On van der Waals friction between two atoms at nonzero temperature

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Abstract. We find the non-retarded van der Waals force between two identical oscillators, in initially uncorrelated mixed states appropriate for a common temperature T and mean energy $\bar{E}$, constrained to move at constant relative velocity on parallel trajectories a fixed finite distance apart. It is shown that the probability distributions of their final states, although correlated, are also thermal; they are appropriate for a slightly higher temperature $T + \Delta T$, with $\Delta \bar{E}$ proportional to $\bar{E}$. Negative friction, i.e. negative $\Delta \bar{E}$, could occur only under conditions where the underlying constraints no longer make physical sense. A crude multi-oscillator multi-collision toy model explores how the temperature might rise with time in a sequence of dynamically similar collisions. An appendix considers conflicting solutions proposed for the same problem.
1. Introduction, preview and conclusions

An earlier calculation (Barton (2010), here referred to as I) found the drag force $F(t)$ between two atoms 1 and 2 modelled as harmonic oscillators, both with natural frequency $\omega$ and zero-frequency polarizability $\alpha$, initially in their ground states and infinitely far apart, constrained to move uniformly with relative velocity $u$ along parallel straight lines a distance $a$ apart. For simplicity, they are taken to be one dimensional, polarized at right angles to the plane of the trajectories. Figure 1 sketches the scenario. The atomic mass is $M$.

The oscillators are coupled by the dipole–dipole interaction Hamiltonian $H_{\text{int}} = \frac{d_1 \cdot d_2}{s^3}$; the interatomic force operator reads $F = -\partial H_{\text{int}}/\partial s = -s^3 H_{\text{int}}/s^5$. Subscripts 1, 2 identify the atoms, $s$ is the relative position vector, $s = 1/\sqrt{u^2 + (ut)^2}$, and the $d = ey$ are the oscillator dipole operators, with $e$ the charge and $y$ the internal coordinate\(^1\). We write the fundamental dipole matrix element as $D \equiv \langle 1 | d | 0 \rangle$; then $D^2 = \alpha \hbar \omega / 2$, and the static van der Waals ground-state potential is $V_0(s) = -\hbar \omega \alpha^2 / 8s^6$, with $F_0 = -\partial V_0 / \partial s = -3\hbar \omega \alpha^2 / 4s^8$.

The overall rise in the mean internal energy\(^2\) of each oscillator is $\Delta E = \int_{-\infty}^{\infty} (u/2) dt F(t)$, readily checked via the far more easily calculated change in its wavefunction from long before to long after the collision. Though there is no uniquely plausible way to split $F$ at finite $s$ into static and velocity-dependent parts, nor into reversible and irreversible parts, evidently the irreversible end-effect $\Delta E$ depends only on the part of $F(t)$ that is odd around passage (where $s$ minimizes); hence with some poetic licence one might perhaps say that it is this part, changing sign under time-reversal, that should be associated with irreversibility and friction as commonly understood. Constraints absent, $\Delta E$ would approximate the loss of kinetic energy, reflected by

\(^1\) The general dipole–dipole interaction $\{(d_1 \cdot d_2)/s^3 - (3/s^5)(d_1 \cdot s)(d_2 \cdot s)\}$ was used in appendix A of I. Here it reduces to the expression $H_{\text{int}}$ just given, because $d_1$ and $d_2$ are in the $y$-direction, while $s$ has only $x$ and $z$ components.

\(^2\) For brevity, the energy of an oscillator will be taken to mean its internal energy. When kinetic energies $Mu^2/2$ are in question, they will be identified as such explicitly. Paper I wrote $E \equiv 2 \int_{-\infty}^{\infty} (u/2) dt F(t)$ for the overall energy rise of the two atoms jointly, so that $(\Delta E \text{ here}) = (E \text{ in } I)/2$. 

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a slight drop in $u$. The condition for the constraints not to be too unrealistic was shown to read
\[
\frac{\hbar \omega}{(Mu^2/2)} \left( \frac{\alpha}{a^3} \right)^2 \ll 1.
\] (1.1)

Here we aim to generalize the results of I, under the same constraints, to oscillators each in a mixed initial state corresponding to a predetermined initial temperature, the same for both in order to avoid entangling the problem of friction with the problems of heat transfer.

As in I, retardation and all other relativistic effects are disregarded, an approximation implemented by taking the limit $c \rightarrow \infty$ right at the outset, i.e. by keeping only the first term in a formal expansion by powers of $1/c$. The approximation applies when $u$ is well below $c$, and $a$ well below both the characteristic wavelength $\Lambda_0$ and the prevailing thermal wavelength $\Lambda_T$, where
\[
\Lambda_0 = \frac{2\pi c}{\omega}, \quad \Lambda_T = \frac{2\pi \hbar c}{k_B T}.
\] (1.2)

Although its accuracy for the potential $V_0$ has been studied thoroughly, for the transition rates governing friction has not; hence appendix C estimates the leading corrections. On dimensional grounds alone they must be of relative orders $(u/c)^2$, $(u/c)(a/\Lambda)$ or $(a/\Lambda)^2$, where each $\Lambda$ could be either $\Lambda_0$ or $\Lambda_T$.

To help set the scene we define conveniently scaled variables, introduce some notation and recall the pertinent results of I. Thermal averages are indicated by overbars; $E$ stands for the energy of one oscillator. Define\footnote{In I, the symbol $\beta$ was used for $\alpha/s^3$.}
\[
v = \frac{u}{\omega a}, \quad \varepsilon = \frac{E}{\hbar \omega}, \quad \tau = \frac{k_B T}{\hbar \omega}, \quad \beta = \frac{1}{\tau};
\] (1.3)
then
\[
\bar{n}(\tau) = \frac{1}{\exp(\beta) - 1}, \quad \bar{\varepsilon}(\beta) = \bar{n} + \frac{1}{2} = \frac{1}{2} \coth \left( \frac{\beta}{2} \right).
\] (1.4)

Given initial $n_1 = n_2 = 0$, paper I calculated the probability, call it
\[
R [(0, 0) \rightarrow (1, 1)] \equiv R_0 = \Delta \varepsilon(0, 0),
\] (1.5)
that the atoms emerge from the collision excited, i.e. with $n_1 = n_2 = 1$, the requisite energy being supplied by the agency enforcing the constraints. Then

$$\Delta \varepsilon = R_0 = \frac{1}{2} \left[ \frac{\alpha^2}{a^6} \right] G, \quad G = \frac{8}{v^4} K_1^2 \left( \frac{2}{v} \right),$$

$$G (v \ll 1) \simeq \left( \frac{2 \pi}{v^2} \right) \exp \left( \frac{-4}{v} \right), \quad G (v \gg 1) \simeq \frac{2}{v^2},$$

with $G$ reaching its one maximum 0.198 at $v \simeq 1.50$. (Here and in (1.10) below, $K_1$, $I_1$ and $L_1$ are the modified Bessel and Struve functions.)

For easy reference, we quote also (correcting a typo) the expectation value of the force operator:

$$\langle F \rangle = F_0 (1 + x^2)^{3/2} \left[ 2 f (x, v) \right], \quad f = \cos \left( \frac{2x}{v} \right) h_i(x) - \sin \left( \frac{2x}{v} \right) h_r(x), \quad x = \frac{ut}{a},$$

$$\left[ \begin{array}{c} h_i \\ h_r \end{array} \right] \equiv \frac{1}{v} \int_{-\infty}^{x} \frac{dx'}{(1 + x'^2)^{3/2}} \left[ \sin (2x'/v) \cos (2x'/v) \right].$$

It is not too difficult to show that $f$ rises monotonically to a maximum at positive $x$, and then falls non-monotonically to its asymptotic form $f(x \gg 1) \simeq h_i(\infty) \sin(2x/v)$, where $h_r(\infty) = (4/v) K_1(2/v)$. Figure 2 of I plots $f(x)$ for the rather high value $v = 0.4$.

At passage, i.e. for $x = 0$, equations (1.8) and (1.9) yield

$$f (0, v) = h_i(0, v) = \frac{1}{v^2} \left[ 2 + \pi L_1(2/v) - \pi I_1(2/v) \right],$$

$$[2 f (0, v \ll 1)] = 1 + \frac{3}{4} v^2 + \cdots, \quad [2 f (0, v \gg 1)] = \frac{4}{v^2} - \frac{2 \pi v^3}{v^3} + \cdots.$$  

Thus at low speeds $\langle F \rangle$ differs only by a factor of $(1 + 3v^2/4)$ from the force $F_0$ which would obtain if the state vector evolved adiabatically.

Since strictly harmonic oscillators cannot dissociate, whereas real atoms are almost wholly ionized well before $k_B T$ reaches the lowest excitation energy (Landau and Lifshitz 1958), results for oscillators are unlikely to have applications for $\tau$ near or higher than unity. Accordingly we focus mainly on scenarios with $\tau \lesssim O(1)$, although the limit $\tau \to \infty$ retains some academic interest, briefly indulged in section 4. Results for lower temperatures are readily transcribed to real atoms, at least qualitatively, by identifying $\omega$ with the frequency and $D$ with the matrix element of the dominant ground-state dipole excitation.

Section 2.1 extends the ground-state results to collisions between atoms in arbitrary initial states $(n_1, n_2)$: it determines the probabilities that they emerge in either of the dipole–dipole-accessible final states $[(n_1 \pm 1), (n_2 \pm 1)]$ having different total energy, and thence the quantum-mechanical mean values $\Delta \varepsilon (n_1, n_2)$ generalizing (1.5). These turn out to depend only on $n_1 + n_2$, i.e. only on the total initial energy. Transition probabilities to final states degenerate with the initial state, i.e. transitions that do not change $n_1 + n_2$, are irrelevant to $\Delta \varepsilon$. Degeneracies will always mean degeneracies of $H_0$, effective either as $t \to \pm \infty$ or fictitiously in the absence of $H_{\text{int}}$. By a slight abuse of language, we shall say that transitions that do or do not change the total energy are non-degenerate or degenerate, respectively. The latter are interesting mainly because they govern the exchange process $(n_1, n_2) \to (n_2, n_1)$, the only transition between states
whose degeneracy is not accidental. The degenerate transition probabilities \( Q \), studied briefly in appendix A, are very different from the \( R \), and much higher.

Section 2.2 determines the probability distributions of the post-collision quantum numbers, which underlie the quantal averages \( \Delta \varepsilon (n_1, n_2) \); averages them over precollision thermal-equilibrium distributions \( P_i(n) \) for initial temperature \( \tau_i \); and shows that the resultant post-collision single-atom energy distributions \( P_f(n) \) are again thermal, with post-collision temperature \( \tau_f = \tau_i + \Delta \tau \). This is not obvious \textit{a priori}; and only when it has been proved is one entitled to say that the collision results in a rise of temperature, and to express the post-collision energies found in section 2 as thermal mean values \( \bar{\varepsilon}(\tau_f) \). The proof is central to this paper, along with the results \((2.11)\)–\((2.13)\) for \( \Delta \tau \) and \( \Delta \bar{\varepsilon} \).

Section 3 explains why our constrained scenario precludes negative friction in the sense of collisions causing the internal energies \( \bar{\varepsilon} \) to fall rather than rise. Section 4 devises a crude toy model featuring two indefinitely extended lines of oscillators, constrained to move antiparallel with fixed velocities. The object is to develop some preliminary idea of how temperatures might rise under repeated collisions. Equation \((4.3)\) gives \( \tau \) and \( \tilde{\varepsilon} = \varepsilon_i \exp(\vartheta) \) as functions of a conveniently scaled time variable \( \vartheta \). The asymptotics of \( \tau \) are spelled out in section 4.2.1 for \( \tau_i = 0 \), and in section 4.2.2 for arbitrary \( \tau_i \). As to the exponential rise of \( \tilde{\varepsilon} \), and eventually of \( \tau \), we recall the caution already expressed about \( \tau \gtrsim O(1) \).

Appendix B merely lists the incongruities between our conclusions and those reported by Hoye and Brevik \((1992, 2010a, 2010b)\).

To resume, our main conclusions are as follows. (i) The internal-energy rise produced by a single collision of the kind envisaged is proportional to the initial internal energy, as described by \((2.5)\); the proportionality constant \( R_0 \), quoted in \((1.6)\), depends strongly on distance and speed. (ii) Consequently, if repeated collisions can be arranged, say as in the toy model from section 4, then the rise of internal energy with the number of collisions, and thence with time, is necessarily exponential. (iii) If the pre-collision internal energies are Boltzmann-distributed with temperature \( T \), then the post-collision distribution is also thermal, with a temperature rise given by \((2.11)\) and \((2.12)\). (iv) Negative friction is precluded under the conditions where our model for the collisions make sense.

2. Excited initial states and thermal averages

2.1. Arbitrary initial quantum numbers

We start by extending the results of I to non-degenerate transitions from arbitrarily prescribed initial levels \( n_1, n_2 \). The familiar dipole selection rules and matrix elements \( |\Delta n| = 1 \) and \( \langle n+1|d|n \rangle = \sqrt{n+1}D, \langle n-1|d|n \rangle = \sqrt{n}D \) entail

\[
R\left[(n_{1i}, n_{2i}) \rightarrow (n_{1i} + 1), (n_{2i} + 1)\right] = (n_{1i} + 1)(n_{2i} + 1)R_0, \tag{2.1}
\]

\[
R\left[(n_{1i}, n_{2i}) \rightarrow (n_{1i} - 1), (n_{2i} - 1)\right] = n_{1i}n_{2i}R_0. \tag{2.2}
\]

For degenerate transitions, the analogous probabilities, e.g. \( R[(n_{1i}, n_{2i}) \rightarrow (n_{1i} \pm 1), (n_{2i} \mp 1)] \), are derived in appendix A, and turn out to be much larger. On the other hand, such transitions are irrelevant to frictional energy dissipation and to the interatomic force.
By virtue of (2.1) and (2.2), the quantum-mechanical expectation values of the energy changes, denoted as \(\Delta \varepsilon\), read

\[
\langle \Delta \varepsilon_1 \rangle = R_0 \{(n_{1i} + 1)(n_{2i} + 1) - n_{1i} n_{2i}\} = R_0 (2n_{2i} + 1),
\]

\[
\langle \Delta \varepsilon_2 \rangle = R_0 (2n_{1i} + 1),
\]

\[
\langle \Delta \varepsilon_1 + \Delta \varepsilon_2 \rangle = 2(1 + n_{1i} + n_{2i})R_0.
\]

That \(\langle \Delta \varepsilon_1 + \Delta \varepsilon_2 \rangle\) is proportional to the total initial energy is of course a peculiarity of simple-harmonic oscillators.

### 2.2. The final probability distributions and a final temperature

The object of this paper is to study the mean energy gain of atoms at a common initial temperature \(\tau_1\), i.e. the average of (2.4) over the common initial thermal-equilibrium distributions \(P_i(n = n_1 \text{ or } n_2)\), where

\[
P_i(n) = \exp(-\beta_i n) [1 - \exp(-\beta_i)], \quad \bar{n}_{1i} = \bar{n}_{2i} = \bar{n}_i = \frac{1}{\exp(\beta_i) - 1},
\]

which entail

\[
\Delta \bar{\varepsilon}_1 = \Delta \bar{\varepsilon}_2 \equiv \Delta \bar{\varepsilon} = 2R_0 \bar{\varepsilon}_i.
\]

To be pedantic, or if one contemplated other initial conditions, one would introduce potentially distinct single-atom probability distributions \(P_{1i}(n_{1i})\) and \(P_{2i}(n_{2i})\). But because our atoms start infinitely far apart, these probabilities are independent, i.e. uncorrelated; and because the atoms start at a common temperature, the two distributions are identical functions of their respective arguments. That is what authorizes the abbreviated notation \(P_i(n)\) with an argument that can be either \(n_1\) or \(n_2\).

By contrast, as yet we cannot talk of a final temperature \(\tau_f\). Although by symmetry the post-collision single-atom distribution too is unique, there is no a priori reason why it should be thermal, given that the excitation mechanism knows nothing about temperatures, and that our model has no post-collision relaxation mechanism. To characterize the post-collision system adequately one must therefore start by determining the probability distributions

\[
P_i(n) = P_i(n) + \Delta P(n)
\]

of the postcollision quantum numbers, given \(P_i(n)\) from (2.5). Since we are working only to first order in the changes \(\Delta \ldots\), we can dispense with subscripts \(i\) on \(\Delta P\) and \(\Delta \bar{\varepsilon}\).

Degenerate transitions are irrelevant to \(\Delta P(n)\): by symmetry, and because by assumption the two \(P_i\) are the same, would-be changes due to such transitions \((n_{1a}, n_{2a}) \rightarrow (n_{1c}, n_{2d})\) are exactly compensated by other transitions \((n_{1c}, n_{2d}) \rightarrow (n_{1a}, n_{2b})\). Hence one finds the \(P_i\) by summing (over all the precollision states that can feed the given final state) the initial \(P_i\) multiplied by the appropriate transition probability from (2.1) or (2.2). This is straightforward but tedious. Eventually, for given \(n_1\) and \(n_2\) and for any probability distribution \(P(n_1)\), one finds

\[
\Delta P(n_1) = R_0 (2n_2 + 1) \times
\]

\[
\times \{ n_1[-2P(n_1) + P(n_1 - 1) + P(n_1 + 1)] - P(n_1) + P(n_1 + 1) \}.
\]
We substitute the thermal distribution \( P_i(n_i) \) from (2.5); replace \((2n_2 + 1)\) with its thermal average \([\exp(\beta_i) + 1]/[\exp(\beta_i) - 1]\); drop the now redundant subscripts; and use hindsight to rearrange the result to read

\[
\Delta P(n) = R_0 \exp[-\beta_i(n + 1)] 2 \sinh(\beta_i) \{n[\exp(\beta_i) - 1] - 1\}.
\]

(2.9)

It remains to compare \( \Delta P \) with the first-order small change \( \Delta \tilde{P} \) induced in a Boltzmann distribution by a small change of temperature:

\[
T \rightarrow T + \Delta T \Rightarrow \beta \rightarrow \beta + \Delta \beta, \quad \Delta \beta = -\frac{\hbar \omega \Delta T}{k_B T^2},
\]

\[
P(n) = \exp(-\beta n)[1 - \exp(-\beta)] \rightarrow P(n) + \Delta \tilde{P}(n),
\]

(2.10)

\[
\Delta \tilde{P}(n) = \Delta \beta \frac{\partial P}{\partial \beta} = -\Delta \beta \exp[-\beta_i(n + 1)] \{n[\exp(\beta_i) - 1] - 1\}.
\]

But inspection of (2.9) and (2.10) shows that \( \Delta P(n) \) is indeed generated by a change

\[
\beta_i \rightarrow \beta_i + \Delta \beta, \quad \Delta \beta = -2R_0 \sinh(\beta_i) = -4R_0 \sinh \left( \frac{\beta_i}{2} \right) \cosh \left( \frac{\beta_i}{2} \right).
\]

(2.11)

\[
\Delta \tau = \Delta \left( \frac{1}{\beta} \right) = 2R_0 \sinh \left( \frac{\beta_1}{\beta_i} \right).
\]

(2.12)

Only now that this has been established are we in a position to reason in terms of postcollision temperatures, and to take advantage of the familiar formulae for thermal equilibrium in order to correlate postcollision mean values. In particular, we can now write

\[
\Delta \tilde{\epsilon} = \frac{1}{2} \Delta \coth \left( \frac{\beta}{2} \right) = -\frac{\Delta \beta}{4 \sinh^2(\beta/2)} \Rightarrow \Delta \tilde{\epsilon} = 2R_0 \tilde{\epsilon}.
\]

(2.13)

Recall that the \( \Delta \ldots \) stand for changes due to the collision, with the velocities kept constant by fiat.

Equations (2.11)–(2.13) are our central results. We see that finite temperatures simply multiply the energy dissipated in zero-temperature collisions by appropriate Bose–Einstein factors \( \tilde{\epsilon}(\tau)/\tilde{\epsilon}(0) = \coth(1/2\tau) \). The same is true for the force \( F(\tau) \), which for \( \tau = 0 \) is quoted in (1.8).

By the same token, \( \coth(1/2\tau) \) is the finite-temperature enhancement factor for the frictional force between two electrically dilute and non-dissipative half-spaces made of identical atoms, reported in Appendix B of I. van der Waals friction between half-spaces that need not be dilute and may be dissipative is discussed elsewhere (Barton 2011); for relativistic calculations, cf Polevoi (1990a).

For completeness, one should note that, contrary to what (2.11) might suggest, the postcollision system is not truly thermal, because its state vector is entangled. For instance, for the two-atom distributions \( \Pi \), one has \( \Pi_1(n_1, n_2) = P_1(n_1)P_1(n_2) \) but \( \Pi_1(n_1, n_2) \neq P_1(n_1)P_1(n_2) \).

3. Negative friction?

Subject to the basic condition (1.1), the introduction has already commented that without constraints a rise \( \Delta \tilde{E} \) of internal energy per atom would entail an equal drop in the kinetic energy \( K = M(u/2)^2/2 = Mu^2/8 \). Although obvious, this reveals an apparently paradoxical feature of our results. Namely, we have found positive \( \Delta \tilde{\epsilon} \) and thereby negative \( \Delta K \) for any internal temperature \( T \) combined with any velocity \( u \), whereas one would expect that, on the
way towards overall thermal equilibrium, high enough $T$ combined with low enough $K$ would entail a drop in $\bar{\varepsilon}$ and a rise in $K$, or in other words, negative friction accelerating instead of retarding the atoms. Indeed a relativistic/retarded calculation by Polevoi (1990a, 1990b) does find negative friction under appropriate conditions. The reason why we do not is that it requires parameters far outside the regime we are considering. This is proved as follows.

The constrained approximation makes sense only if even appreciable fractional changes in $E$ entail only small fractional changes in $u$, i.e. only if

$$\frac{\Delta u}{u} \ll \frac{\Delta E}{E}, \quad (3.1)$$

while energy conservation yields

$$\Delta \left( \frac{M u^2}{8} \right) = \Delta E \Rightarrow \Delta u = \frac{4 \Delta E}{M u} \Rightarrow \frac{\Delta u}{u} = \frac{4 \Delta E}{M u^2}. \quad (3.2)$$

Combining these relations we see that our model requires

$$\frac{\Delta u}{u} = \frac{4 \Delta E}{M u^2} \ll \frac{\Delta E}{E} \Rightarrow M u^2 \gg 4E. \quad (3.3)$$

The crucial point is that this is incompatible with conditions anywhere near thermal equilibrium, which is where the paradox in question might have become operative, and where

$$\frac{M u^2}{8} = \frac{k_B T}{2} = \frac{\hbar \omega}{2}, \quad \tilde{E} = \frac{\hbar \omega}{2} \coth \frac{1}{2\tau}. \quad (3.4)$$

But these two conditions jointly with (3.3) entail

$$(2\tau) \tanh \left( \frac{1}{2\tau} \right) \gg 1, \quad (3.5)$$

which is impossible because $0 < z \tanh(1/z) < 1$. ■

4. Evolution in a multi-collision toy model

4.1. The model

Instead of just two atoms, we now envisage infinitely many along each trajectory, all having the same fixed velocity $\pm u/2$. Their mean spacing is $l$, whence the mean number of collisions that a given atom undergoes in unit time is $\mu = u/l$. The atoms on both trajectories start at a common temperature, with their quantum numbers distributed accordingly; moreover, we take this initial distribution to be thermal also in the further sense that there are no correlations between different atoms. Interactions between atoms on the same trajectory are ignored. This is a crude way of arranging for the quantum number of every atom to be governed by a sequence of dynamically identical collisions with atoms on the opposite trajectory. The artificialities of the model are obvious. For one thing, although the motion must start at some finite time, the model simply disregards the oscillations caused before then by the van der Waals (vdW) interactions between atoms on one trajectory with those on the other. Correspondingly,
in looking for the drag force we ignore transients, and thereby also the finite temperature rise that such transients must have produced: hence it is only a pretence that the initial temperature could be strictly zero. For another thing, as explained in the introduction, the model becomes seriously misleading at large times, when it predicts exponentially rising temperatures. Meanwhile, however, we derive its predictions without further apologies. Evidently all the atoms are described by a common probability distribution for all $t$.

If the entire system is maintained at its initial temperature $T$, say by immersing both trajectories in black-body radiation, the paragraph just below (2.13) tells us that the power $p$ dissipated per atom, and the drag force $f$ experienced by each, are just $\coth(1/2\tau)$ times that for $T = 0$:

$$p = uf = \hbar \omega \mu \Delta \tilde{\epsilon}/2 = 2\hbar \omega \mu \tilde{R}_0 \tilde{\epsilon} = \hbar \omega \mu \tilde{R}_0 \coth(1/2\tau), \quad \mu = u/l.$$  \hfill (4.1)

4.2. Frictional heating

In an alternative and more interesting scenario, the probability distribution $P(t)$ evolves through the succession of collisions just described. Then (2.13) transcribes into the differential equation

$$\frac{d\tilde{\epsilon}}{d\vartheta} = \tilde{\epsilon}, \quad \vartheta \equiv 4\mu \tilde{R}_0 t = \frac{4u \tilde{R}_0 t}{l}. \hfill (4.2)$$

Hence

$$\tilde{\epsilon} = \tilde{\epsilon}_i \exp(\vartheta), \quad \tau = \frac{1}{2 \coth^{-1}\{\exp(\vartheta) \coth(1/2\tau_i)} \}. \hfill (4.3)$$

In the special case where the atoms start in their ground states,

$$\tau_i = 0 \Rightarrow \tau = \frac{1}{2 \coth^{-1}\{\exp(\vartheta)\}} = \frac{1}{\log\{\coth(\vartheta/2)\}}. \hfill (4.4)$$

To elucidate the asymptotics of the temperature one needs

$$\coth(z \ll 1) = 1 + \frac{z}{3} + O(z^3), \quad \coth(z \gg 1) = 1 + 2\{\exp(-2z) + \exp(-4z) + \cdots\}, \hfill (4.5)$$

$$\coth^{-1}(z) = \frac{1}{z} + \frac{1}{3z^3} + O\left(\frac{1}{z^5}\right). \hfill (4.6)$$

4.2.1. Initial temperature zero. For $\vartheta \ll 1$, we expand (4.4) by brute force:

$$\tau(\vartheta \ll 1) = \frac{1}{\log(2/\vartheta)} - \frac{1}{12} \left[\frac{\vartheta}{\log(\vartheta/2)}\right]^2 + O\left(\frac{\vartheta^4}{\log^2(2/\vartheta)}\right). \hfill (4.7)$$

For $\vartheta \gg 1$, expanding first $\cot(\vartheta/2)$ by (4.5), and then $1/\log\{\ldots\}$ in powers of $\exp(-\vartheta)$:

$$\tau(\vartheta \gg 1) = \frac{1}{2} \exp(\vartheta) + \frac{1}{3} \exp(-\vartheta) + O(\exp(-2\vartheta)). \hfill (4.8)$$
Figure 2. The scaled temperature \( \tau \) as a function of scaled time \( \vartheta \). Upper curve: \( \tau \) rising from initial \( \tau_i = 0.1 \). Lower curve: \( \tau \) rising from initial \( \tau_i = 0 \). Note how fast the difference shrinks (recalling that as \( \vartheta \to \infty \) both rise exponentially but with different coefficients as given by (4.10)).

Figure 3. The function \( \chi \) defined by (4.11) rising with scaled time \( \vartheta \), from initial \( \chi_i = 0.19998 \), corresponding to \( \tau_i = 0.1 \) as in figure 2 (to illustrate the approach of \( \tau \) to its long-time asymptotic form).

4.2.2. Initial temperature nonzero. For \( \vartheta \ll 1 \), we expand (4.3) in a Taylor series, finding the coefficients by brute force. Eventually one obtains

\[
\tau (\vartheta \ll 1) = \tau_i + \{\tau_i^2 \sinh(1/\tau_i)\} \vartheta^2 + \mathcal{O}(\vartheta^2).
\]  

(4.9)
Unfortunately, for small \( \tau \), this approximation is next to useless, because exponentially large \( \sinh(1/\tau) \) restricts it to exponentially small \( \vartheta \).

For \( \vartheta \gg 1 \), we expand \( \coth^{-1}\{\ldots\} \) in (4.3) appropriately to large argument, and find

\[
\tau (\vartheta \gg 1) = \frac{1}{2} \exp(\vartheta) \coth\left(\frac{1}{2\tau}\right) - \frac{3}{2} \exp(-\vartheta) \coth^3\left(\frac{1}{2\tau}\right) + \mathcal{O} \exp(-3\vartheta). \tag{4.10}
\]

One sees that eventually the temperature rises exponentially with time from any \( \tau \). However, the introduction has already warned that this rise, once it produces large \( \tau \), is one of the least applicable consequences of the model; and it is a peculiarity of oscillators to begin with.

Figure 2 plots \( \tau \) rising from \( \tau_i = 0 \) (equation (4.4)), alongside \( \tau \) rising from \( \tau_i = 0.1 \) (equation (4.3)), to show how fast they approach each other while \( \tau \) is still quite reasonably small. By contrast, to help visualize what happens at (unrealistically) higher \( \vartheta \), figure 3 plots, again with \( \tau_i = 0.1 \), an auxiliary function

\[
\chi = 2\tau \tanh(1/2\tau_i) \exp(-\vartheta), \quad \lim_{\vartheta \to \infty} \chi = 1. \tag{4.11}
\]

Contrast the horizontal scales of the two figures.

Appendix A. Degeneracies

Although our atoms are identical, their trajectories are, by assumption, far enough apart to prevent their wavefunctions from overlapping, so that they are effectively distinguishable, and their joint state vector need not be symmetrized. In particular, \( |n_1, n_2\rangle \) and \( |n_2, n_1\rangle \) are distinct zero-order basis states. For our purposes, it will suffice to analyse only the first-excited case\(^4\) \( n_1 + n_2 = 1 \). Diagonalizing \( H_{\text{int}} \) on the basis of \( |1, 0\rangle, |0, 1\rangle \), where \( \langle 0, 1|H_{\text{int}}|1, 0\rangle = D^2/s^3 \), yields the eigenvalues \( \pm D^2/s^3 = \pm h\omega\alpha/2s^3 \); these are the static vdW potentials in the eigenstates \((1, 0) \mp (0, 1))/\sqrt{2} \) of \( H \). They may be contrasted with the potential \(-h\omega\alpha^2/8s^6 \) in the ground state \( |0, 0\rangle \).

However, as regards friction, degeneracies are irrelevant, because then one is concerned not with energy eigenvalues but with transition probabilities, requiring time-dependent rather than time-independent perturbation theory. For the first-excited state this yields

\[
|\Psi(t)\rangle \simeq \exp(-2i\omega t) \{|1, 0\rangle + c(t)|0, 1\rangle\}, \tag{A.1}
\]

\[
c(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' \langle 0, 1|H_{\text{int}}(t')|1, 0\rangle \tag{A.2}
\]

\[
= -\frac{iD^2}{\hbar u a^2} \int_{-\infty}^{x} \frac{dx'}{(1 + x'^2)^{3/2}} \nonumber
\]

\[
= -\frac{i\alpha\omega}{2ua^2} \varphi, \quad \varphi \equiv 1 + \frac{x}{(1 + x^2)^{3/2}}, \tag{A.3}
\]

whence we write the transition probability as

\[
Q \{(1, 0) \rightarrow (0, 1)\} = |c(\infty)|^2 = \frac{\omega^2\alpha^2}{u^2a^4} = \frac{\alpha^2}{a^6v^2} \equiv Q_0. \tag{A.4}
\]

\(^4\) For higher states, the equal level-spacing of oscillators entails further and accidental zero-order degeneracies without counterparts for real atoms: for instance, \( |2, 1\rangle \) is zero-order degenerate not only with \( |1, 2\rangle \) but also with \( |3, 0\rangle \) and \( |0, 3\rangle \).
Thus $Q_0$ is comparable to its non-degenerate analogue $R_0$ for $v \gg 1$, but much larger for $v \ll 1$, when $R_0$ falls exponentially.

In fact, if one restricts the state vector to a linear combination of $|1, 0\rangle$ and $|0, 1\rangle$, it is easily found without further approximation:

$$|\Psi(t)\rangle \simeq \cos\left[\frac{\alpha^2 \varphi}{2a^3 v}\right] + i \sin\left[\frac{\alpha^2 \varphi}{2a^3 v}\right],$$

(A.5)

reducing for small $\varphi$ to (A.1) and (A.3) as it should.

For degenerate transitions in general, the same argument as in section 2 yields

$$Q[(n_1, n_2) \rightarrow (n_1 + 1, n_2 - 1)] = Q_0 (n_1 + 1) n_2.$$  

(A.6)

These are the only kind in question, because $H_{\text{int}}$ links no other oscillator-degenerate pairs of states.

Appendix B. Other theories?

Hoye and Brevik (1992, 2010a, 2010b) have considered friction between two oscillators, not necessarily identical, a finite distance apart, and kept at a common constant temperature. Translated into our notation, their result (equation (19) in Hoye and Brevik (2010a), cited as HB) reads

$$F_{\text{HB}} = \frac{\pi \beta \hbar^2}{8m_1 m_2 \omega_1^2} \sinh^2(\beta \hbar \omega_1 / 2) \delta (\omega_1 - \omega_2),$$

(B.1)

where $\psi = e_1 e_2 / s^3$, with $\omega_{1,2}$, $e_{1,2}$ and $m_{1,2}$ the frequencies, charges and internal masses of the oscillators. (Recall that $\alpha = e^2 / m \omega^2$.) They say that ‘. . . there is friction only when the oscillators have the same frequency, and $\beta$ should be finite, i.e. $T > 0$’.  

The present writer does not understand how to make sense of a factor $\delta(\omega_1 - \omega_2)$ in an expression for the frictional force between individually identifiable oscillators. However, even apart from this factor, equation (B.1) taken at face value is at all points incompatible with the results here and in paper I:

(i) it is linear in $u$ (presumably as a leading approximation at low speed);

(ii) it vanishes at zero temperature;

(iii) it vanishes for oscillators with different frequencies, whereas appendix C of I spells out that our results do not.

To derive (B.1), HB (as translated into our notation) consider two oscillators with initial separation $s_i$, and follow their evolution over a short time lapse $\Delta t$ during which $s(t) = s_i + u \cdot t$, leading them to approximate $H_{\text{int}}(t) \simeq H_{\text{int}}(s_i) + u \cdot \nabla H_{\text{int}}(s)|_{s=s_i}$. But then they retain this approximation while exploiting standard response-function formalism, which requires integrals

5 The 1992 and the first 2010 papers refer, in a spirit apparently of compatibility, to results of Levitov (1989) on friction between half-spaces, with which other recent papers have disagreed (see e.g. Pendry (1997)). Regarding the non-retarded regime, Levitov fails through inconsistency in handling gauges: he assigns to a term $L_0$ of his Lagrangian all effects not stemming directly from the quantized radiation field, but then never returns to $L_0$. The oversight might have been invited by uncritical reliance on path integrals plus Lifshitz theory. (The effects governed by $L_0$ are described as ‘short-wavelength’, probably a slip of the pen or a mistranslation of ‘short-distance’.) These points are discussed further elsewhere (Barton 2011).
\[ f^\infty dt \ldots , \] an incompatibility that may be responsible for the discrepancy noted in (i). (For instance, their approximation (10) cannot be taken under the integral in their equation (9).

In fact it is readily shown that to first order in \( \Delta t \) (and thereby in \( u \)), i.e. when the approximation does apply, there is no frictional (i.e. non-adiabatic) energy change \( \Delta E \) in any pure state, and therefore none in the statistical mixture of such states appropriate to any temperature whether zero or finite. Label the initial and final states by \( i, f \), so that

\[ s_0 = s + \Delta t u, \quad H(s) = H(s_0) + \Delta t \partial H(s)/\partial t|_{s=s_0} = H(s) + \Delta t u \cdot \nabla H(s); \tag{B.2} \]

then the non-adiabatic energy change reads

\[ \Delta E \equiv |\langle f | H(s) | f \rangle - \langle i | H(s) | i \rangle| - \Delta t u \cdot \nabla V_0(s), \tag{B.3} \]

where \( V_0(s) \) is the vdW potential in the state \( |i\).

The Schrödinger equation entails

\[ |f\rangle \simeq \left[ 1 - i\frac{\Delta t H(s)}{\hbar} \right]|i\rangle \quad \Rightarrow \tag{B.4} \]

\[ \Delta E + \Delta t u \cdot \nabla V_0(s) = \langle i | \left[ \left[ 1 + i\frac{\Delta t H(s)}{\hbar} \right] \times \left[ H(s) + \Delta t u \cdot \langle \nabla H(s) \rangle \right] \left[ 1 - \frac{i\Delta t H(s)}{\hbar} \right] - H(s) \right] |i\rangle \]

\[ = \langle i | \Delta t u \cdot \langle \nabla H(s) \rangle |i\rangle + {\cal O}((\Delta t)^2)), \tag{B.5} \]

Finally,

\[ \langle i | \langle \nabla H(s) \rangle |i\rangle = \nabla \langle i | H(s) | i\rangle = \nabla [\hbar \omega (n_1 + n_2 + 1) + V_0(s)] = \nabla V_0(s), \tag{B.7} \]

where the first step follows from the Hellmann–Feynman theorem\(^6\). Substitution into (B.6) yields \( \Delta E = 0. \square \)

**Appendix C. The non-retarded approximation**

We consider the contributions to friction of order \( 1/c^2 \), following the suggestion of an anonymous referee that they might warrant more attention than the dimensional estimates of at most second order in \( u/c, a/\Lambda_0 \) and \( a/\Lambda_T \) jointly\(^7\). In fact we shall derive (in outline) only the zero-temperature correction. Finite-temperature effects would require a major research programme, and for them we can appeal only to the somewhat loose analogy with the problem of the adiabatic potential \( V(s) \) between isotropic 3D oscillators, which has been studied exhaustively. At \( T = 0 \) the standard treatment (e.g. Feinberg et al 1989, Power and Thirunamachandran 1994) yields the well-known result

\[ V(s, T = 0) = -\frac{3a^2\hbar\omega}{4s^6} \left\{ 1 - \frac{1}{3} \left( \frac{\omega s}{c} \right)^2 + {\cal O} \left( \frac{\omega s}{c} \right)^4 \right\}. \tag{C.1} \]

\(^6\) Risking the obvious we note that, as in (B.2), for our purposes \( \Delta t u \cdot \nabla \) is the same as \( \Delta t \partial/\partial t \).

\(^7\) Although \( s/\Lambda_0 \) and \( s/\Lambda_T \) become large long before and long after passage, one can ignore this complication because those regions do not in any case contribute to the accuracy being envisaged.

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At finite $T$ the most accessible introduction is probably the original one by McLachlan (1963a, 1963b), specialized to oscillators (with vivid numerical illustrations) by Goedecke and Wood (1999). Here we consider only $k_B T / \hbar \omega = \Lambda_0 / \Lambda_T \ll 1$; then the leading correction (Barton (2001); equation (2.9) and footnote 8) yields

$$ V(s, T) \simeq - \frac{3 \alpha^2 \hbar \omega}{4 s^6} \left\{ 1 - \frac{1}{3} \left( \frac{\omega \delta}{c} \right)^2 - \frac{1408 \pi^5}{2835} \left( \frac{k_B T}{\hbar \omega} \right)^6 \left( \frac{\omega \delta}{c} \right)^5 \right\} $$

$$ = - \frac{3 \alpha^2 \hbar \omega}{4 s^6} \left\{ 1 - \frac{4 \pi^2}{3} \left( \frac{s}{\Lambda_0} \right)^2 - \frac{45056 \pi^{10}}{2835} \left( \frac{\Lambda_0}{\Lambda_T} \right)^6 \left( \frac{s}{\Lambda_0} \right)^5 \right\}, \quad \text{(C.2)} $$

where \([\ldots]\) \(\approx 1.49 \times 10^6\). Remarkably, the temperature-dependent component is only of order \(1/e^5\).

To allow for retardation, the electromagnetic interaction between two particles separated by \(\rho_{ij} = \mathbf{r}_i - \mathbf{r}_j\), with charges \(e_{i,j}\) and velocities \(w_{i,j} = \mathbf{v}_{i,j}\), is written as

$$ U_{ij} = \frac{e_i e_j}{\rho_{ij}} + h_{ij}, \quad h_{ij} \equiv - \frac{e_i e_j}{2c^2} \left[ (\mathbf{w}_i \cdot \mathbf{w}_j) + \left( \frac{\mathbf{w}_i \cdot \mathbf{r}_{ij}}{\rho_{ij}} \right) \left( \frac{\mathbf{w}_j \cdot \mathbf{r}_{ij}}{\rho_{ij}} \right) \right]. \quad \text{(C.3)} $$

In classical physics \(h_{ij}\) is called the Darwin interaction (Landau and Lifshitz 1975); in quantum mechanics it enters the Breit equation which governs the motion of two electrons in the Pauli approximation (Bethe and Salpeter 1957). A stationary oscillator has \(e_i, \mathbf{w}_i = \mathbf{d}_i\), and it is straightforward to verify that in the dipole approximation interference between \(h_{ij}\) and \(e_i e_j / \rho_{ij}\) yields the correction given by \((C.1)\).

Regarding zero-temperature friction, one must start with the addend to \(H_{\text{int}}\), call it \(\tilde{H}_{\text{int}}\), produced by the Darwin term. Without loss of generality we picture the oscillator initially on the left as made of one particle of charge \(-e\) at the prescribed position \(\mathbf{r}_1 = (a, 0, z = ut/2)\) indicated in figure 1, plus another particle of charge \(+e\) at \(\mathbf{r}_1' = (a, y_1, ut/2)\); the other oscillator is made of one charge \(-e\) at the other prescribed position \(\mathbf{r}_2 = (0, 0, z = -ut/2)\) plus a charge \(e\) at \(\mathbf{r}_2' = (0, y_2, -ut/2)\). The \(y_{1,2}\) are just the internal coordinates we have already used; while, for example, \(\mathbf{w}_i' = (0, \dot{y}_1, u/2)\) and \(\rho_{1,2}' = (a, y_1 - y_2, ut)\). We need the dipole approximation to the \(h_{ij}\) summed over the pairs 12, 12', 1'2, 1'2'. To find it one expands all the \(\rho_{ij}\) in the pertinent denominators up to second order in the \(y/s\) and \(\dot{y}/s\) severally or jointly; drops terms of order zero (which do not contribute to friction because they cannot excite the oscillators); and keeps only the leading survivors, which are of second order. The calculation is straightforward but tedious, though in our model it is eased by the internal coordinates being orthogonal to \(\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2\) and to \(\mathbf{t} = \mathbf{u}\). Eventually one finds:

$$ \tilde{H}_{\text{int}} = \tilde{H}_1 + \tilde{H}_2, \quad \tilde{H}_1 = \frac{u^2}{8c^2} H_{\text{int}}. \quad \text{(C.4)} $$

The component \(\tilde{H}_2\) contains terms that excite each oscillator singly and others that excite just one oscillator doubly. Only the former can contribute to order \(1/c^2\), because they alone can interfere with \(H_{\text{int}}\); dropping the latter we get

$$ \tilde{H}_2 = \frac{1}{2c^2} \left\{ \frac{1}{s} d_1 d_2 - \frac{(\mathbf{u} \cdot \mathbf{s})}{2 s^3} (d_1 d_2 + d_1 d_2) - \frac{3 (\mathbf{u} \cdot \mathbf{s})^2}{4 s^5} d_1 d_2 \right\}. \quad \text{(C.5)} $$

The positive sign of \(\tilde{H}_1\), contrasting with the minus in \((C.1)\), comes from the fact that overall the prescribed velocities \(\pm ut/2\) contribute negatively to \([\ldots]\) in \((C.3)\).

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The transition matrix element follows after a few steps, which require mainly book-keeping and which we merely list. (i) Replace $\dot{d} \to i \omega d$. (ii) Scale to the dimensionless variables $x, v$ as before, and compare with the already-known matrix element of $H_{\text{int}}$. (iv) Insert into the integral $\int_{-\infty}^{\infty} dx \exp(-2ix/v) \ldots$, on the pattern of (1.9), which echoes equations (2.4) and (2.5) in I. (v) Discard the integrands odd in $x$, and integrate the others, which yields modified Bessel functions times powers of $v$. (vi) Combine with the contribution from $\tilde{H}_1$. (vii) Call the result $\delta J$; let $J_{\text{NR}}$ be the corresponding integral from $H_{\text{int}}$; note that both are real, whence the relative correction factor in $|J_{\text{NR}} + \delta J|^2$ and thence to the rate $R_0$ reads

$$\delta R_0 / R_0 = 2 \delta J / J_{\text{NR}} \equiv \eta.$$  

(C.6)

One finds

$$\eta = \frac{1}{4} \left( \frac{u}{c} \right)^2 - \left( \frac{\omega a}{c} \right)^2 g(v), \quad g \equiv 1 + \frac{vK_0(2/v)}{K_1(2/v)}, \quad v \equiv \frac{u}{\omega a},$$  

where the first term of $\eta$ stems from $\tilde{H}_1$ and the second from $\tilde{H}_2$.

Thus, of the three dimensionally admissible parameters, $\eta$ appears to feature the two squares but not the cross-term. But in principle the distinction is arbitrary, since $(\omega a/c)^2/(u/c)^2 = 1/v^2$ allows one to re-write $\eta$ as $(u/c)^2 \lambda(v)$, with $\lambda = 1/4 - g/v^2$.

Asymptotically

$$g(v \ll 1) = 1 + v - v^2/4 + \mathcal{O}(v^3), \quad g(v \gg 1) = 2(\log v - \gamma) + 1 + \mathcal{O}((\log v)/v)^2.$$  

(C.8)

Finally, we note that some temperature-dependent corrections to $R$ follow automatically on replacing $R_0 \to R_0(1 + \eta)$ in sections 2 and 4. The nontrivial problem is to find these corrections to $R_0$ itself; and, as already explained, at present one has no hard information about these. However, for what it is worth, the analogy with adiabatic potential $V$ suggests that to order $1/c^2$ there might be none.

References

Barton 2001 J. Phys. A: Math. Gen. A 34 5781
Barton 2010 New J. Phys. 12 113044
Barton 2011 On van der Waals friction between half-spaces at low temperature, Sussex preprint
Bethe H A and Salpeter E E 1957 Quantum Mechanics of One- and Two-Electron Atoms (Berlin: Springer) sections 38 and 39
Feinberg G, Sucher J and Au K C 1989 Phys. Rep. 180 83
Goedecke G H and Wood R C 1999 Phys. Rev. A 60 2577
Hoye J S and Brevik I 1992 Physica A 181 413
Hoye J S and Brevik I 2010a Europhys. Lett. 91 60003
Hoye J S and Brevik I 2010b arXiv:1009.3135v1 [quant-ph]
Landau L D and Lifshitz E M 1958 Statistical Physics (Oxford: Pergamon) section 103
Landau L D and Lifshitz E M 1975 The Classical Theory of Fields 4th edn (Oxford: Pergamon) equation (65.8)
Levitov L S 1989 Europhys. Lett. 8 499
McLachlan A D 1963a Proc. R. Soc. A 271 387
McLachlan A D 1963b Proc. R. Soc. A 274 80
Pendry J B 1997 J. Phys.: Condens. Matter 9 10301
Polevoi V G 1990a Sov. Phys.—JETP 71 1119 (Engl. Transl.)
Polevoi V G 1990b Zh. Eksp. Teor. Fiz. 98 1990 (in Russian)
Power E A and Thirunamachandran T 1994 Phys. Rev. A 50 3929

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