# Correlation functions in classical gases at high frequency

Max Teubner
*Max-Planck-Institut für Biophysikalische Chemie, Postfach 2841, 37077 Göttingen, Germany*

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A general procedure is outlined to determine the exact asymptotic form of spectra in classical gases at high frequency. Examples are the force-force correlation or the velocity autocorrelation function of a tagged particle. For purely repulsive potentials of the form $\mathrm{Ar}^{-n}$, the asymptotic spectra are proportional to $\omega^{\sigma}\exp[-(\omega\tau)^{\nu}]$. Exponent $\nu$ and time constant $\tau$ depend only on the interparticle potential, while exponent $\sigma$ depends in addition on the correlation studied. The analysis makes use of the fact that the high-frequency spectra are dominated by high-energy binary collisions. It is argued that for arbitrary potentials the spectra decay slower than $\exp(-\mathrm{const}\times\omega^{2/3})$ and that the results are also relevant for dense fluids. The frequency range is estimated where quantum effects become important.

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## I. INTRODUCTION

Theoretical studies of high-frequency spectra in classical fluids seem to be rare. This is somewhat surprising, since such spectra play an important role for the dynamics of chemical reactions. For example, the process of vibrational energy relaxation of excited molecules in solution is of central importance for the understanding of reaction dynamics in the gas and liquid phase. The elementary step in this process involves the transfer of a quantum of vibrational energy into translational degrees of freedom of the solvent. The theoretical description usually is based on first order perturbation theory. This predicts for the relaxation rate of a harmonic oscillator with frequency $\omega_0$ in a thermal environment the Landau-Teller formula [1–4]

$$k=\frac{1}{2\mu\, k_B T}S_F(\omega_0), \tag{1}$$

where

$$S_F(\omega)=\int_{-\infty}^{+\infty}dt\, e^{i\omega t}\langle F(t)F(0)\rangle \tag{2}$$

is the spectrum of the fluctuating solvent force $F(t)$ exerted on the vibrational coordinate of the solute and $\mu$ is the mass of the oscillator. In principle, the right-hand side should be evaluated at the quantum level, but usually just the classical correlation function is inserted.

In real systems, oscillator frequencies range up to $\omega_0 \sim 10^{15}\ \mathrm{sec}^{-1}$ which corresponds to the H-H oscillation. At such frequencies all collective motion of the solvent is frozen. The only processes which contribute to the spectra in this frequency range are rare high-energy binary collisions (IBC model [5–7]). This is a vast simplification. In the frequency range of interest the many-body dynamics reduces to the two-body problem of binary collisions in a static potential. In the gas phase the potential is simply the binary potential between the molecules. In a fluid phase one must add the potential which arises from the (frozen) environment. In the high-frequency, high-energy range this is a small perturbation. Therefore the spectra in the fluid and in the gas phase are expected to be proportional [4,6]. I comment on this point later.

We conclude that the spectra in the high-frequency domain are known once the two-body problem is controlled. Apparently the first authors to use this approach were again Landau and Teller [1]. For the special case of an exponential potential and considering central collisions only, they found in the asymptotic domain

$$S_F(\omega)\sim e^{-(\omega\tau)^{2/3}}, \tag{3}$$

where the time constant $\tau$ depends on the potential, the temperature, and the mass of the molecules.

Landau and Teller's result, Eq. (3), does not seem to have received the attention it deserves. The reason, presumably, is that Eq. (3) is not a true asymptotic relation and cannot be used to calculate rate constants. These authors were only interested in qualitative features of the asymptotic spectrum. They neglected all noncentral collisions, and did not bother about the solvent density which determines the collision frequency. Such effects generate additional frequency-dependent factors which, however, vary less rapidly than the exponential. It is the purpose of this paper to supply these additional factors, at least for some potentials in the gas phase. This will transform Landau and Teller's result into a true asymptotic relation which can be used to quantitatively predict rate constants in the high-frequency domain.

In particular we will pose and partially answer the following questions.

(1) Is it possible to sharpen Eq. (3) into a true asymptotic relation and what is the form of the preexponential factors?

(2) How can one calculate the time constant $\tau$ for arbitrary potentials?

(3) Do all spectra decay weaker than exponentially?

(4) Does the exponent 2/3 have any significance beyond the exponential potential considered by Landau and Teller?

As argued above, the answer to these questions is not only an amusing exercise in statistical mechanics and complex variables, but of considerable importance to chemical dynamics. An additional motivation for analytical studies comes from certain difficulties in the numerical simulation of the high-frequency spectra which apparently have not been sufficiently appreciated.

The classical spectrum $S_F(\omega)$ can, in principle, be calculated from an equilibrium molecular dynamics (MD) simulation. However, there are several obstacles to reliably determine the spectra in the high-frequency domain. First, since the numerical accuracy is usually limited to 16 orders of magnitude, the high-frequency spectral range often is not accessible. Second, the high-frequency domain displays a considerable and unexpected dependence on the number $N$ of particles used in the simulation [8]. One can show that for any $N$ there is a frequency $\omega_N$ so that the MD spectrum is qualitatively in error for $\omega \geqslant \omega_N$ even for infinite simulation time. The most serious limitation of a MD simulation of the spectra, however, stems from the finite simulation time. High-frequency spectra are generated by almost central collisions of high energy. The highest energy $E_{max}$ in the course of a simulation sets an upper limit $\omega_{max}$ beyond which the MD spectra are qualitatively in error. Since $E_{max}$ increases only logarithmically with simulation time, the simulation time becomes prohibitively large for the spectral regions of interest. These matters are more fully discussed in Ref. [8].

In this paper I present a method to calculate the asymptotics of high-frequency spectra. The procedure is quite general and applicable to all potentials which can be analytically continued into a part of the complex $r$ plane. From a practical standpoint the Lennard-Jones potential

$$V_{LJ}(r) = \text{const} \times \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \tag{4}$$

is of much greater interest than the exponential potential studied by Landau and Teller. The spectra of this potential will be published elsewhere [8]. As a relatively simple example and a prerequisite to the Lennard-Jones potential I present in this paper a detailed calculation of spectra of gases interacting with the repulsive potential

$$V(r) = \frac{A}{r^n}, \quad n \geqslant 2. \tag{5}$$

The value $n=2$, while artificial, is interesting, since in this case some spectra can be calculated analytically for all frequencies. For $n>2$ we find simple analytical results only in the high-frequency region. In this way we obtain the true asymptotic expression for spectra for potentials of this type. This will answer the first three questions above for these potentials.

The paper is organized as follows. In Sec. II I present a simple expression for correlation functions in dilute gases composed of spherical molecules. This expression is the classical limit of a well known quantum mechanical formula, and reduces the calculation of correlation functions to the two-body problem. Section III discusses a few simple and well known applications. Section IV contains results for the special case $n=2$ where many spectra can be calculated analytically by elementary methods. A discussion of the general procedure to calculate asymptotic spectra follows in Sec. V. Section VI contains the asymptotic form of high-frequency spectra of the potential $V(r)$ for general $n$ including the spectrum of the velocity autocorrelation function of a tagged particle. In this section I also determine precisely in which sense the collisions seen in the high-frequency spectra are "almost central." I continue in Sec. VII with a qualitative discussion of high-frequency spectra in fluids. After a brief remark on general potentials in Sec. VIII, I turn to question 4 in Sec. IX. After presenting a conjecture for the upper bound on exponent $\nu$, the paper closes in Sec. X with an estimate of the frequency range where quantum effects become important.

## II. AVERAGES AND CORRELATIONS IN DILUTE GASES

Consider a tagged particle in a dilute gas of density $\rho$. We are interested in observables like the force and potential energy with the neighbors. The latter is given by

$$V_i(t) = \sum_{j \neq i} V(\mathbf{r}_{ij}(t)), \tag{6}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. We search to express quantities like $\langle V_i(t+\tau) V_i(t) \rangle$ by the dynamics of the two-body collisions.

$V_i(t)$ is an example of a simple but important class of observables. A relative binary observable $A_i = A_i(t_1, t_2, \ldots)$ associated with a tagged particle $i$ is a sum of local observables

$$A_i = \sum_{j \neq i} A_{loc}, \tag{7}$$

where each $A_{loc} = A_{loc}(t_1, t_2, \ldots) = A_{loc}(\mathbf{r}(t_1), \mathbf{r}(t_2), \ldots)$ depends only on the relative distance $\mathbf{r} = \mathbf{r}_{ij}$ of a pair of particles at times $t_1, t_2, \ldots$ . By considering limits this includes a possible dependence on relative velocities. We also require that $A_{loc}$ tends to zero for large separation. Since all particles are identical, we will often omit the index $i$.

Other simple examples of local observables are

$$\delta(r_{ij}(t) - r) \tag{8}$$

or

$$e^{\beta V(r_{ij}(t))} - 1, \quad \beta = (k_B T)^{-1}, \tag{9}$$

and products of these at different times. The time average of the first one leads to the radial distribution function $g(r)$ (see Sec. III C). By the same method one can show that the second one leads to the second virial coefficient $B_2$. Further examples are

$$(\mathbf{v}_{ij}(t+\tau) - \mathbf{v}_{ij}(t)) \cdot \mathbf{v}_{ij}(t) \tag{10}$$

or

$$\frac{l^2}{r_{ij}^2(t)}, \tag{11}$$

where $l$ is the angular momentum in the two-body problem. The first one is essentially the velocity autocorrelation function of a tagged particle. It is shown in Sec. III C that the second one leads to a well known expression of $B_2$ in terms of the scattering angle. As a final example consider the collision-induced dipole moment of a pair of dissimilar rare gas atoms [9]. These atoms do not possess a permanent dipole moment, but a transient moment

$$\mu(r_{ij}(t),E,l) \tag{12}$$

appears during a collision due to the distortion of the electron distribution. Apparently $\mu$ depends only on relative quantities (distance and velocity) and vanishes between collisions.

I will now give a derivation of the basic expression Eq. (17) used extensively throughout the rest of the paper. For the moment we also assume that the potential is purely repulsive.

In a dilute gas, subsequent collisions of the tagged particle are random and uncorrelated events, widely separated in time. Since $A_{loc}(t)$ is nonzero only for particles closely together, we expect

$$\langle A\rangle = Z\langle A_{loc}\rangle, \tag{13}$$

where $Z$ is the number of collisions per unit time and $\langle A_{loc}\rangle$ is an average over all collisions. This should be correct provided the time span covered by the $t_i$ is small versus the time $t_{coll}$ between collisions.

Since a collision involves only two particles interacting with a spherically symmetric potential, a collision is completely characterized by the following quantities: The velocity $v_s$ of the center of gravity, the angular momentum vector $\mathbf{l}$ which also determines the plane of motion, the energy $E$ in the center of mass frame, and the time $t$. By definition, $A_{loc}$ is independent of $v_s$ and the direction of $\mathbf{l}$. For a given collision, characterized by $E$ and $l$, the average is given by the time average

$$\langle A_{loc}\rangle_{E,l} = \int_{-\infty}^{\infty} d\tau\, A_{loc}(\tau+t_1,\tau+t_2,\ldots). \tag{14}$$

Therefore we may write

$$\langle A\rangle = \int_0^{\infty} dE \int_0^{\infty} dl\, Z(E,l) \times \int_{-\infty}^{\infty} d\tau\, A_{loc}(\tau+t_1,\tau+t_2,\ldots), \tag{15}$$

where $Z(E,l)$ is the number density of collisions with energy $E$ and angular momentum $l$ per unit time. This quantity is well known from the kinetic theory of gases [10]. We have

$$Z(E,l) = 4\pi\rho(2\pi\mu k_B T)^{-3/2} e^{-\beta E} 2\pi\, l, \tag{16}$$

where $\rho$ is the density, $\mu = m/2$ the reduced mass, $l$ the angular momentum, $E$ the energy in the center of mass frame, and $\beta = (k_B T)^{-1}$. Inserting, we obtain the following expression for the average of a relative observable [9,11]

$$\langle A\rangle = 4\pi\rho(2\pi\mu k_B T)^{-3/2} \int_0^{\infty} dE\, e^{-\beta E} \int_0^{\infty} 2\pi l\, dl \times \int_{-\infty}^{\infty} d\tau A_{loc}(\tau+t_1,\tau+t_2,\ldots). \tag{17}$$

On the right-hand side the $A_{loc}$ refer to the unique solution of the two-body problem at definite energy $E$ and angular momentum $l$.

We have derived this equation for purely repulsive potentials so that there are no bound states. If the potential is not purely repulsive, certain values of $E$ and $l$ admit several possible trajectories. For $E>0$, at most one of these is a scattering state, the others corresponding to periodic motion (in the radial coordinate). Let $\{T_i(E,l)\}$ be the collection of periods for a given pair $(E,l)$ where $T=\infty$ corresponds to scattering. Then the generalization of Eq. (17) to arbitrary potentials is given by

$$\langle A\rangle = 4\pi\rho(2\pi\mu k_B T)^{-3/2} \int_{E_{min}}^{\infty} dE\, e^{-\beta E} \int_0^{\infty} 2\pi l\, dl \times \sum_i \int_0^{T_i(E,l)} d\tau\, A_{loc}(\tau+t_1,\tau+t_2,\ldots). \tag{18}$$

The proof is somewhat lengthy and relegated to Appendix A.

The quantum analog of this relation is probably better known than its classical limit. It is simply

$$\langle A\rangle = \frac{1}{Z}\mathrm{Tr}\, e^{-\beta H} A \tag{19}$$

in a representation where $H$ and $\mathbf{L}$ are simultaneously diagonal. As in the classical case, $A$ must vanish for widely separated particles and depend only on relative coordinates and velocities. The trace over the center of mass can be performed and cancels the corresponding factor in the partition function $Z$. The remaining term in $Z$ is the partition function of a single structureless particle with reduced mass $\mu$,

$$Z = V\left(\frac{\mu k_B T}{2\pi\hbar^2}\right)^{3/2}. \tag{20}$$

An additional factor of $N$ is generated by taking the trace over all particles.

For operators which commute with the angular momentum operator $\mathbf{L}$, a complete orthonormal set $\{\psi_{nl}\}$ of eigenfunctions to $H$ and $\mathbf{L}$ can be chosen and we obtain the quantum analog of Eq. (18),

$$\langle A\rangle = \rho\left(\frac{2\pi\hbar^2}{\mu k_B T}\right)^{3/2} \sum_{nl} (2+1) e^{-\beta E_{nl}} \langle\psi_{nl}|A|\psi_{nl}\rangle. \tag{21}$$

Formally, the classical limit is obtained by the replacements

$$\sum (2l+1) \to \hbar^{-2} \int 2l\, dl \tag{22}$$

$$\sum_n e^{-\beta E_n} \langle \cdot \rangle_n \to h^{-1} \int dE e^{-\beta E} \int dt, \tag{23}$$

where $\langle \cdot \rangle$ denotes a quantum average in state $n$.

We wish to apply the above result to correlations of relative observables $A$ and $B$. Suppose for ease of notation that both depend only on the distances $r_j$ to the reference particle, possibly at different times,

$$A = \sum_j A_{loc}(r_j), \tag{24}$$

$$B = \sum_k B_{loc}(r_k). \tag{25}$$

In the product

$$AB = \sum_j A_{loc}(r_j) B_{loc}(r_j) + \sum_{j \neq k} A_{loc}(r_j) B_{loc}(r_k) \tag{26}$$

the second term on the right is of order $\rho^2$ and, up to higher order, its average is equal to $\langle A \rangle \langle B \rangle$. We obtain

$$\langle AB \rangle - \langle A \rangle \langle B \rangle = \left\langle \sum_j A_{loc}(r_j) B_{loc}(r_j) \right\rangle. \tag{27}$$

The sum on the right-hand side is again a relative observable. We apply Eq. (18) and obtain

$$\begin{aligned} &\langle A(t)B(0)\rangle - \langle A \rangle \langle B \rangle \\ &\quad = 4\pi\rho(2\pi\mu k_B T)^{-3/2} \int_{E_{min}}^{\infty} dE\, e^{-\beta E} \int_0^{\infty} 2\pi l\, dl \\ &\quad \times \sum_i \int_0^{T_i(E,l)} d\tau\, A_{loc}(\tau+t) B_{loc}(\tau). \end{aligned} \tag{28}$$

In the rest of this paper we will be mainly concerned with purely repulsive potentials. In this case we obtain for the spectrum

$$\begin{aligned} S_A(\omega) &= \int_{-\infty}^{\infty} dt\, e^{i\omega t} [\langle A(t)A(0)\rangle - \langle A \rangle^2] \\ &= 4\pi\rho(2\pi\mu k_B T)^{-3/2} \\ &\quad \times \int_0^{\infty} dE\, e^{-\beta E} \int_0^{\infty} 2\pi l\, dl |A_{loc}(\omega)|^2, \end{aligned} \tag{29}$$

where

$$A_{loc}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} A_{loc}(t) \tag{30}$$

is the Fourier transform of $A_{loc}$ on the trajectory characterized by $E,l$.

## III. SOME SIMPLE APPLICATIONS

Before we proceed to the spectra, let us apply the results of Sec. II to a few simple and well known problems. This section contains no new material and only serves to gain some practice in applying Eq. (18) and to introduce some notation. It may be skipped by most readers.

### A. Radial distribution function

Let us first show that

$$\left\langle \sum_j \delta(r_{ij}(t) - r) \right\rangle = 4\pi r^2 \rho e^{-\beta V(r)}. \tag{31}$$

To prove it note that the motion is confined to a plane. In this plane we may decompose the radius vector $\mathbf{r} = \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ as

$$\mathbf{r}(t) = r(t)\mathbf{n}(t), \quad \mathbf{n}(t) = \begin{pmatrix} \cos\theta(t) \\ \sin\theta(t) \end{pmatrix}, \tag{32}$$

where $\mathbf{n}$ is a two-dimensional unit vector. The equations of motion for $r(t)$ and $\theta(t)$ are

$$\frac{\mu}{2}\dot{r}^2 + V(r) + \frac{l^2}{2\mu r^2} = E \tag{33}$$

and

$$\dot{\theta} = \frac{l}{\mu r^2}, \tag{34}$$

where

$$\mu = \frac{m}{2} \tag{35}$$

is the reduced mass and $l$ is the angular momentum.

In the time integrals

$$\sum_i \int_0^{T_i(E,l)} dt\, \delta(r_{ij}(t) - r) \tag{36}$$

introduce $r_{ij}$ as a new variable. Since every point is transversed twice, this becomes

$$2\sum_i \int_{a_i}^{b_i} \delta(r_{ij} - r) \frac{dr_{ij}}{\dot{r}_{ij}}, \tag{37}$$

where $\dot{r}_{ij} > 0$ and $a_i$ and $b_i$ are the two turning points for periodic motion. (In the case of collisions the upper bound is infinite.) This is equal to

$$\frac{2}{\dot{r}_{ij}(r)} = 2\sqrt{\frac{\mu}{2}} \frac{1}{\sqrt{E - V - \frac{l^2}{2\mu} r^{-2}}}, \tag{38}$$

provided $r$ is located in one of the intervals $(a_i, b_i)$ and vanishes otherwise. This condition means that the argument of the square root must be non-negative.

Now we can perform the energy integration. Multiplying by $e^{-\beta E}$ and setting

$$E = V + \frac{l^2}{2\mu} r^{-2} + x^2, \quad \frac{dE}{x} = 2dx, \tag{39}$$

we obtain

$$\begin{aligned}\int_0^\infty dE\, e^{-\beta E} \sum_i \int_0^{T_i(E,l)} dt\, \delta(r_{ij}(t) - r) &= 4\sqrt{\frac{\mu}{2}} \int_0^\infty dx\, e^{-\beta V - \beta(l^2/2\mu) r^{-2} - \beta x^2} \\ &= \sqrt{2\pi\mu k_B T} e^{-\beta V - \beta(l^2/2\mu) r^{-2}}.\end{aligned} \tag{40}$$

We multiply by $2\pi l$ and integrate over the angular momenta. The right-hand side becomes

$$(2\pi\mu k_B T)^{3/2} r^2 e^{-\beta V}. \tag{41}$$

This must be multiplied by $4\pi\rho(2\pi k_B T)^{-3/2}$ and proves the assertion.

### B. Number of bound particles

It is sometimes interesting to decompose the total radial distribution function $g(r)$ into contributions from the bound and scattering states separately. Setting $A = 1$ in Eq. (18) and performing the sum over the finite periods only, we obtain the average number of bound particles for any given particle,

$$\begin{aligned}\langle n_b \rangle = {} & 4\pi\rho(2\pi\mu k_B T)^{-3/2} \\ & \times \int dE\, e^{-\beta E} \int 2\pi l\, dl \sum_i T_i(E,l).\end{aligned} \tag{42}$$

The radial distribution function $g_b(r)$ due to the bound particles only is obtained by replacing $\Sigma_i T_i$ by

$$\frac{2}{\dot{r}} = \frac{\sqrt{2\mu}}{\sqrt{E - V - \frac{l^2}{2\mu} r^{-2}}}. \tag{43}$$

Integration is over those $E, l$ which render the square root positive and admit a finite turning point to the right of $r$. A detailed discussion is given elsewhere [8]. Again, the quantum mechanical counterparts are formally much simpler,

$$\langle n_b \rangle = \rho \left( \frac{2\pi\hbar^2}{\mu k_B T} \right)^{3/2} \sum_n e^{-\beta E_n} \tag{44}$$

and

$$g_b(r) = \rho \left( \frac{2\pi\hbar^2}{\mu k_B T} \right)^{3/2} \sum_n e^{-\beta E_n} |\psi_n(r)|^2, \tag{45}$$

where the sums run over the bound states.

### C. Virial coefficient and scattering angle

Consider the local observable

$$A_{loc}(t) = \frac{l^2}{r^2(t)} = \mu l \dot{\theta}(t). \tag{46}$$

After time and energy integration we find as previously

$$\begin{aligned}&\int dE\, e^{-\beta E} \int dt \frac{1}{r(t)^2} \\ &\quad = \int_0^\infty r^{-2} \sqrt{2\pi\mu k_B T}\, e^{-\beta V(r)} e^{-\beta(l^2/2\mu) r^{-2}} dr.\end{aligned} \tag{47}$$

On the other hand, integrating the expression involving $\theta$ over time yields the sum of the changes $\Delta_i \theta$ for all periods. Comparing we find

$$\begin{aligned}& l^2 \sqrt{2\pi\mu k_B T} \int_0^\infty r^{-2} e^{-\beta V(r)} e^{-\beta(l^2/2\mu) r^{-2}} dr \\ &\quad = \mu l k_B T \int d(\beta E) e^{-\beta E} \sum_i \Delta_i \theta.\end{aligned} \tag{48}$$

Now we subtract

$$l^2 \sqrt{2\pi\mu k_B T} \int_0^\infty r^{-2} \; e^{-\beta(l^2/2\mu) r^{-2}} dr = \pi\mu l k_B T, \tag{49}$$

multiply by $2\pi l\, dl$, and integrate. The left-hand side becomes

$$(2\pi\mu k_B T)^{3/2} 2\mu k_B T \int_0^\infty r^2 (e^{-\beta V(r)} - 1) dr \tag{50}$$

and we obtain for the second virial coefficient

$$\begin{aligned}& 2\pi \int_0^\infty r^2 (e^{-\beta V(r)} - 1) dr \\ &\quad = 2\pi^2 (2\pi\mu k_B T)^{-3/2} \int d(\beta E) e^{-\beta E} \\ &\qquad \times \int_0^\infty l^2 dl \left( \sum_i \Delta_i \theta - \pi \right).\end{aligned} \tag{51}$$

In particular, for purely repulsive potentials the sum contains only one term and $\Delta\theta - \pi$ is equal to minus the scattering angle $\chi$. We obtain

$$2\pi\int_0^\infty r^2(1-e^{-\beta V(r)})dr$$
$$=2\pi^2(2\pi\mu k_BT)^{-3/2}\int_0^\infty d(\beta E)e^{-\beta E}\int_0^\infty l^2 dl\chi(E,l), \tag{52}$$

which is equivalent to the expression in Ref. [12].

## IV. POTENTIAL $V(r)=Ar^{-2}$

In this section we start with the calculation of the high-frequency spectra. Gases with inverse square potentials are particularly simple and we do not need the general apparatus discussed in Sec. V. Many features of the spectra can be calculated analytically by elementary means.

From the equation of motion Eq. (33), we obtain the turning point $r_0$

$$r_0^2=\frac{1}{E}\left(A+\frac{l^2}{2\mu}\right) \tag{53}$$

and write the equation of motion in the form

$$\dot{r}^2=g^2\left(1-\frac{r_0^2}{r^2}\right), \tag{54}$$

where $g$ is the relative velocity at infinity and

$$E=\frac{1}{2}\mu g^2$$

is the energy. If the origin of time is defined by $\dot{r}(0)=0$, the solution is

$$r(t)=\sqrt{r_0^2+g^2t^2}. \tag{55}$$

### A. Observable $r^{-2}$

The simplest local observable is the potential itself. We have

$$r^{-2}(\omega)\equiv\int_{-\infty}^\infty dt\, e^{i\omega t}r^{-2}(t)=\frac{\pi}{r_0 g}e^{-\omega r_0/g}. \tag{56}$$

With $\lambda=\sqrt{\mu A/2}$ we find after some algebra

$$\int_0^\infty |r^{-2}(\omega)|^2 2\pi l\, dl=2\pi^3\mu^2\int_1^\infty e^{-2\omega\lambda z/E}\frac{dz}{z}. \tag{57}$$

To integrate over the energy we use

$$\int_0^\infty e^{-\beta E-2\omega\lambda z/E}dE=\beta^{-1}\sqrt{\omega\tau z}K_1(\sqrt{\omega\tau z}), \tag{58}$$

where $K_1$ is the modified Bessel function and the time constant $\tau$ is defined by

$$\tau=4\beta\sqrt{2\mu A}. \tag{59}$$

We find

$$\int_0^\infty dE\int_0^\infty 2\pi l\, dl|r^{-2}(\omega)|^2$$
$$=2\pi^3\mu^2\beta^{-1}\int_1^\infty \sqrt{\omega\tau z}K_1(\sqrt{\omega\tau z})\frac{dz}{z} \tag{60}$$

and, setting $x^2=\omega\tau z$,

$$\int_0^\infty dE\int_0^\infty 2\pi l\, dl|r^{-2}(\omega)|^2=4\pi^3\mu^2\beta^{-1}K_0(\sqrt{\omega\tau}). \tag{61}$$

For potentials without a hard core let us define a "thermal radius" by

$$V(r_{th})=k_BT. \tag{62}$$

At the distance $r=r_{th}$ the potential energy is just equal to the thermal energy. In the present case we may replace $A$ by

$$A=k_BTr_{th}^2. \tag{63}$$

Using this notation we finally obtain for the spectrum of the potential energy correlations on a tagged particle

$$\int_{-\infty}^\infty dt\, e^{i\omega t}\langle V_i(t)V_i(0)\rangle=\pi^{5/2}(k_BT)^2\rho r_{th}^3\tau K_0(\sqrt{\omega\tau}). \tag{64}$$

This relation is exact for all $\omega$ in a dilute gas.

The example displays a typical feature of high-frequency spectra: They always seem to decay slower than exponentially. In the example here, inserting $K_0(x)\sim\sqrt{\pi/x}\,e^{-x}$ for large $\omega\tau$, the right-hand side becomes

$$\frac{\pi^3}{\sqrt{2}}(k_BT)^2\rho r_{th}^3\tau(\omega\tau)^{-1/4}e^{-\sqrt{\omega\tau}}. \tag{65}$$

Below we will discuss many more examples of spectra of this type. The first authors who discovered a spectrum $\sim e^{-(\omega\tau)^\nu}$ with $\nu=2/3$ seem to be Landau and Teller [1] for the exponential potential $e^{-r/a}$.

Let us replace $A$ in Eq. (59) by Eq. (63). Then we obtain the suggestive form

$$\tau=4\frac{r_{th}}{v_{th}}, \tag{66}$$

where

$$v_{th}=\sqrt{\frac{k_BT}{2\mu}} \tag{67}$$

is the mean square thermal velocity along the $x$ axis (say). Therefore $\tau$, which measures the duration of a collision, is proportional to the time it takes a thermal particle to travel its own diameter. Very similar features will be found for the other potentials.

One further point is noteworthy. Checking the calculation one verifies that for a given $\omega$ the main contribution to the spectrum comes from almost central collisions $(l\sim 0)$ with energies near

$$\frac{\partial}{\partial E}(\beta E+2\omega\lambda/E)=0, \tag{68}$$

i.e., near

$$\beta E\sim\frac{\sqrt{\omega\tau}}{2}. \tag{69}$$

### B. Velocity autocorrelation function

A complete analytic calculation is possible but somewhat involved. Since the problem is discussed again in Sec. VI F for general $n$, I only present the result. In the high-frequency region the spectrum of the velocity fluctuations of a tagged particle is given by

$$\int_{-\infty}^{\infty}dt\, e^{i\omega t}\langle\dot{\mathbf{r}}_i(t)\cdot\dot{\mathbf{r}}_i(0)\rangle$$

$$\sim 32\pi^2\rho r_{th}^4\sqrt{\frac{k_BT}{\mu}}(\omega\tau)^{-5/4}e^{-\sqrt{\omega\tau}}. \tag{70}$$

Comparing with the spectrum of the potential we observe that both display the same subexponential decay and differ only in the algebraic prefactors. We will see that this is a general phenomenon. The spectra of generic local observables belonging to the same potential have the same (subexponential) decay. They differ only in prefactors that usually vary less rapidly with $\omega$.

## V. GENERAL REMARKS ON ASYMPTOTIC SPECTRA

According to Eq. (29) the first step in calculating spectra is to estimate the Fourier transform $A(\omega)$ on individual trajectories. In a second step these are averaged over energies and angular momenta.

To have something concrete in mind, let $A(r)$ be some inverse power of the distance and consider

$$r^{-p}(\omega)\equiv\int_{-\infty}^{\infty}dt\frac{e^{i\omega t}}{r^p(t)}, \tag{71}$$

where the exponent $p$ is positive. (We will see later in Sec. VI H that the observables $r^{\pm p}$ are in fact representative for a very large class of observables.)

It is well known, that the asymptotics of the Fourier transform is governed by the singularity structure of the integrand in the complex plane. Suppose that $r(t)$, as a function of the complex variable $t$, can be analytically continued into some strip containing the real axis. Let $t^*$ be the minimum of the imaginary parts of the singularities of $r(t)$ in the upper half plane so that $r(t)$ is analytic in the strip $0<\mathrm{Im}(t)<t^*$. Since $r^{-p}(t)$ is even in $t$ we may assume $\omega>0$. We can move the contour of integration to a parallel to the real axis through $it^*$ (if necessary we can avoid the singularity itself by some small indentation in the contour). Then we obtain

$$r^{-p}(\omega)=e^{-\omega t^*}\int_{-\infty}^{\infty}dt\frac{e^{i\omega t}}{r^p(t+it^*)}. \tag{72}$$

If some information is available about the behavior of $r(t)$ near the singularity, the integral can be processed further. The important point to note is that the asymptotic behavior is dominated by the singularity in the upper half plane with the smallest imaginary part $t^*$ [1].

$r(t)$ satisfies the equation of motion, Eq. (33),

$$\frac{dr}{dt}=\pm\sqrt{\frac{2}{\mu}}\sqrt{E-V(r)-\frac{l^2}{2\mu r^2}} \tag{73}$$

in the whole domain of analyticity. According to a theorem of Cauchy, $r(t)$ is analytic everywhere except possibly at singularities of the right-hand side. These are given by $r=0$ (for $l\neq 0$), the singularities of $V(r)$, and the zeros of the expression in the square root. At these zeros, however, $r(t)$ is analytic. Indeed, near such a point $r_1$, the differential equation simplifies to

$$\frac{dr}{dt}=\text{const}\times\sqrt{r-r_1}. \tag{74}$$

The solution is $r(t)=r_1+\text{const}\times t^2$ which is analytic at $r_1$. We conclude, that the possible singularities are located at $r=0$ and at the singularities of $V(r)$.

In the simplest situation $V(r)$ has a single singularity at $r=0$. The case $V(r)=\mathrm{A}r^{-n}$ is studied in detail below. The Lennard-Jones potential, Eq. (4), is another example. It will be discussed in a future paper [8]. In such cases, $t^*$ is given by the imaginary part of

$$\sqrt{\frac{\mu}{2}}\int_{r_0}^{0}\frac{dr}{\sqrt{E-V(r)-\frac{l^2}{2\mu}r^{-2}}}, \tag{75}$$

where $r_0$ is the turning point.

## VI. POTENTIAL $V(r)=\mathrm{A}r^{-n}$

For simplicity we assume $n>2$. A few remarks about the case $n<2$ are made in Sec. VI G. As previously, we often replace the factor $A$ by the "thermal radius" defined by

$$A=k_BTr_{th}^{\,n}. \tag{76}$$

The value of $t^*$ is given by

$$t^*(E,l)=\sqrt{\frac{\mu}{2}}\int_0^{r_0}\frac{dr}{\sqrt{\mathrm{A}r^{-n}+\frac{l^2}{2\mu}r^{-2}-E}}, \tag{77}$$

where the turning point $r_0=r_0(E,l)$ is given by

$$\mathrm{A}r_0^{-n}+\frac{l^2}{2\mu}r_0^{-2}-E=0. \tag{78}$$

### A. Fourier transform on individual trajectories

Our first task is to evaluate

$$\int_{-\infty}^{\infty}dt\,\frac{e^{i\omega t}}{r^p(t+it^*)} \tag{79}$$

for large positive $\omega$. In the vicinity of the singularity where $r\sim 0$, the equation of motion simplifies to

$$\frac{\mu}{2}\dot{r}^2+\mathrm{A}r^{-n}\sim 0. \tag{80}$$

(Here we need the assumption $n>2$.) We insert the ansatz

$$r(t)\sim\xi c(t-it^*)^{\lambda}, \tag{81}$$

where $\xi$ is some root of unity, $c>0$, and the complex plane has a cut from $it^*$ to $i\infty$. We find

$$\lambda=\frac{2}{n+2}, \tag{82}$$

$$c^{2+n}=\frac{2A}{\mu}\lambda^{-2}, \tag{83}$$

$$\xi^{2+n}=-1. \tag{84}$$

Therefore the singularity at $r=0$ is an algebraic branch point. In the asymptotic region we may insert the solution (81) and obtain for $p>0$

$$\int_{-\infty}^{\infty}dt\,\frac{e^{i\omega t}}{r^p(t+it^*)}\sim\xi^{-p}\,c^{-p}\int_{-\infty}^{\infty}\frac{e^{i\omega t}}{t^{\lambda p}}dt$$
$$=\xi^{-p}\,c^{-p}\,\frac{2\pi}{\Gamma(\lambda p)}e^{(i\pi/2)p\lambda}\omega^{\lambda p-1}. \tag{85}$$

Here the contour has been deformed to a loop along the imaginary axis cut from infinity to 0 and back to infinity on the other side of the cut.

The right-hand side must be real for all $p$. Therefore

$$\xi=e^{(i\pi/2)\lambda} \tag{86}$$

which also satisfies $\xi^{n+2}=-1$. We obtain for the spectrum on a single trajectory in the asymptotic region

$$r^{-p}(\omega)\sim\frac{2\pi}{\Gamma(\lambda p)}c^{-p}\omega^{\lambda p-1}\,e^{-\omega t^*(E,l)}. \tag{87}$$

For $l=0$ and $n\to 2$ the right-hand side should tend to the corresponding results for $n=2$. Using Sec. IV this is checked easily.

Before we proceed let us ask under what conditions this result is expected to be valid. We expect the error to be small if the terms neglected in the equation of motion are small versus the terms retained. This means

$$\frac{A}{r^n}\gg E,\quad \frac{A}{r^n}\gg\frac{l^2}{2\mu r^2}. \tag{88}$$

Inserting $r\sim ct^{\lambda}$ and defining

$$\tau_{th}=\frac{r_{th}}{v_{th}} \tag{89}$$

we find after some algebra the conditions

$$\omega\tau_{th}\gg\frac{n+2}{2}(\beta E)^{(1/2)+(1/n)},$$
$$\omega\tau_{th}\gg\frac{n+2}{2}\left(\frac{l^2}{2\mu k_BTr_{th}^2}\right)^{(1/2)+[2/(n-2)]}. \tag{90}$$

We will verify later that these conditions are indeed satisfied in the asymptotic region. The next step is to evaluate the double integral

$$\int_0^{\infty}2\pi l\,dl\int_0^{\infty}dE\,e^{-\beta E-2\omega t^*(E,l)} \tag{91}$$

for large $\omega$.

### B. Central collisions

It will be argued in Sec. VI E that almost central collisions make the dominant contribution to the spectra. In particular, they determine the exponential factor in the spectra. In order to introduce some notation, let us consider purely central collisions in this section.

We must estimate the integral

$$\int_0^{\infty}dE\,e^{-\beta E-2\omega\,t^*(E,0)} \tag{92}$$

for large $\omega$. Using Laplace's method the integral is dominated by the energy $E=E(\omega)$ satisfying

$$\frac{\partial}{\partial E}[\beta E+2\omega t^*(E,0)]=0. \tag{93}$$

For $l=0$, $t^*$ can be calculated,

$$t^*(E,0)=\frac{\sqrt{\pi}}{2}\,\frac{\Gamma\left(\frac{1}{2}+\frac{1}{n}\right)}{\Gamma\left(\frac{1}{n}\right)}\,\frac{r_{th}}{v_{th}}(\beta E)^{-(1/2)-(1/n)}, \tag{94}$$

where again $v_{th}=(k_BT/2\mu)^{1/2}$. Let

$$\nu=\left(\frac{3}{2}+\frac{1}{n}\right)^{-1} \tag{95}$$

and define a time constant

$$\tau = c_0 \frac{r_{th}}{v_{th}}, \tag{96}$$

where

$$c_0 = \sqrt{\pi}(1-\nu)^{-1/\nu} \frac{\Gamma\left(\frac{1}{\nu}\right)}{\Gamma\left(\frac{1}{n}\right)}. \tag{97}$$

Up to the numerical constant $c_0$, $\tau$ is the time it takes a thermal particle to travel its own diameter.

From Eq. (93) we find that the dominant energies for collisions with frequency $\omega$ are close to

$$\beta E(\omega) = (1-\nu)(\omega\tau)^{\nu} \tag{98}$$

and that

$$\int_0^\infty dE\, e^{-\beta E - 2\omega\, t^*(E,0)} \sim k_B T \sqrt{2\pi\nu(1-\nu)}(\omega\tau)^{\nu/2} e^{-(\omega\tau)^{\nu}}. \tag{99}$$

It is also interesting to estimate the width of energies around the dominant energy $E(\omega)$ which contribute to the spectrum. This is given by

$$\langle[\beta E - \beta E(\omega)]^2\rangle \sim \nu(1-\nu)(\omega\tau)^{\nu}. \tag{100}$$

The width increases with $\omega$, but the relative width $\langle[E - E(\omega)]^2\rangle/E(\omega)^2$ decreases $\sim \nu(1-\nu)^{-1}(\omega\tau)^{-\nu}$.

### C. Double integral for large frequencies

In this section we evaluate the double integral (91) in the high-frequency domain. In Eq. (77) we set $r = r_0 u$ and obtain

$$t^*(E,l) = \sqrt{\frac{\mu}{2}} \frac{1}{\sqrt{A}} r_0^{(n/2)+1} \times \int_0^1 \frac{du}{\sqrt{u^{-n} - 1 + \frac{l^2}{2\mu A} r_0^{n-2}(u^{-2}-1)}}. \tag{101}$$

Defining $s$ by

$$r_0 = \left(\frac{A}{E}\right)^{1/n} s \tag{102}$$

we have

$$\frac{l^2}{2\mu A} r_0^{n-2} = s^n - 1 \tag{103}$$

and we write $t^*$ in the form

$$t^*(E,l) = \sqrt{\frac{\mu}{2}} A^{1/n} E^{-(1/2)-(1/n)} s^{(n/2)+1} \times \int_0^1 \frac{du}{\sqrt{u^{-n} - 1 + (s^n - 1)(u^{-2}-1)}} \equiv \sqrt{\frac{\mu}{2}} A^{1/n} E^{-(1/2)-(1/n)} f(s). \tag{104}$$

We shall later need

$$f(1) = \sqrt{\pi} \frac{\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)}{\Gamma\left(\frac{1}{n}\right)},$$

$$f'(1) = \frac{\sin\left(\frac{\pi}{n}\right)}{\sqrt{\pi}} \Gamma\left(\frac{3}{2} - \frac{1}{n}\right) \Gamma\left(\frac{1}{n}\right). \tag{105}$$

The function $f(s)$ is monotonically increasing for $s > 1$. Indeed, denoting the expression under the square root by $\alpha$, we have

$$f'(s) = s^{n/2} \int_0^1 \frac{du}{\alpha^{3/2}} \left\{ \left(\frac{n}{2} + 1\right)[u^{-n} - 1 + (s^n - 1)(u^{-2} - 1)] - \frac{n}{2} s^n (u^{-2} - 1) \right\}. \tag{106}$$

Since $u^{-n} - 1 > u^{-2} - 1$ the braces are larger than

$$(u^{-2} - 1)\left[\left(\frac{n}{2} + 1\right) s^n - \frac{n}{2} s^n\right] = (u^{-2} - 1) s^n \tag{107}$$

which shows that $f'(s) > 0$.

Using

$$l^2 = 2\mu A^{2/n} E^{1-(2/n)}(s^2 - s^{2-n}), \quad s > 1 \tag{108}$$

we change integration over $l$ into integration over $s$ with

$$2l\, dl = 2\mu A^{2/n} E^{1-(2/n)}[2s - (2-n)s^{1-n}]ds \tag{109}$$

and obtain

$$\int_0^\infty 2\pi l\, dl\, e^{-2\omega t^*(E,l)} = 2\pi\mu A^{2/n} E^{1-(2/n)} \int_1^\infty ds[2s - (2-n)s^{1-n}] e^{-2\omega t^*(E,s)} \tag{110}$$

and

$$\int_0^\infty dE \int_0^\infty 2\pi l dl e^{-\beta E-2\omega t^*(E,l)}$$
$$=2\pi\mu A^{2/n}\int_1^\infty ds(2s-(2-n)s^{1-n})$$
$$\times\int_0^\infty dE\, E^{1-(2/n)}e^{-\beta E-2\omega t^*(E,s)}. \quad (111)$$

Using Appendix B we can estimate the integral over $E$ for large $\omega$. In the notation of Appendix B we have

$$y=\omega\tau\frac{f(s)}{f(1)}, \quad \eta=1-\frac{2}{n} \quad (112)$$

and the integral over $E$ is asymptotically for large $\omega$

$$\beta^{(2/n)-2}\sqrt{2\pi\nu(1-\nu)}(1-\nu)^\eta y^{\nu[(1/2)+\eta]}e^{-y^\nu}. \quad (113)$$

We obtain

$$\int_0^\infty dE\int_0^\infty 2\pi l\, dl\, e^{-\beta E-2\omega t^*(E,l)}$$
$$\sim 2\pi\mu\beta^{-2}(\beta A)^{2/n}\sqrt{2\pi\nu(1-\nu)}(1-\nu)^\eta$$
$$\times\int_1^\infty ds(2s-(2-n)s^{1-n})y^{\nu[(1/2)+\eta]}e^{-y^\nu}. \quad (114)$$

Since $f(s)$ is monotonically increasing in $s$, for large $\omega$ the dominant contribution to the integral comes from $s\sim 1$. Therefore the right-hand side is asymptotically

$$\sim 2\pi\mu\beta^{-2}(\beta A)^{2/n}n\sqrt{2\pi\nu(1-\nu)}(1-\nu)^\eta$$
$$\times\int_1^\infty ds\, y^{\nu[(1/2)+\eta]}\, e^{-y^\nu}$$
$$\sim 2\pi\mu\beta^{-2}(\beta A)^{2/n}n\sqrt{2\pi\nu(1-\nu)}(1-\nu)^\eta$$
$$\times(\omega\tau)^{\nu[(1/2)+\eta]}\int_1^\infty ds\, e^{-(\omega\tau)^\nu\{1+\nu[f'(1)/f(1)](s-1)\}} \quad (115)$$

and we obtain finally

$$\int_0^\infty dE\int_0^\infty 2\pi l\, dl\, e^{-\beta E-2\omega t^*(E,l)}$$
$$\sim 2\pi\mu\beta^{-2}(\beta A)^{2/n}\frac{n}{\nu}\sqrt{2\pi\nu(1-\nu)}\,(1-\nu)^\eta$$
$$\times\frac{f(1)}{f'(1)}(\omega\tau)^{\nu[-(1/2)+\eta]}\, e^{-(\omega\tau)^\nu}. \quad (116)$$

### D. The asymptotic spectra

Collecting terms we write our result for the spectra of the observable

$$r_i^{-p}=\sum_{j\neq i}\frac{1}{r_{ij}^p(t)} \quad (117)$$

in the asymptotic region in the form

$$S(\omega)=\int_{-\infty}^\infty dt\, e^{i\omega t}\langle r_i^{-p}(t)r_i^{-p}(0)\rangle\sim a\,(\omega\tau)^\sigma\, e^{-(\omega\tau)^\nu}. \quad (118)$$

The exponents $\nu$ and $\sigma$ are given by

$$\nu=\frac{2n}{3n+2} \quad (119)$$

and

$$\sigma=\frac{4p}{n+2}-\frac{5n+8}{3n+2}. \quad (120)$$

The time constant $\tau$ is defined in Eq. (96). The amplitude $a$ has the form

$$a=\alpha\,(\rho\, r_{th}^3)\,\tau\, r_{th}^{-2p}, \quad (121)$$

where $\alpha$ is a dimensionless constant. The dimensions of the other terms are obvious: $\rho\, r_{th}^3$ corresponds to a dimensionless volume fraction, $\tau$ corresponds to the integration over time in $S(\omega)$, and $r_{th}^{-2p}$ stems from the correlation $\langle r(0)^{-p}\, r(t)^{-p}\rangle$ considered. $\alpha$ is given by

$$\alpha=4\pi\, c_0\left(\frac{2\pi}{\Gamma(p\lambda)}\right)^2[(n+2)c_0]^{-2p\lambda}\frac{n}{\nu}$$
$$\times\sqrt{2\nu(1-\nu)}\,(1-\nu)^{1-(2/n)}$$
$$\times\frac{\Gamma\left(\frac{1}{2}+\frac{1}{n}\right)\Gamma\left(1-\frac{1}{n}\right)}{\Gamma\left(\frac{3}{2}-\frac{1}{n}\right)\Gamma\left(\frac{1}{n}\right)}. \quad (122)$$

$\lambda$ and $c_0$ are defined in Eqs. (82) and (97), respectively. In particular, for $n=p=2$ we recover the previous results in Sec. IV with $\alpha=\pi^3/\sqrt{2}$.

### E. Dominant energy, angular momentum, and deflection angle seen at frequency $\omega$

At this point let us summarize what we have learned about the nature of the collisions seen at frequency $\omega$ in the spectra. In Sec. VI B it was shown that the energy of the collisions seen at frequency $\omega$ is given by Eq. (98). The higher the frequency, the more energetic the collisions that contribute to a spectrum at this frequency.

Concerning the angular momentum, we obtain from Eq. (108)

$$\frac{l^2}{2\mu\, k_B T\, r_{th}^2} = (\beta E)^{1-(2/n)}\, s^2(1-s^{-n}). \tag{123}$$

For high frequency $s$ is close to 1. More precisely, it follows from Eq. (115) that $s-1$ is exponentially distributed and

$$\langle s-1\rangle \sim \frac{f(1)}{\nu f'(1)}(\omega\tau)^{-\nu}. \tag{124}$$

This implies, in conjunction with Eq. (98), that the dominant angular momenta seen at frequency $\omega$ satisfy

$$\left\langle \frac{l^2}{2\mu\, k_B T\, r_{th}^2}\right\rangle \sim \gamma\,(\omega\tau)^{-2\nu/n}, \tag{125}$$

where the constant is $\gamma=(n/\nu)[f(1)/f'(1)](1-\nu)^{1-(2/n)}$. The higher the frequency, the smaller the angular momenta of the collisions contributing to a spectrum.

The fact that $l^2$ is so small in the asymptotic region suggests a more transparent albeit less rigorous way to estimate the double integral. Expanding $t^*(E,l)$ about $l=0$ and keeping only the first two terms, the double integral becomes

$$\int_0^\infty dE\, e^{-\beta E}\int_0^\infty 2\pi l\, dl\, e^{-2\omega t^*(E,0)-2\omega(\partial t^*/\partial l^2)(E,0)\, l^2}. \tag{126}$$

This suggests that $l^2$ is distributed exponentially with

$$\langle l^2\rangle \sim \left(2\omega\frac{\partial t^*}{\partial l^2}(E(\omega),0)\right)^{-1} \tag{127}$$

which indeed coincides with Eq. (125). The double integral then becomes asymptotically

$$\pi\langle l^2\rangle\int_0^\infty dE\, e^{-\beta E-2\omega t^*(E,0)} = \pi\, k_B T\langle l^2\rangle\sqrt{2\pi\nu(1-\nu)} \times(\omega\tau)^{\nu/2}\, e^{-(\omega\tau)^{\nu}}, \tag{128}$$

which coincides with Eq. (116) as it should.

We have stated repeatedly that the dominant collisions for high frequency are almost central. Now we can make this more precise. After some algebra one obtains for the angle of deflection $\chi$ of a collision with angular momentum $l$ and energy $E$,

$$\pi-\chi=\sqrt{\frac{2\,l^2}{\mu k_B T\, r_{th}^2}}\,(\beta E)^{-(1/2)+(1/n)}\, s^{(n/2)-1} \times\int_0^1\frac{du}{\sqrt{1-u^n+(s^n-1)(1-u^2)}}, \tag{129}$$

where $s$ has the same meaning as previously. Letting $s\to 1$ on the right-hand side and using Eqs. (98) and (125) we obtain after a short calculation

$$\langle(\pi-\chi)^2\rangle \sim \gamma_\chi(\omega\tau)^{-\nu}, \tag{130}$$

where the constant is given by

$$\gamma_\chi=\frac{3n+2}{n(n-2)}\cot\frac{\pi}{n}. \tag{131}$$

The deflection angle of the collisions seen in the spectra at large frequencies indeed tends to $\pi$.

Let us finally check the conditions (90). Inserting $\beta E(\omega)$ from Eq. (98), the first condition amounts to $1>\nu[(1/2)+(1/n)]$ which is satisfied. From Eq. (125) it follows that the second condition is also amply satisfied.

### F. Application: Velocity autocorrelation function

As a simple application let us calculate the spectrum of the velocity fluctuations of a tagged particle in the high-frequency domain. We must first show that the angular velocity can be neglected versus the radial velocity $\dot r$. Indeed, from $\mathbf{r}=r\,\mathbf{n}$ we obtain using Eq. (34)

$$\dot{\mathbf{r}}=\dot r\,\mathbf{n}+\frac{l}{\mu r}\hat{\mathbf{n}}, \tag{132}$$

where $\hat{\mathbf{n}}$ is a unit vector normal to $\mathbf{n}$. The asymptotics is determined by the region near the singularity at $r=0$ as explained in Sec. VI A. The angular velocity can be neglected provided

$$|\dot r(t)| \gg \frac{l}{\mu|r(t)|} \tag{133}$$

in that region. This amounts to

$$\text{const} \gg l|t-it^*|^{1-2\lambda}. \tag{134}$$

Since the relevant $l$ are small and $1-2\lambda=(n-2)/(n+2)\geqslant 0$, this is satisfied.

From Sec. VI A we obtain further

$$\dot r \sim \sqrt{-\frac{2A}{\mu}}\, r^{-n/2} \tag{135}$$

near the singular point. This implies that up to a constant factor the spectrum of $\dot r$ is the same as of $r^{-n/2}$. In particular the exponent $\sigma$ is given by

$$\sigma_{vaf}=\frac{n^2-14n-16}{(n+2)(3n+2)}. \tag{136}$$

Since for particle $i$ in a collision

$$m\ddot{\mathbf{r}}_i=\mu\ddot{\mathbf{r}}, \tag{137}$$

we obtain the spectrum of the velocity autocorrelation function in the high-frequency region

$$\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\dot{\mathbf{r}}_i(t)\cdot\dot{\mathbf{r}}_i(0)\rangle \sim \alpha_{vaf}\, v_{th}^2\,\tau\,(\rho\, r_{th}^3)\,(\omega\tau)^{\sigma_{vaf}}\, e^{-(\omega\tau)^{\nu}}, \tag{138}$$

where $\alpha_{vaf}$ is given by $\alpha$ for $p=n/2$.

An alternative calculation could proceed as follows: In the high-frequency domain the equation of motion for the $i$th particle

$$m\ddot{\mathbf{r}}_i=-\sum_{j\neq i}\mathbf{n}_{ij}V'(r_{ij}) \tag{139}$$

can again be replaced by the radial part

$$m\ddot{r}_i=-\sum_{j\neq i}V'(r_{ij})=nA\sum_{j\neq i}\frac{1}{r_{ij}^{n+1}(t)}. \tag{140}$$

Utilizing Eq. (118) for $p=n+1$ we obtain

$$\int_{-\infty}^{\infty}dt\, e^{i\omega t}\langle\ddot{\mathbf{r}}_i(t)\cdot\ddot{\mathbf{r}}_i(0)\rangle \sim\frac{n^2A^2}{m^2}\alpha\,(\rho\, r_{th}^3)\,\tau\, r_{th}^{-2n-2}\,(\omega\tau)^{\sigma}\,e^{-(\omega\tau)^{\nu}}, \tag{141}$$

where $\alpha$ and $\sigma$ must be evaluated for $p=n+1$. A short calculation verifies that the two expressions for the velocity autocorrelation function are equivalent.

### G. Potentials with $n<2$

Up to now we have always assumed $n\geqslant 2$. Softer potentials with $n<2$ can also be studied, but off central collisions play an increasingly important role. This complicates the analysis and somewhat modifies the preexponential factor. For example, in the case of the Coulomb potential one can show that the high-frequency spectra are proportional to

$$(\omega\tau)^{\sigma_c}e^{-(\omega\tau)^{2/5}}, \tag{142}$$

where the exponent is given by

$$\sigma_c=\frac{20p-37}{15}. \tag{143}$$

This exponent is almost equal to the previous $\sigma$ when one formally puts $n=1$ in Eq. (120). This would predict

$$\sigma=\frac{20p-39}{15}. \tag{144}$$

### H. Other binary observables

For definiteness we have concentrated on the observables $r^{-p}(t)$. However, for most other local observables $A(r)$ the results are very similar.

As usual, the spectrum is dominated by the singularity of $A(r(t))$ with the smallest imaginary part in the upper half plane. Several possibilities can arise.

It may happen that $A(r(t))$ becomes singular at some point $r'$ even before the singularity in $V(r)$ is encountered. Consider for example the observable $(1+r^2)^{-1}$. This has a pole at $r=i$ and, depending on the potential, there may be a $t'$ with $r(t')=i$ and $0<\mathrm{Im}(t')<t^*$. The arguments of the preceding sections can be applied with little change to this situation provided $t^*$ is replaced by $\mathrm{Im}(t')$ with

$$t'=\sqrt{\frac{\mu}{2}}\int_{r_0}^{r'}\frac{dr}{\sqrt{E-V(r)-\frac{l^2}{2\mu}r^{-2}}}. \tag{145}$$

In the high-energy region we have

$$\mathrm{Im}(t')\sim E^{-1/2}. \tag{146}$$

This leads to the exponent $\nu=2/3$ (see the discussion in Sec. IX).

Another possibility is that $A(t)$ is regular at $it^*$ even though $V(r(t))$ is singular there. This happens, for example, for $n=2$ and the observable $e^{-r(t)^2}$. This is one of the exceptional cases where the spectrum decays exponentially. Such situations must be studied separately.

In the generic case the relevant singularity in $A(r(t))$ is the one inherited from $V(r)$. In this case almost all of the work has been done. The asymptotic evaluation of the double integral in Sec. VI C is independent of the observable. It remains to determine the spectrum in the vicinity of the singularity at $r=0$. This has been done in Sec. VI A for $r^{-p}$. Suppose first that

$$A(r)=r^{-p}B(r), \tag{147}$$

where $p>0$ and $B(0)$ is finite and nonzero. Then, because the spectrum depends only on the behavior of $A(r)$ near $r=0$, asymptotically

$$A(\omega)=B(0)\,r^{-p}(\omega). \tag{148}$$

The spectrum of $A(r)$ is proportional to the spectrum of $r^{-p}$ of Sec. VI D.

Now let

$$A(r)=r^{q}B(r), \tag{149}$$

where $q>0$ and $B(0)$ is finite and nonzero. In the integration along the loop mentioned in Sec. VI A, we have $r=ce^{i\pi\lambda}|s|^{\lambda}$ on the right edge of the cut and $r=c\,e^{-i\pi\lambda}|s|^{\lambda}$ on the left edge. Therefore the integral over the loop becomes

$$i\int_0^{\infty}c^q\,e^{i\pi q\lambda}\,s^{q\lambda}\,e^{-\omega s}ds-i\int_0^{\infty}c^q\,e^{-i\pi q\lambda}\,s^{q\lambda}\,e^{-\omega s}ds =-2c^q\sin(\pi q\lambda)\,\Gamma(q\lambda+1)\,\omega^{-q\lambda-1} \tag{150}$$

and we obtain asymptotically

$$A(\omega)\sim -B(0)2\,c^q\sin(\pi q\lambda)\,\Gamma(q\lambda+1)\,\omega^{-q\lambda-1}\,e^{-\omega t^*(E,l)}. \tag{151}$$

Using the relation $\Gamma(-x)\Gamma(1+x)=-\pi/\sin(\pi x)$, we note that this is just the analytic continuation of Eq. (148) to negative $p$ [compare Eq. (87)]. Equation (151) is correct only if $q\lambda$ is not an integer. Otherwise the singularity of $r^q$ at $r=0$ is of lower order and must be studied separately.

Finally, if $A(0)$ is finite and nonzero, we must replace $A(r)$ by $A(r)-A(0)$ in order to obtain an observable which is singular at $r=0$.

For small values of $p$ and $q$, the convergence to the asymptotic expressions above is quite slow. To see this and to obtain an expression valid for a larger range of $\omega$, consider for example the observable $A(r)=e^{-b\,r(t)}$ where $b$ is some inverse length. Inserting the singular solutions $ce^{\pm i\pi\lambda}|s|^{\lambda}$ we obtain

$$(e^{-b\,r})(\omega)\sim f\,e^{-\omega t^*}, \tag{152}$$

where

$$\begin{aligned} f&=i\int_0^\infty ds\,e^{-\omega s}(e^{-bce^{i\pi\lambda}s^\lambda}-e^{-bce^{-i\pi\lambda}s^\lambda})\\ &=i\int_0^\infty ds\,e^{-\omega s-bc\cos\pi\lambda\,s^\lambda}\\ &\quad\times(e^{-bci\sin\pi\lambda\,s^\lambda}-e^{bci\sin\pi\lambda\,s^\lambda})\\ &=2\int_0^\infty ds\,e^{-\omega s-bc\cos(\pi\lambda)s^\lambda}\sin[bc\sin(\pi\lambda)s^\lambda]. \end{aligned} \tag{153}$$

For large $\omega$ this tends to Eq. (151) for $q=1$ and $B(0)=-b$ with a relative error $O(\omega)^{-\lambda}$. The same method can be used to obtain approximations for most other observables in the high-frequency domain.

## VII. DENSE LIQUIDS

In dense liquids the low-frequency spectra are quite different from their gaseous counterparts. At high-frequency, however, the situation greatly simplifies. As in gases, the high-frequency spectra are due to rare binary collisions with high energy.

It has been argued that these collisions are not independent but occur in groups [6]. While this is true, we have seen previously that the collisions dominating the high-frequency spectra are almost central. According to Eq. (130) the deflection angle $\chi$ of the collisions seen in the high-frequency spectra tends to $\pi$. An alternative quantity to gauge centrality is the impact parameter

$$b=\frac{l}{\sqrt{2\mu E}}. \tag{154}$$

A dimensionless measure for centrality is the expectation value of $(b/r_{th})^2$. From Eq. (125) we obtain in the asymptotic region

$$\left\langle\frac{b^2}{r_{th}^2}\right\rangle\sim\frac{\gamma}{1-\nu}(\omega\tau)^{-(2n+4)/(3n+2)}. \tag{155}$$

This tends to zero for large $\omega\tau$ and demonstrates that the collisions which contribute to the high-frequency spectra are almost central even in fluids.

Now we can return to the argument that collisions in liquids are not necessarily independent. Of all the collisions in a group (a ‘‘hot spot’’) there is rarely a collision sufficiently central to satisfy Eqs. (130) or (155) and to be seen in the spectra. Even if one of these collisions is central enough, the preceding or subsequent collisions in this group have an overwhelmingly small probability to make a second central collision. It is this stringent condition on centrality that guarantees that the collisions seen in the high-frequency spectra are independent, even in a dense liquid.

The spectra are dominated by a small region near the turning point where the particle spends only a very short time. During this time the configuration of the environment is practically unchanged. Therefore, we again have independent scattering events in a time-independent potential. The potential, however, differs in several aspects from the gas. It is different in every collision; it is in general not spherically symmetrical, and it has no well defined limit for large $r$.

The high-frequency spectra are determined by the trajectories of a pair of nearby particles in the vicinity of the turning point. The number density of such a pair at distance $r$ and with velocities $v_1,v_2$ is given by

$$\rho\,g(r)\varphi(v_1)\varphi(v_2), \tag{156}$$

where $\varphi(v)$ is the Maxwell velocity distribution. The trajectories are determined by Newtons equations with initial conditions

$$r_1(0)=0,\quad \dot{r}_1=v_1, \tag{157}$$

$$r_2(0)=r,\quad \dot{r}_2=v_2. \tag{158}$$

Suppose for a moment that the potentials in the fluid and in the gas are identical. Then, with the same initial conditions, the trajectories are also identical. This suggests for the ratio of the high-frequency spectra in the fluid and in the gas [6,4]

$$\frac{S_{fl}(\omega)}{S_{gas}(\omega)}=\frac{\rho_{fl}\quad g_{fl}(r_0)}{\rho_{gas}g_{gas}(r_0)}, \tag{159}$$

where $r_0$ is the turning point.

In the high-frequency domain the force from the environment is very small compared to the force from the direct potential $V(r)$. This suggests that Eq. (159) might be exact at the asymptotic limit. This, however, is not true. It turns out that a small and bounded perturbation of the potential generates an additional factor which varies slowly with the frequency [8]. In any case, the preceding arguments suggest that the exponential factor $e^{-(\omega\tau)^\nu}$ is also present in dense liquids.

## VIII. OTHER POTENTIALS

The method used in this paper can be applied to many other potentials. Essentially the only restriction is that the potential can be analytically continued into the complex $r$ plane. This rules out potentials with hard core like the hard-sphere potential. In a future paper [8] various perturbations of $V(r)=\mathrm{Ar}^{-n}$ will be studied as well as potentials with inaccessible regions. The qualitative result is similar: In the high-frequency domain the spectra are dominated by almost central collisions with high energy. Up to a prefactor which usually varies less rapidly with $\omega$, generic high frequency spectra behave as

$$\sim e^{-Min\{\beta E+\omega\, t^*(E)\}}, \tag{160}$$

where $t^*$ is that singularity of $V(r(t))$ in the upper-half $t$ plane closest to the real axis and the minimum is over $E>0$.

### IX. UNIVERSAL UPPER BOUND ON EXPONENT $\nu$

It seems that for all potentials the generic spectra ultimately decay slower than exponentially [13]. In fact, the ultimate decay seems to be not faster than $\sim e^{-\mathrm{const}\times\omega^{2/3}}$. The inequality

$$\nu\leqslant\frac{2}{3} \tag{161}$$

follows from Eq. (160), provided $t^*(E)$ decays for large energies at least as fast as $E^{-1/2}$. I present a few arguments in favor of the latter conjecture.

Consider first a potential $V(r)$ with a single singular point at $r=0$ where it diverges to infinity. Every decent potential of this kind satisfies for sufficiently small $r$

$$V''(r)>0. \tag{162}$$

In

$$t^*(E)=\sqrt{\frac{\mu}{2}}\int_0^{r_0}\frac{dr}{\sqrt{V(r)-E}}, \tag{163}$$

where $r_0$ is the turning point with $V(r_0)=E$, we introduce

$$V(r)-E=V(r)-V(r_0)\geqslant(r-r_0)V'(r_0) \tag{164}$$

and find the inequality

$$t^*(E)<\sqrt{2\mu}\,\sqrt{\frac{r_0}{-V'(r_0)}}. \tag{165}$$

We employ the trivial inequality $[e^r V(r)]'<0$ or $V'(r)+V(r)<0$ and obtain

$$t^*(E)<\sqrt{2\mu}\,\sqrt{\frac{r_0}{E}}. \tag{166}$$

This proves the conjecture for this class of potentials. In addition, if $V(r)$ increases stronger than any power for $r\to 0$, it is easy to see that $\nu=2/3$ in this case.

A more qualitative argument for potentials with a singularity on the real axis runs as follows. Let $V(r)$ be singular at $r=0$ and expand $V$ into a Laurent series

$$V(r)\sim\sum_{n>0}a_n r^{-n} \tag{167}$$

with $a_n\geqslant 0$ for sufficiently large $n$. For collisions with higher and higher energy, steeper and steeper portions of the potential are probed. This roughly corresponds to a potential $\sim r^{-n}$ where $n$ increases with the collision energy. Taking $n\to\infty$ in Eq. (119) leads to $\nu=2/3$. This suggests that the exponent $\nu$ is always equal to its upper limit for potentials which grow stronger than any power at their singularity.

Consider now potentials with an inaccessible region like $V(r)=(r-a)^{-n}$. With regard to central collisions, this potential behaves like $r^{-n}$ with a trivial shift of the origin. Since the exponential factors are determined by the central collisions, they are identical.

Suppose next that $V(r)$ is analytic and bounded on the real axis and that the relevant singularity is at a finite point $r_s$ in the complex plane. Then $t^*$ is given by the imaginary part of

$$\sqrt{\frac{\mu}{2}}\int_0^{r_s}\frac{dr}{\sqrt{E-V(r)}}. \tag{168}$$

The problem is simple if the potential is finite at $r_s$. In this case we have $t^*\sim E^{-1/2}$ for large $E$ which again implies $\nu=2/3$.

If the potential is infinite at $r_s$, the situation is not so transparent. For simplicity suppose that the singularity is at $ix_s$ and that $V(ix)$ is real for $0<x<x_s$. Suppose also that $V(ix)$ and $[\ln V(ix)]'$ are monotonically increasing to infinity for $x\to x_s$. The imaginary part of

$$\int_0^{ix_s}\frac{dx}{\sqrt{E-V(x)}}=i\int_0^{x_s}\frac{dx}{\sqrt{E-V(ix)}} \tag{169}$$

is given by

$$\frac{1}{\sqrt{E}}\int_0^{x_e}\frac{dx}{\sqrt{1-\dfrac{V(ix)}{V(ix_e)}}}, \tag{170}$$

where $V(ix_e)=E$. We want to show that the integral is bounded away from 0 and infinity for $E\to\infty$. We do this by constructing upper and lower bounds.

Since the integrand is $>1$, a lower bound to the integral is $x_e$ which tends to $x_s$. To construct an upper bound we use the monotonicity of $[\ln V(ix)]'$. This implies

$$\ln V(ix_e)-\ln V(ix)\geqslant[\ln V(ix)]'(x_e-x) \tag{171}$$

or

$$1-\frac{V(ix)}{V(ix_e)}\geqslant 1-e^{-[\ln V(ix)]'(x_e-x)}. \tag{172}$$

Inserting we obtain for the integral the upper bound

$$\int_0^{x_e} dx(1-e^{-[\ln V(ix)]'(x_e-x)})^{-1/2} \tag{173}$$

which tends to a finite limit for $x_e \to x_s$. As a result $t^* \sim E^{-1/2}$ for large $E$ which implies again $\nu = 2/3$.

As an example consider the potential

$$V(r) = \cosh^{-2} r. \tag{174}$$

Similar to the exponential potential it permits an analytic solution. Omitting physical constants, for $E>1$ the solution to

$$\dot{r}^2 + \cosh^{-2} r = E \tag{175}$$

is given by

$$r(t) = \sinh^{-1}\left(\sqrt{\frac{E-1}{E}}\sinh(\sqrt{E})t\right). \tag{176}$$

The singular points are logarithmic branch points at

$$\sqrt{E}\, t_n = \pm \ln\frac{\sqrt{E}+1}{\sqrt{E-1}} + \left(n+\frac{1}{2}\right)\pi i, \tag{177}$$

where $n$ is any integer. Here

$$t^* = \frac{\pi}{2\sqrt{E}} \tag{178}$$

for all $E$ which implies $\nu = 2/3$. In conclusion, it seems that for generic potentials (where the relevant singularity is an essential singularity) the exponent $\nu$ is equal to 2/3. Only if the order of the relevant singularity is finite (a pole or an algebraic branch point) $\nu$ takes values smaller than 2/3.

## X. QUANTUM MECHANICS

It is well known that for very high frequencies collisions must be treated quantum mechanically. As a rule of thumb, quantum mechanical effects can be neglected in dynamic phenomena at equilibrium whenever

$$\frac{\hbar\omega}{k_B T} \ll 1. \tag{179}$$

An interesting by-product of the theory presented above is a more precise location of the classical quantum boundary for equilibrium correlations.

Two conditions must be met if the spectra can be treated classically. One condition is that the angular momenta of the dominant collisions are much greater than $\hbar$. Using Eq. (125) this can be written as

$$\frac{\lambda_B}{r_{th}} \ll 2\pi\sqrt{\gamma}\,(\omega\tau)^{-\nu/n}, \tag{180}$$

where

$$\lambda_B = \frac{2\pi\hbar}{\sqrt{2\mu k_B T}} \tag{181}$$

is the thermal de Broglie wavelength.

The second condition stems from central collisions in the radial coordinate. I briefly sketch the results. A detailed discussion will be published elsewhere [14].

Let $\{\psi_E(r)\}$ be the eigenfunctions of the scattering states in the energy representation normalized according to

$$\int_0^\infty \psi_E^*(x)\psi_E(y)\, dE = 2\pi\hbar\ \ \delta(x-y) \tag{182}$$

and let

$$C(E,E') = \langle \psi_E | A | \psi_{E'} \rangle \tag{183}$$

be the matrix elements of some operator $A$. One derives the standard relations

$$\int_{-\infty}^\infty dt\, e^{i\omega t}\langle A(t)A(0)\rangle = \int_0^\infty dE\, e^{-\beta E}|C(E,E+\hbar\omega)|^2 \tag{184}$$

and

$$\begin{aligned}\int_{-\infty}^\infty dt\, e^{i\omega t}\langle A(0)A(t)\rangle &= \int_{\hbar\omega}^\infty dE\, e^{-\beta E}|C(E,E-\hbar\omega)|^2\\ &= e^{-\beta\hbar\omega}\int_{-\infty}^\infty dt\, e^{i\omega t}\langle A(t)A(0)\rangle,\end{aligned} \tag{185}$$

where the operator $A$ is in the Heisenberg representation and $\omega>0$.

In the classical limit the matrix elements must tend to the Fourier coefficients of the corresponding classical observable $A_{cl}(t)$, i.e.,

$$C(E,E+\hbar\omega) \to \int_{-\infty}^\infty dt\, e^{i\omega t} A_{cl}(t). \tag{186}$$

Consider first the diagonal matrix elements. Up to an uninteresting factor from normalization, for operators $r^{-p}$ the diagonal $C(E,E)$ depends on the single dimensionless parameter

$$\frac{r_{th}}{\lambda_B}(\beta E)^{(1/2)-(1/n)}. \tag{187}$$

For $n>2$ the classical limit $\hbar \to 0$ is identical to the high-energy limit at fixed $\hbar$. Therefore, for high-energy collisions, the diagonal matrix elements take their classical values. In the off-diagonal matrix elements there appears the second dimensionless parameter $\hbar\omega/E$. These matrix elements tend to their classical counterparts provided

$$\frac{\hbar\omega}{E} \ll 1. \tag{188}$$

The dominant energies seen in the spectra at frequency $\omega$ are close to $E(\omega)$ of Eq. (98). Inserting we obtain after some rearrangement the condition

$$\frac{\lambda_B}{r_{th}} \ll 2\pi c_0(1-\nu)(\omega\tau)^{-1+\nu}, \tag{189}$$

where $c_0$ is defined in Eq. (97). For sufficiently low frequencies both inequalities (180) and (189) are satisfied which indicates classical behavior. When they fail quantum effects become important.

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## APPENDIX A: PROOF OF EQ. (18)

Consider a relative binary observable $A$ that depends on the position vector $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ of two particles at times $t_1, t_2, \ldots$ . By considering limits, this includes a possible dependence on relative velocities.

Let the positions and momenta of the particles at some initial time $t_0$ be $\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2$. Newton's equations then determine the value of the $\mathbf{r}_i(t)$ and $\mathbf{p}_i(t)$ for all times in the future and in the past. Inserting the values for $t=t_1, t_2, \ldots$ into $A$, the observable becomes a function of the initial values $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ and $2\mathbf{p}=\mathbf{p}_1-\mathbf{p}_2$ which we denote by $A(\mathbf{r},\mathbf{p})$. The average of $A$ is an average of $A(\mathbf{r},\mathbf{p})$ over the initial ensemble.

For a dilute gas of density $\rho$ the probability density of the initial ensemble is

$$\rho\, \varphi(p_1)\varphi(p_2)\, e^{-\beta V(r)}\, d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}, \tag{A1}$$

where

$$\varphi(p)=(2\pi m k_B T)^{-3/2}\, e^{-p^2/(2mk_BT)} \tag{A2}$$

is the Maxwell velocity distribution. Therefore

$$\langle A\rangle=\rho\int d\mathbf{p}_1\,\varphi(p_1)\int d\mathbf{p}_2\,\varphi(p_2)\int d\mathbf{r}\, e^{-\beta V(r)}A(\mathbf{r},\mathbf{p}). \tag{A3}$$

Our first task is to integrate out the motion of the center of mass.

Let $\mathbf{p}_s$ be the momentum of the center of mass and $\mathbf{p}$ be the relative momentum. Then

$$\mathbf{p}_1=\mathbf{p}+\frac{1}{2}\mathbf{p}_s, \tag{A4}$$

$$\mathbf{p}_2=-\mathbf{p}+\frac{1}{2}\mathbf{p}_s. \tag{A5}$$

The Jacobian for this transformation is equal to 1 and

$$\varphi(p_1)\varphi(p_2)=(2\pi m k_B T)^{-3}\, e^{-p^2/(2\mu k_BT)}\, e^{-p_s^2/(4mk_BT)}. \tag{A6}$$

Integration over $\mathbf{p}_s$ produces a factor $(4\pi m k_B T)^{3/2}$, and the result of integrating out the motion of the center of mass is

$$\langle A\rangle=\rho\,(2\pi\mu k_B T)^{-3/2}\int\int d\mathbf{r}\, d\mathbf{p}\, e^{-\beta E}A(\mathbf{r},\mathbf{p}), \tag{A7}$$

where

$$E=\frac{p^2}{2\mu}+V(r) \tag{A8}$$

is the energy in the center of mass system.

Now we make use of the fact that the problem is rotationally invariant and the motion is confined to a plane. In the following we often omit the integrand $e^{-\beta E}A(\mathbf{r},\mathbf{p})$.

We write

$$\int\int d\mathbf{r}\, d\mathbf{p}=\int\int d\mathbf{r}\, d\mathbf{p}\int d\mathbf{L}\,\delta^{(3)}(\mathbf{L}-\mathbf{r}\times\mathbf{p}), \tag{A9}$$

rotate the angular momentum vector into the $z$ axis, and obtain for the right-hand side

$$4\pi\int\int d\mathbf{r}\, d\mathbf{p}\int_0^\infty dl\, l^2\,\delta^{(3)}(l\,\mathbf{e}_3-\mathbf{r}\times\mathbf{p}), \tag{A10}$$

where $\mathbf{e}_3$ is the unit vector in the $z$ direction. This is equal to

$$\begin{aligned}&4\pi\int\int d\mathbf{r}\, d\mathbf{p}\int_0^\infty dl\, l^2\,\delta((\mathbf{r}\times\mathbf{p})_1)\,\delta((\mathbf{r}\times\mathbf{p})_2)\,\delta(l-(\mathbf{r}\times\mathbf{p})_3)\\ &=4\pi\int\int d\mathbf{r}\, d\mathbf{p}\,((\mathbf{r}\times\mathbf{p})_3)^2\,\delta((\mathbf{r}\times\mathbf{p})_1)\,\delta((\mathbf{r}\times\mathbf{p})_2).\end{aligned} \tag{A11}$$

The region of integration in the second line is $(\mathbf{r}\times\mathbf{p})_3>0$. Now we use the fact that the integrand is independent of $r_3$ and $p_3$. The integral over $r_3$ and $p_3$ is

$$\int dr_3\int dp_3\,\delta(r_2p_3-r_3p_2)\,\delta(r_1p_3-r_3p_1). \tag{A12}$$

Setting

$$\begin{pmatrix}x\\ y\end{pmatrix}=\begin{pmatrix}r_2 & -p_2\\ -r_1 & p_1\end{pmatrix}\begin{pmatrix}p_3\\ r_3\end{pmatrix} \tag{A13}$$

and noting that the determinant is nonzero we obtain for this integration

$$\frac{1}{(\mathbf{r}\times\mathbf{p})_3}. \tag{A14}$$

Therefore we obtain

$$\int\int d\mathbf{r}\, d\mathbf{p}=4\pi\int\int d^2\mathbf{r}\, d^2\mathbf{p}(\mathbf{r}\times\mathbf{p}), \tag{A15}$$

where integration is over the region $\mathbf{r}\times\mathbf{p}>0$.

Now we introduce polar coordinates

$$x=r\cos\theta,\quad y=r\sin\theta. \tag{A16}$$

The conjugate momenta are

$$p_r = \mu \dot{r}, \quad p_\theta = \mu r^2 \dot{\theta}. \tag{A17}$$

Because every point transformation is canonical and the phase volume is invariant under canonical transformations, we obtain

$$\int\int d^{18}r\ d^3p = 4\pi \int\int\int\int p_\theta\, dr\, d\theta\, dp_r\, dp_\theta . \tag{A18}$$

We perform a second canonical transformation from the coordinates $r,\theta$ and momenta $p_r$, $p_\theta$ to new coordinates $t$, $\theta_0$ and new momenta $E,l$. To this end, consider Hamilton's characteristic function $W(r,\theta)$. It satisfies the Hamilton-Jacobi equation

$$\frac{1}{2\mu}\left[\left(\frac{\partial W}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial W}{\partial \theta}\right)^2\right] + V(r) = E. \tag{A19}$$

$\theta$ is a cyclic coordinate and the Hamilton-Jacobi equation is separable. We insert the ansatz

$$W = W_r(r,l,E) + l\ \theta \tag{A20}$$

and obtain

$$\frac{1}{2\mu}\left[\left(\frac{\partial W_r}{\partial r}\right)^2 + \frac{l^2}{r^2}\right] + V(r) = E. \tag{A21}$$

$W$ depends on the old coordinates $r,\theta$ and the new momenta $E,l$. As a canonical transformation, $W$ transforms the Hamiltonian into the constant $E$ and generates new coordinates via

$$Q_1 = \frac{\partial W}{\partial E}, \tag{A22}$$

$$Q_2 = \frac{\partial W}{\partial l}. \tag{A23}$$

Hamilton's canonical equations with $H \equiv E$ produce the equations of motion $\dot{Q}_1 = 1, \dot{Q}_2 = 0$. Therefore $Q_1$ is equal to the time with respect to some reference time $t_0$, and $Q_2$ is constant. According to Eq. (A20) $Q_2$ is equal to a reference angle $\theta_0$.

Using again the invariance of the phase volume with respect to canonical transformations we obtain

$$\int\int d\mathbf{r}\, d\mathbf{p} = 4\pi \int dE \int l\, dl \int d\theta_0 \int dt. \tag{A24}$$

The integrand is invariant with respect to rotations in the plane of the motion. Therefore the integral becomes

$$\int\int d\mathbf{r}\, d\mathbf{p} = 4\pi \int dE \int 2\pi l\, dl \int dt. \tag{A25}$$

This completes the formal development.

We must now study the mapping

$$(r,p_r,p_\theta) \leftrightarrow (E,l,t) \tag{A26}$$

in some more detail. In particular we must know under what conditions the mapping is bijective. Since $p_\theta = l$, it is sufficient to study the one-dimensional canonical transformation

$$(r,p_r,) \leftrightarrow (E,t) \tag{A27}$$

induced by the effective potential

$$V_{eff} = V(r) + \frac{l^2}{2\mu r^2}. \tag{A28}$$

Every possible motion is either unbounded or bounded. Unbounded trajectories are scattering states, beginning and ending at infinity with a single turning point in between. If the motion is bounded it is, apart from certain singular cases, periodic in $r$. As $(r,p_r)$ traverses such a trajectory, the image in the $(E,t)$ plane is an interval parallel to the $E$ axis. For unbounded motion the time extends from $-\infty$ to $+\infty$. For periodic motion $r$ and $p_r$ take the same values after one period $T$. The time interval then extends over this period.

A fixed energy $E$ may admit a finite number of trajectories, at most one of these is unbounded. As $(r,p_r)$ traverses these trajectories, each trajectory maps onto the corresponding time interval. In such a case, the integral over time becomes the sum over all periods admitted

$$\sum_i \int_0^{T_i} dt. \tag{A29}$$

## APPENDIX B

We want to estimate the integral

$$\int_0^\infty e^{-x-\omega x^{-\alpha}}\, dx \tag{B1}$$

for large $\omega$. Setting $x = \omega^\nu y$ with

$$\nu = \frac{1}{1+\alpha}. \tag{B2}$$

The integral becomes

$$\omega^\nu \int_0^\infty e^{-\omega^\nu (y+y^{-\alpha})}\, dy. \tag{B3}$$

Now we can apply Laplace's method. The minimum of $f(y) = y + y^{-\alpha}$ is located at

$$y_m = \alpha^{1/(\alpha+1)} \tag{B4}$$

and the value at the minimum is

$$f_m = y_m + y_m y_m^{-\alpha-1} = (1+\alpha^{-1}) y_m . \tag{B5}$$

Therefore we obtain for large $\omega$

$$\int_0^\infty e^{-x-\omega x^{-\alpha}}\,dx \sim \sqrt{\frac{2\pi}{f''_m}}\,\omega^{\nu/2}\,e^{-\omega^\nu f_m}. \tag{B6}$$

Inserting

$$\frac{1}{f''_m} = \frac{\alpha}{(\alpha+1)^2} f_m \tag{B7}$$

we obtain

$$\int_0^\infty e^{-x-\omega x^{-\alpha}}\,dx \sim \frac{\sqrt{2\pi\alpha}}{\alpha+1}\,y^{\nu/2}\,e^{-y^\nu}, \tag{B8}$$

where

$$y = (f_m)^{1/\nu}\,\omega. \tag{B9}$$

In a similar manner we find

$$\int_0^\infty x^\eta\,e^{-x-\omega x^{-\alpha}}\,dx \sim \frac{\sqrt{2\pi\alpha}}{\alpha+1}(1-\nu)^\eta\,y^{\nu[(1/2)+\eta]}e^{-y^\nu}. \tag{B10}$$

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