, the force is decreased (Eq.126).

5.2 Meaning and implication

Unlike most researches studying N-body systems in the framework of statistical mechanics or kinetic theory, we take a mechanical approach to a one-dimensional weakly interacting gas in thermal equilibrium. With the help from a detailed analysis of how gas particles interact, we have successfully gained some more interesting physics that the traditional approach doesn't readily tell us. Our work is an example demonstrating the possibility to study weakly interacting N-body systems from a mechanical viewpoint working with particle trajectory.

Though the derivation here is focused on the equation of state, the spirit of this

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mechanical model is investigating the physics of particle-particle interaction and trying to have a deeper understanding of a seemingly simple system. The equation of state is just a part of physics that the mechanical model can tell us. With this mechanical model, we obtain some understanding for issues other than the equation of state.

Our mechanical model consists of three elements: (1) A mechanical picture of an unperturbed system (in which there is no particle-particle interaction), (2) plausible assumptions concerning things such as the velocity distribution and homogeneity of the system that we put in by hand, and (3) assumed form of (weak) particle-particle interaction. For one-dimensional interacting gas at thermal equilibrium, the mechanical picture for the unperturbed system is just a bunch of particles doing constant velocity motions and reversing their velocities when hitting the walls. Building mechanical model on this picture, and then put in the effect of particle-particle interaction, we capture some interesting physics. The essence of such mechanical approach lies in the fact that the effect of particle-particle interaction is weak ($\mathcal{O}\left(\rho r_0\right) < \mathcal{O}\left(1\right)$ and $\mathcal{O}\left(\frac{U}{k_B T}\right) < \mathcal{O}\left(1\right)$), and so we can focus on two-body interaction and build on the idea of particle trajectories. To study the influence of background particles on the main particle, instead of regarding background particles as a bunch of neighbor particles surrounding the main particle, we introduce the idea of particle trajectory. For a system different from one-dimensional interacting gas (some colloidal systems or granular systems, for example), if we can figure out its free particle model and then put in particle-particle interaction, maybe we can have some interesting physics. We think it is possible to extend the idea to other systems usually studied in a statistical mechanics or kinetic theory point of view.

Statistical mechanics works with partition function. Traditional kinetic theory adopting Boltzmann equation considers a particle interacting with its neighbor particles. But our mechanical approach works with a slightly more detailed analysis of the particle trajectory, the number of collisions and the effect of each collision. Here

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we had restricted ourselves to the first-order calculations only, hoping that future work might extend our result. The merit of this mechanical approach is that it does provide us with more physics insight about how the individual effect affects the final answer.

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Appendix A: Calculation of $\frac{1}{2}\Delta T_j^0$ (without putting square well potential)

In this appendix, we calculate $\frac{1}{2}\Delta T_j^0$ starting with Eq.26. Plugging Eq.23, $\frac{1}{L}\int_0^L dx_k^0$ $\#_L\left(v_j^0, v_k^0, x_k^0\right)$ shown in Fig. 9 and Eq.24 into Eq.26, we have

$$\frac{1}{2}\Delta T_j^0 = \frac{N}{v_j^0}\int_{-\infty}^{\infty} dv_k^0 f(v_k^0)\left\{-r_0 + \frac{1}{L}\int_0^L dx_k^0\left[\#_R\frac{v_j^0 - H\left(v_k^0\right)}{2}\Delta t_{interaction}\left(v_j^0, H\left(v_k^0\right)\right)\right.\right.$$
$$\left.\left.+\#_L\frac{v_j^0 + H\left(v_k^0\right)}{2}\Delta t_{interaction}\left(v_j^0, -H\left(v_k^0\right)\right)\right]\right\} \tag{143}$$

$$\begin{aligned}
\frac{1}{2}\Delta T_j^0 &= -r_0\frac{N}{v_j^0} + \frac{N}{v_j^0}\frac{1}{L}\int_{-\infty}^{\infty} dv_k^0 f(v_k^0)\int_0^L dx_k^0\left[\#_R\frac{v_j^0 - H\left(v_k^0\right)}{2}\Delta t_{interaction}\left(v_j^0, H\left(v_k^0\right)\right)\right.\\
&\left.+\#_L\frac{v_j^0 + H\left(v_k^0\right)}{2}\Delta t_{interaction}\left(v_j^0, -H\left(v_k^0\right)\right)\right]\\
&= -r_0\frac{N}{v_j^0}\\
&+\frac{N}{v_j^0}\frac{1}{L}\int_0^L dx_k^0\int_0^{v_j^0\left(1-\frac{x_k^0}{L}\right)} dv_k^0 f(v_k^0)\frac{v_j^0 - v_k^0}{2}\Delta t_{interaction}\left(v_j^0, v_k^0\right)\\
&+\frac{N}{v_j^0}\frac{1}{L}\int_0^L dx_k^0\int_{v_j^0\left(1-\frac{x_k^0}{L}\right)}^{v_j^0} dv_k^0 f(v_k^0)\frac{v_j^0 + v_k^0}{2}\Delta t_{interaction}\left(v_j^0, -v_k^0\right)\\
&+\frac{N}{v_j^0}\int_{-\infty}^{0} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0\#_R\left(v_j^0, v_k^0, x_k^0\right)\right)\frac{v_j^0 - v_k^0}{2}\Delta t_{interaction}\left(v_j^0, v_k^0\right)\\
&+\frac{N}{v_j^0}\int_{v_j^0}^{\infty} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0\#_R\left(v_j^0, v_k^0, x_k^0\right)\right)\frac{v_j^0 + v_k^0}{2}\Delta t_{interaction}\left(v_j^0, -v_k^0\right)\\
&+\frac{N}{v_j^0}\int_{-\infty}^{0} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0\#_L\left(v_j^0, v_k^0, x_k^0\right)\right)\frac{v_j^0 + v_k^0}{2}\Delta t_{interaction}\left(v_j^0, -v_k^0\right)\\
&+\frac{N}{v_j^0}\int_0^{\infty} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0\#_L\left(v_j^0, v_k^0, x_k^0\right)\right)\frac{v_j^0 - v_k^0}{2}\Delta t_{interaction}\left(v_j^0, v_k^0\right)
\end{aligned} \tag{144}$$

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Combining the second term and the third term, we have

$$
\begin{aligned}
\frac{1}{2}\Delta T_j^0 = &-r_0\frac{N}{v_j^0} + \frac{N}{v_j^0}\int_0^{v_j^0} dv_k^0 f(v_k^0) \\
&\times\left[\left(1-\frac{v_k^0}{v_j^0}\right)\frac{v_j^0-v_k^0}{2}\Delta t_{interaction}\left(v_j^0,v_k^0\right)+\frac{v_k^0}{v_j^0}\frac{v_j^0+v_k^0}{2}\Delta t_{interaction}\left(v_j^0,-v_k^0\right)\right] \\
&+\frac{N}{v_j^0}\int_{-\infty}^{0} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0 \#_R\left(v_j^0,v_k^0,x_k^0\right)\right)\frac{v_j^0-v_k^0}{2}\Delta t_{interaction}\left(v_j^0,v_k^0\right) \\
&+\frac{N}{v_j^0}\int_{v_j^0}^{\infty} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0 \#_R\left(v_j^0,v_k^0,x_k^0\right)\right)\frac{v_j^0+v_k^0}{2}\Delta t_{interaction}\left(v_j^0,-v_k^0\right) \\
&+\frac{N}{v_j^0}\int_{-\infty}^{0} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0 \#_L\left(v_j^0,v_k^0,x_k^0\right)\right)\frac{v_j^0+v_k^0}{2}\Delta t_{interaction}\left(v_j^0,-v_k^0\right) \\
&+\frac{N}{v_j^0}\int_{0}^{\infty} dv_k^0 f(v_k^0)\left(\frac{1}{L}\int_0^L dx_k^0 \#_L\left(v_j^0,v_k^0,x_k^0\right)\right)\frac{v_j^0-v_k^0}{2}\Delta t_{interaction}\left(v_j^0,v_k^0\right)
\end{aligned}
\tag{145}
$$

Using the following properties

$$
\int_{v_j^0}^{\infty} dv_k^0\left[\frac{1}{L}\int_0^L dx_k^0\#_R\left(v_j^0,v_k^0,x_k^0\right)+\frac{1}{L}\int_0^L dx_k^0\#_R\left(v_j^0,-v_k^0,x_k^0\right)\right]=\int_{v_j^0}^{\infty} dv_k^0\left(1+\frac{v_k^0}{v_j^0}\right)
\tag{146}
$$

$$
\int_{0}^{\infty} dv_k^0\left[\frac{1}{L}\int_0^L dx_k^0\#_L\left(v_j^0,v_k^0,x_k^0\right)+\frac{1}{L}\int_0^L dx_k^0\#_L\left(v_j^0,-v_k^0,x_k^0\right)\right]=\int_{v_j^0}^{\infty} dv_k^0\left(-1+\frac{v_k^0}{v_j^0}\right)
\tag{147}
$$

and the symmetry of velocity distribution, namely $f(v) = f(-v)$, we get

$$
\begin{aligned}
\frac{1}{2}\Delta T_j^0 = &-r_0\frac{N}{v_j^0} \\
&+\frac{N}{2}\int_{-v_j^0}^{\infty} dv_k^0 f(v_k^0)\left(1+\frac{v_k^0}{v_j^0}\right)^2\Delta t_{interaction}\left(v_j^0,-v_k^0\right) \\
&-\frac{N}{2}\int_{v_j^0}^{\infty} dv_k^0 f(v_k^0)\left(1-\frac{v_k^0}{v_j^0}\right)^2\Delta t_{interaction}\left(v_j^0,v_k^0\right)
\end{aligned}
\tag{148}
$$

To simplify the equation further, we utilize the feature that the interaction time is a function of the relative velocity, but not the magnitudes of the two velocities (Eq.16).

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That is,

$$\Delta t_{interaction}\left(v_1, v_2\right) = \Delta t_{interaction}\left(\mid v_1 - v_2 \mid\right) \tag{149}$$

Equipped with this feature and some change of variables for Eq.148, finally, we obtain

$$\frac{1}{2}\Delta T_j^0 = -r_0\frac{N}{v_j^0} + \frac{N}{2}\int_0^\infty dv_k^0\left[f\left(v_k^0 - v_j^0\right) - f\left(v_k^0 + v_j^0\right)\right]\left(\frac{v_k^0}{v_j^0}\right)^2 \Delta t_{interaction}\left(0, v_k^0\right). \tag{150}$$

Let's stop and think about what we have done. In order to calculate ΔT_j^0, we need to calculate the number of collisions and the effect of each collision. For the effect of each collision, the effect of particle-particle interaction enters through spatial displacement and time interval during the process that the main particle interacts with a background particle (Eq.17). In Section 3.1, we see that the information of displacement can be translated into the information of interaction time (Eq.13 and Eq.14), with the help of center-of-mass velocity. In other words, the effect of each particle-particle interaction is all embedded in $\Delta t_{interaction}$. All the information of the form of particle-particle interaction is hidden in $\Delta t_{interaction}$. As for the number of collisions, which is an idea independent of the form of particle-particle interaction, we attack this part by introducing free particle model, and the problem reduces to the counting of line-crossings of trajectories of a bunch of free particles. The validity of such free particle model relies on the fact that we are considering particle-particle interaction effect only to order one.

In deriving the above equation of ΔT_j^0 (Eq.150), we have used the symmetry of velocity distribution, the assumption of spatial distribution being homogeneous, the feature that $\Delta t_{interaction}$ only depends on the absolute value of the relative velocity. Notice that we haven't put in Maxwell's velocity distribution (so there is still $f(v)$) and the information of particle-particle interaction (so there is still $\Delta t_{interaction}$). In other words, Eq.150 is valid for any potential that vanishes for $r > r_0$.

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Putting in Maxwell's velocity distribution (Eq.7), we derive

$$\frac{1}{2}\Delta T_j^0 = -r_0\frac{N}{v_j^0}+\frac{N}{2}\frac{1}{\sqrt{a\pi}\left(v_j^0\right)^2}\int_0^\infty dv_k^0\left[e^{-\frac{\left(v_k^0-v_j^0\right)^2}{a}}-e^{-\frac{\left(v_k^0+v_j^0\right)^2}{a}}\right]\left(v_k^0\right)^2\Delta t_{interaction}\left(0,v_k^0\right). \tag{151}$$

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Appendix B: Probability of $N-2$ background particles under thermodynamic limit

In this appendix, we calculate the probability of $N-2$ background particles under thermodynamic limit. We start with the probability of a single background particle in Eq.59. Defining $\xi \equiv \rho d_3$ and changing d_3 to $\xi\left(\frac{L}{N}\right)$, we note that Eq.59 becomes

$$\begin{aligned}&\text{probability of a single background particle}\\&=\frac{1}{2L}\left\{\left[2L-\xi\left(\frac{L}{N}\right)\right]\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\left[\frac{2N}{\xi}-1\right]\right)-\xi\left(\frac{L}{N}\right)\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)\right.\\&\left.+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}\xi\left(\frac{L}{N}\right)\left(e^{-\frac{\left(v_j^0\right)^2}{a}\left[\frac{2N}{\xi}-1\right]^2}-e^{-\frac{\left(v_j^0\right)^2}{a}}\right)\right\}\end{aligned} \tag{152}$$

We rewrite Eq.152 with the spirit of $x=1-(1-x)=1-\frac{1}{N}(N-Nx)$ as

$$\begin{aligned}&\text{probability of a single background particle}\\&=1-\frac{1}{N}\left\{N-\frac{N}{2L}\left[2L-\xi\left(\frac{L}{N}\right)\right]\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\left[\frac{2N}{\xi}-1\right]\right)\right.\\&\left.+\frac{\xi}{2}\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)-\frac{\xi}{2}\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}\left(e^{-\frac{\left(v_j^0\right)^2}{a}\left[\frac{2N}{\xi}-1\right]^2}-e^{-\frac{\left(v_j^0\right)^2}{a}}\right)\right\},\end{aligned} \tag{153}$$

and then rewrite Eq.153 as

$$\begin{aligned}&\text{probability of a single background particle}\\&=1-\frac{1}{N}\left(\frac{\xi}{2}\left[1+\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\right)\\&-\frac{1}{N}\left(-\frac{\xi}{2}\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}\left[\frac{2N}{\xi}-1\right]^2}\right)\\&-\frac{1}{N}\left(N\left[1-\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\left[\frac{2N}{\xi}-1\right]\right)\right]\right)\\&-\frac{1}{N}\left(\frac{\xi}{2}\left[\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\left[\frac{2N}{\xi}-1\right]\right)-1\right]\right).\end{aligned} \tag{154}$$

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When taking the thermodynamic limit that $N \to \infty$ and $L \to \infty$ while $\frac{N}{L}$ is fixed, and the condition that ξ is fixed (that is, $d_3 = \xi\left(\frac{L}{N}\right)$ is fixed under the thermodynamic limit), we have

$$\lim_{N\to\infty}\left(-\frac{\xi}{2}\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}\left[\frac{2N}{\xi}-1\right]^2}\right) = 0 \tag{155}$$

$$\lim_{N\to\infty}\left(N\left[1-\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\left[\frac{2N}{\xi}-1\right]\right)\right]\right) = 0 \tag{156}$$

$$\lim_{N\to\infty}\left(\frac{\xi}{2}\left[\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\left[\frac{2N}{\xi}-1\right]\right)-1\right]\right) = 0. \tag{157}$$

The part dealing with the probability of the remaining $N-2$ background particles is

$$\begin{aligned} &\text{probability of } (N-2) \text{ background particles} \\ = \;& (\text{probability of a single background particle})^{N-2}. \end{aligned} \tag{158}$$

Combining Eq.154, Eq.155, Eq.156 Eq.157 and Eq.158, and taking the thermodynamic limit with ξ being fixed, the remaining $N-2$ background particles part of the probability under thermodynamic limit is given by

$$\begin{aligned} &\lim_{N\to\infty}(\text{probability of a single background particle})^{N-2} \\ &= \lim_{N\to\infty}\left(1-\frac{1}{N}\left(\frac{\xi}{2}\left[1+\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\right)\right)^{N-2} \\ &= e^{-\frac{\xi}{2}\left[1+\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]} \\ &= e^{-\left(\frac{1}{2}\left[1+\operatorname{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\right)\rho d_3}. \end{aligned} \tag{159}$$

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Appendix C: Simplification of the exponential decay probability distribution

In this appendix, we argue that the exponential decay probability distribution in Eq.95 can be replaced by unity. The basic idea is trying to show that $\exp\left(-\frac{1}{2}\left[1+\text{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)\right.\right.$ $\left.\left.+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\rho d_3\right)$ decays with d_3 in a slow manner so that it can be replaced by unity. To deal with the idea of "decays in a slow manner", we define the "decay depth" as

$$\text{decay depth} \equiv \left(\frac{1}{2}\left[1+\text{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\rho\right)^{-1}. \tag{160}$$

That is, the decay depth is defined by

$$\left[e^{-\left(\frac{1}{2}\left[1+\text{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\right)\rho d_3}\right]_{d_3=\text{decay depth}} = \frac{1}{e}. \tag{161}$$

To simplify the decay depth, we consider its order of magnitude. Using $1 \leq \left[1+\text{erf}\left(\frac{v_j^0}{\sqrt{a}}\right)\right]$ ≤ 2, the order of the decay depth is given by

$$\mathcal{O}\left(\text{decay depth}\right) = \mathcal{O}\left(\left(\left[1+\frac{\sqrt{a}}{\sqrt{\pi}v_j^0}e^{-\frac{\left(v_j^0\right)^2}{a}}\right]\rho\right)^{-1}\right) \tag{162}$$

Switching to the representation by dimensionless velocity $u_j^0 = \frac{v_j^0}{\sqrt{a}}$ and dropping the numerical factor of $\sqrt{\pi}$, we get

$$\mathcal{O}\left(\text{decay depth}\right) = \mathcal{O}\left(\left(\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\rho\right)^{-1}\right) \tag{163}$$

This is the order of magnitude of the decay depth of the probability distribution. How about the range of d_3 for non-trivial interaction we are interested in? From Fig.

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17 and Fig. 20, the maximum of relevant d_3 to be considered is

$$\begin{aligned}\text{maximum of relevant } d_3 &= d_2 + (d_2 - d_1)\frac{\frac{v_j^0+v_k^0}{2}}{\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2+\frac{\epsilon}{m}}} \\ &= d_2 + (d_2 - d_1)\frac{\frac{u_j^0+u_k^0}{2}}{\sqrt{\left(\frac{u_j^0-u_k^0}{2}\right)^2+\frac{\epsilon}{2k_BT}}}, \end{aligned} \tag{164}$$

so we have

$$\begin{aligned} &\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right) \\ =\ &\mathcal{O}\left(\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\rho\left(d_2+(d_2-d_1)\frac{\frac{u_j^0+u_k^0}{2}}{\sqrt{\left(\frac{u_j^0-u_k^0}{2}\right)^2+\frac{\epsilon}{2k_BT}}}\right)\right) \\ =\ &\mathcal{O}\left(\rho\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\left(d_2+(d_2-d_1)\frac{u_j^0+\alpha}{\sqrt{(\alpha)^2+\frac{\epsilon}{2k_BT}}}\right)\right) \end{aligned} \tag{165}$$

where $\alpha \equiv \frac{1}{2}\left(u_k^0 - u_j^0\right)$.

What is the order of magnitude of this $\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right)$? If we can argue that $\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right) < \mathcal{O}(1)$, then we are safe. But things are not so straightforward. There are v_k^0 that $\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right)$ is not small. For example, if $v_k^0 - v_j^0$ is quite small, that is, the velocities of the two particles are almost the same, the interaction time will be very long and hence d_3 is large in this case. This kind of v_k^0 do exist, but their population is quite small. They exist only in a small neighborhood around v_j^0, and so their population and hence their contribution to Δv_j^0 is small. This is the basic idea behind the calculation and argument we will show in the following.

Now let's check $\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right)$ with Eq.165. If $\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right)$ is not smaller than unity, then we are in trouble. Fortunately, we will see these trouble

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makers actually have negligible contributions. First, we rewrite Eq.165 as

$$\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right)$$
$$= \mathcal{O}\left(\rho d_2\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]+\rho\left(d_2-d_1\right)\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\frac{u_j^0+\alpha}{\sqrt{\left(\alpha\right)^2+\frac{\epsilon}{2k_BT}}}\right) \tag{166}$$

The first term in Eq.166 is not a function of α, that is, it is independent of v_k^0. Does the first term cause trouble? For the first term, troubles happen if

$$\rho d_2\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\geq 1, \tag{167}$$

that is, we have troubles if

$$1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\geq\frac{1}{\rho d_2}. \tag{168}$$

Since ρd_2 is small, Eq.168 means

$$u_j^0\leq\rho d_2, \tag{169}$$

and hence

$$\mathcal{O}\left(\text{population}\left(u_j^0\right)\right)\leq\mathcal{O}\left(\rho d_2\right), \tag{170}$$

in view of the fact that Maxwell's velocity distribution is $\frac{1}{\sqrt{\pi}}due^{-u^2}$ in its dimensionless form. Since the order of the population is negligible compared with the order we are willing to keep, the troubles in the first term of Eq.166 give negligible contributions.

Now let's deal with the second term, that is

$$\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right)=\mathcal{O}\left(\rho\left(d_2-d_1\right)\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\frac{u_j^0+\alpha}{\sqrt{\left(\alpha\right)^2+\frac{\epsilon}{2k_BT}}}\right). \tag{171}$$

To deal with this guy, we separate the situations to Case 1 and Case 2 by the order of α.

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Case 1 : $\mathcal{O}(\alpha) \geq \mathcal{O}\left(\sqrt{\frac{\epsilon}{k_B T}}\right)$

In this case, Eq.171 can be simplified as

$$\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right) = \mathcal{O}\left(\rho\left(d_2 - d_1\right)\left[1 + \frac{1}{u_j^0} e^{-\left(u_j^0\right)^2}\right]\left(1 + \frac{u_j^0}{\alpha}\right)\right). \tag{172}$$

Troubles happen if

$$\rho\left(d_2 - d_1\right)\left[1 + \frac{1}{u_j^0} e^{-\left(u_j^0\right)^2}\right]\left(1 + \frac{u_j^0}{\alpha}\right) \geq 1. \tag{173}$$

Case 1-1 : If $\mathcal{O}\left(u_j^0\right) \leq \mathcal{O}(\alpha)$, by Eq.173, troubles happen if

$$\rho\left(d_2 - d_1\right)\left[1 + \frac{1}{u_j^0} e^{-\left(u_j^0\right)^2}\right] \geq 1, \tag{174}$$

that is, we have troubles if

$$1 + \frac{1}{u_j^0} e^{-\left(u_j^0\right)^2} \geq \frac{1}{\rho\left(d_2 - d_1\right)}. \tag{175}$$

Since $\rho\left(d_2 - d_1\right)$ is small, Eq.175 means

$$u_j^0 \leq \rho\left(d_2 - d_1\right), \tag{176}$$

which means

$$\mathcal{O}\left(\text{population}\left(u_j^0\right)\right) \leq \mathcal{O}\left(\rho\left(d_2 - d_1\right)\right). \tag{177}$$

So the trouble makers do give negligible contributions.

Case 1-2 : If $\mathcal{O}\left(u_j^0\right) \geq \mathcal{O}(\alpha)$, by Eq.173, troubles happen if

$$\rho\left(d_2 - d_1\right)\left[1 + \frac{1}{u_j^0} e^{-\left(u_j^0\right)^2}\right] \frac{u_j^0}{\alpha} \geq 1. \tag{178}$$

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That is, we have troubles if

$$\alpha \leq \rho\left(d_2-d_1\right)\left[u_j^0+e^{-\left(u_j^0\right)^2}\right]. \tag{179}$$

Since $\alpha \equiv \frac{1}{2}\left(u_k^0-u_j^0\right)$, $d\alpha=\frac{1}{2}du_k^0$, Eq.179 implies

$$\mathcal{O}\left(\text{population}\left(u_j^0,u_k^0\right)\right) \leq \mathcal{O}\left(\rho\left(d_2-d_1\right)\int du_j^0 e^{-\left(u_j^0\right)^2}\left[u_j^0+e^{-\left(u_j^0\right)^2}\right]\right)=\mathcal{O}\left(\rho\left(d_2-d_1\right)\right). \tag{180}$$

So the potential troubles still give negligible contributions.

Case 2 : $\mathcal{O}\left(\alpha\right) \leq \mathcal{O}\left(\sqrt{\frac{\epsilon}{k_BT}}\right)$

In this case, Eq.171 can be simplified as

$$\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right)=\mathcal{O}\left(\rho\left(d_2-d_1\right)\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\frac{u_j^0+\alpha}{\sqrt{\frac{\epsilon}{k_BT}}}\right). \tag{181}$$

Here we drop the factor of two in $\frac{\epsilon}{2k_BT}$. Troubles happen if

$$\rho\left(d_2-d_1\right)\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\frac{u_j^0+\alpha}{\sqrt{\frac{\epsilon}{k_BT}}} \geq 1. \tag{182}$$

By $\mathcal{O}\left(\alpha\right) \leq \mathcal{O}\left(\sqrt{\frac{\epsilon}{k_BT}}\right)$, we have

$$\frac{1}{\alpha} \geq \frac{1}{\sqrt{\frac{\epsilon}{k_BT}}} \tag{183}$$

and hence

$$\frac{u_j^0}{\alpha}+1 \geq \frac{u_j^0+\alpha}{\sqrt{\frac{\epsilon}{k_BT}}}. \tag{184}$$

By Eq.184 and Eq.182, the necessary condition for Case 2 to have troubles is

$$\rho\left(d_2-d_1\right)\left[1+\frac{1}{u_j^0}e^{-\left(u_j^0\right)^2}\right]\left(1+\frac{u_j^0}{\alpha}\right) \geq 1 \tag{185}$$

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But Eq.185 is just the same condition as Eq.173 for Case 1, which we have already checked that all the troubles give negligible contributions. So we are done.

In summary, there are some $\left(u_j^0, u_k^0\right)$ that don't respect

$$\mathcal{O}\left(\frac{\text{maximum of relevant } d_3}{\text{decay depth}}\right) < \mathcal{O}\left(1\right). \tag{186}$$

However, the violations happen for small u_j^0 (Eq.169 and Eq.176) or the case that u_k^0 is very close to u_j^0 (Eq.179). The result is, the contributions given by these trouble makers are negligible in the order being considered, due to the fact that their population is small.

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Appendix D: Contribution of $\Delta v_j^0 \mid_{region-3}$

In this appendix, we argue that the contribution of $\Delta v_j^0 \mid_{region-3}$ is negligible when we sum over all velocities to get the correction in momentum transferred. In view of the equation of state (Eq.11), Δv_j^0 appears with the form as

$$\sum_j \frac{2m\Delta v_j^0}{T_j^0} = \frac{2N}{\sqrt{a\pi}} \int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}} 2m\frac{v_j^0}{2L}\Delta v_j^0 = \frac{2m\rho}{\sqrt{a\pi}} \int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}} v_j^0 \Delta v_j^0 \quad (187)$$

For $u_j^0 < \sqrt{\frac{\epsilon}{k_B T}}$, we have $\Delta v_j^0 \mid_{region-3} = -v_j^0$. So we get

$$\begin{aligned} &\left[\sum_j \frac{2m\Delta v_j^0}{T_j^0}\right]_{u_j^0<\sqrt{\frac{\epsilon}{k_B T}},\text{Class3}} \\ &= \left[-\frac{2m\rho}{\sqrt{a\pi}} \int_0^\infty dv_j^0 e^{-\frac{\left(v_j^0\right)^2}{a}} \left(v_j^0\right)^2 \rho \int d(d_3) \int_{v_j^0}^{\frac{2\frac{\epsilon}{m}}{v_j^0}} dv_k^0 f\left(v_k^0\right) \mid 1 - \frac{v_k^0}{v_j^0} \mid \right]_{u_j^0<\sqrt{\frac{\epsilon}{k_B T}}} \\ &= -\frac{4}{\pi}\rho^2 k_B T \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} \left(u_j^0\right)^2 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} \left(1 - \frac{u_k^0}{u_j^0}\right) \int d(d_3)\right]. \end{aligned} \quad (188)$$

What is the order of magnitude of this guy? Our strategy is to bound this guy and show that its order of magnitude is smaller compared with the accuracy we are retaining.

By Eq.91 and Fig. 20, the integral of d_3 is bounded by

$$\int d(d_3) < (d_2 - d_1) \frac{\frac{v_j^0+v_k^0}{2}}{\sqrt{\left(\frac{v_j^0-v_k^0}{2}\right)^2 + \frac{\epsilon}{m}}} = (d_2 - d_1) \frac{u_j^0 + u_k^0}{\sqrt{\left(u_j^0 - u_k^0\right)^2 + 2\frac{\epsilon}{k_B T}}} \quad (189)$$

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And so we have

$$\begin{aligned}
& \rho^2 k_B T \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} \left(u_j^0\right)^2 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} \left(1 - \frac{u_k^0}{u_j^0}\right) \int d(d_3) \right] \\
< \; & \rho^2 k_B T \left(d_2 - d_1\right) \\
& \times \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} u_j^0 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} \left(u_j^0 - u_k^0\right) \frac{u_j^0 + u_k^0}{\sqrt{\left(u_j^0 - u_k^0\right)^2 + 2\frac{\epsilon}{k_B T}}} \right] \\
= \; & \rho^2 k_B T \left(d_2 - d_1\right) \\
& \times \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} u_j^0 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} \left(u_j^0 + u_k^0\right) \frac{u_j^0 - u_k^0}{\sqrt{\left(u_j^0 - u_k^0\right)^2 + 2\frac{\epsilon}{k_B T}}} \right] \\
< \; & \rho^2 k_B T \left(d_2 - d_1\right) \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} u_j^0 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} \left(u_j^0 + u_k^0\right) \right] \\
= \; & \rho^2 k_B T \left(d_2 - d_1\right) \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} \left(u_j^0\right)^2 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} \right] \\
& + \rho^2 k_B T \left(d_2 - d_1\right) \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} u_j^0 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} u_k^0 \right] \qquad (190)
\end{aligned}$$

Since $\int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} < \int_0^{\infty} du_k^0 e^{-\left(u_k^0\right)^2} = \mathcal{O}\left(1\right)$ and $\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} \left(u_j^0\right)^2 < \left(\sqrt{\frac{\epsilon}{k_B T}}\right)^3$ $= \left(\frac{\epsilon}{k_B T}\right)^{1.5}$, the first term in the final form of Eq.190 is bounded by $\left(\rho^2 \left(d_2 - d_1\right) \epsilon\right) \sqrt{\frac{\epsilon}{k_B T}}$ and thus is negligible. The term needed to be checked is

$$\rho^2 k_B T \left(d_2 - d_1\right) \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} u_j^0 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} u_k^0 \right] \qquad (191)$$

Using the property that $e^{-x^2} x < 1$ for $x \geq 0$, we have

$$\int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} u_k^0 < \frac{\epsilon}{k_B T}\frac{1}{u_j^0} - u_j^0 \qquad (192)$$

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Put Eq.192 into Eq.191, and we get

$$
\begin{aligned}
&\rho^2 k_B T \left(d_2 - d_1\right) \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} u_j^0 \int_{u_j^0}^{\frac{\epsilon}{k_B T}\frac{1}{u_j^0}} du_k^0 e^{-\left(u_k^0\right)^2} u_k^0\right] \\
&< \rho^2 k_B T \left(d_2 - d_1\right) \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} u_j^0 \left(\frac{\epsilon}{k_B T}\frac{1}{u_j^0} - u_j^0\right)\right] \\
&= \rho^2 \left(d_2 - d_1\right) \epsilon \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2}\right] \\
&- \rho^2 k_B T \left(d_2 - d_1\right) \left[\int_0^{\sqrt{\frac{\epsilon}{k_B T}}} du_j^0 e^{-\left(u_j^0\right)^2} \left(u_j^0\right)^2\right] \\
&= \mathcal{O}\left(\left[\rho^2 \left(d_2 - d_1\right) \epsilon\right] \sqrt{\frac{\epsilon}{k_B T}}\right) + \mathcal{O}\left(\left[\rho^2 \left(d_2 - d_1\right) \epsilon\right] \sqrt{\frac{\epsilon}{k_B T}}\right),
\end{aligned}
\tag{193}
$$

and so we are done. When putting the effect of Δv_j^0 in the correction of equation of state, the contribution of $\Delta v_j^0 \mid_{region-3}$ is negligible, due to the fact that $\Delta v_j^0 \mid_{region-3}$ appears only for small v_j^0 and thus the population is small.

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Appendix E: Particle-particle repulsion

In this appendix, we argue that particle pairs that their separations cannot reach $r = d_1$ due to the potential barrier give negligible correction, due to the fact that their population is quite small. By Eq.128, all we need to consider is $\sum_j \frac{2mv_j^0}{T_j^0}\frac{\Delta T_j^0}{T_j^0}$. By Eq.129, for $\Delta u < \Delta u\mid_{critical} = \sqrt{\frac{2U_{max}}{k_B T}}$, the interaction time is given by

$$\Delta t_{interaction}\left(0, v_k^0\right) = \int_{d_{min}\left(v_k^0\right)}^{r_0} \frac{dr}{\sqrt{\left(\frac{v_k^0}{2}\right)^2 - \frac{U(r)}{m}}} \tag{194}$$

where d_1 is replaced by $d_{min}\left(v_k^0\right)$, and this is the only difference. By Eq.130, Eq.131, Eq.132 and Eq.194, the effect of replacing d_1 with $d_{min}\left(v_k^0\right)$ for $\Delta u < \Delta u\mid_{critical}$ in $\frac{1}{2}\Delta T_j^0$ is

$$\begin{aligned}
&\frac{1}{2}\Delta T_j^0 \mid_{\text{correction for } \Delta u < \Delta u|_{critical}} \\
&= \frac{N}{2}\frac{\sqrt{a}}{\sqrt{\pi}\left(v_j^0\right)^2}\int_0^{\sqrt{\frac{2U_{max}}{k_BT}}} du_k^0 \left[e^{-(u_k^0-u_j^0)^2} - e^{-(u_k^0+u_j^0)^2}\right]\left(u_k^0\right)^2 \int_{d_1}^{d_{min}\left(u_k^0\right)} \frac{dr}{\sqrt{\left(\frac{u_k^0}{2}\right)^2 - \frac{1}{2}\frac{U(r)}{k_BT}}} \\
&= \frac{N}{2}\frac{\sqrt{a}}{\sqrt{\pi}\left(v_j^0\right)^2}\int_0^{\sqrt{\frac{2U_{max}}{k_BT}}} du_k^0 \left[e^{-(u_k^0-u_j^0)^2} - e^{-(u_k^0+u_j^0)^2}\right]\left(u_k^0\right)^2 \\
&\left(\frac{2\left(d_{min}\left(u_k^0\right) - d_1\right)}{u_k^0} - \frac{2}{\left(u_k^0\right)^3}\int_{d_1}^{d_{min}\left(u_k^0\right)} dr\left[\frac{-U(r)}{k_BT}\right]\right) \\
&= \frac{N}{2}\frac{\sqrt{a}}{\sqrt{\pi}\left(v_j^0\right)^2}\int_0^{\sqrt{\frac{2U_{max}}{k_BT}}} du_k^0 \left[e^{-(u_k^0-u_j^0)^2} - e^{-(u_k^0+u_j^0)^2}\right] 2u_k^0\left(d_{min}\left(u_k^0\right) - d_1\right) \\
&- \frac{N}{2}\frac{\sqrt{a}}{\sqrt{\pi}\left(v_j^0\right)^2}\int_0^{\sqrt{\frac{2U_{max}}{k_BT}}} du_k^0 \left[e^{-(u_k^0-u_j^0)^2} - e^{-(u_k^0+u_j^0)^2}\right]\frac{2}{u_k^0}\int_{d_1}^{d_{min}\left(u_k^0\right)} dr\left[\frac{-U(r)}{k_BT}\right]
\end{aligned} \tag{195}$$

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Expand $\left[e^{-(u_k^0-u_j^0)^2}-e^{-(u_k^0+u_j^0)^2}\right]$ as

$$\begin{aligned}\left[e^{-(u_k^0-u_j^0)^2}-e^{-(u_k^0+u_j^0)^2}\right] &= e^{-\left(u_k^0\right)^2}e^{-\left(u_j^0\right)^2}\left(e^{2u_j^0u_k^0}-e^{-2u_j^0u_k^0}\right)\\ &= e^{-\left(u_k^0\right)^2}e^{-\left(u_j^0\right)^2}\left(4u_j^0u_k^0+\text{higher order of } u_k^0\right) \qquad (196)\end{aligned}$$

By Eq.196, $\left[e^{-(u_k^0-u_j^0)^2}-e^{-(u_k^0+u_j^0)^2}\right]$ contributes one order of u_k^0 when u_k^0 is small. Therefore, the order of the first term in Eq.195 is $\left(\sqrt{\frac{2U_{max}}{k_BT}}\right)^3=\left(\frac{2U_{max}}{k_BT}\right)^{1.5}$ and the order of the second term in Eq.195 is $\sqrt{\frac{2U_{max}}{k_BT}}\left(\left[\frac{-U(r)}{k_BT}\right]\right)=\mathcal{O}\left(\left(\frac{2U_{max}}{k_BT}\right)^{1.5}\right)$. Hence the effect of replacing d_1 with $d_{min}\left(v_k^0\right)$ for $\Delta u<\Delta u\mid_{critical}$ in $\frac{1}{2}\Delta T_j^0$ is negligible, and so the effect is negligible in equation of state, due to the fact that the population is too small to cause relevant effect.

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