Fusion mechanism in fullerene-fullerene collisions: The deciding role of giant oblate-prolate motion

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Abstract – We provide answers to long-lasting questions in the puzzling behavior of fullerene-fullerene fusion: Why are the fusion barriers so exceptionally high and the fusion cross sections so extremely small? An \textit{ab initio} nonadiabatic quantum molecular-dynamics (NA-QMD) analysis of $C_{60} + C_{60}$ collisions reveals that the dominant excitation of an exceptionally “giant” oblate-prolate $H_g(1)$ mode plays the key role in answering both questions. From these microscopic calculations, a macroscopic collision model is derived, which reproduces the NA-QMD results. Moreover, it predicts analytically fusion barriers for different fullerene-fullerene combinations in excellent agreement with experiments.

Introduction. – After the pioneering $C_{60} + C_{60}$ collision experiment of Campbell \textit{et al.} in 1993 \cite{1}, cluster-cluster collisions became a versatile new field of research (for reviews see \cite{2–5}) with lasting interest \cite{6–20}. In particular, fusion between fullerenes has been studied in great detail, both experimentally and theoretically \cite{1,21–37}. Fusion is a universal phenomenon in collisions between complex particles covering many orders in size and energy from heavy-ion collisions in nuclear physics \cite{38} to macroscopic liquid droplets \cite{39,40} or even colliding galaxies \cite{41}. It is a great challenge of ongoing interest to reveal universal similarities and basic differences of these mechanisms.

Usually, the gross features of fusion can be understood with macroscopic arguments \cite{3,38,40,42} leading to the general expression for the fusion cross-section $\sigma$ as a function of the center-of-mass energy $E_{\text{c.m.}} \equiv E$ of

\begin{equation}
\sigma(E) = \pi R_{12}^2 \left(1 - \frac{V_B}{E}\right)
\end{equation}

with $R_{12} = R_1 + R_2$ the sum of the radii of the colliding partners and $V_B$ the fusion barrier (for a derivation see, \textit{e.g.}, \cite{3,38,43}). This formula (known as “critical distance model” in nuclear physics \cite{38} or “absorbing sphere model” in chemistry \cite{43}) describes quantitatively the experimental fusion cross-section for atomic nuclei (with $V_B > 0$) and liquid droplets (with $V_B = 0$) \cite{10,39,40} in the low-energy range with $E \gtrsim V_B$ (see footnote 1). It is expected to hold also for collisions between metallic clusters \cite{10} (even with $V_B < 0$); see last paper in the series \cite{6–9}. The physics behind formula (1) is indeed simple: fusion takes place, if the colliding partners touch, owing to the larger binding energy of the fused compound \cite{42}. For colliding fullerenes one naturally expects a fusion barrier $V_B$ of at least the $sp^2$ bond breaking energy, or more pertinently the Stone-Wales transformation energy \cite{33,34} of a few eV \cite{44} and, according to (1), a fusion cross-section of the order of the geometrical one, $\pi R_{12}^2 \sim 150\,\text{Å}^2$ \cite{29}. Experimentally, however, the fusion barriers are about one order of magnitude larger (around 80 eV) \cite{29} and the cross-sections are even two magnitudes smaller (a few Å$^2$) \cite{31}.

Up to now, there is no definite explanation for these findings, albeit some possible phenomenological reasons have been discussed \cite{3–5,31,32}. In addition, previous (at that time still approximate) microscopic quantum molecular-dynamics (QMD) calculations predicted the large fusion barriers \cite{28}. From these studies it is also well known that only very few mutual initial orientations of the colliding cages lead to fusion (without identifying them). Anyway, fullerenes typically do not fuse if they touch, even at high impact energies, and the question remains: why? In this work, we provide a clear answer to this longstanding question.

Footnote:

1We do not consider here the high energy range, where the cross-sections generally decreases with $E_{\text{c.m.}}$, see \cite{10}.
Microscopic results. — Motivated by our recent findings of the dominating role of the \( A_2(1) \) breathing mode in \( C_{60} \)-laser interaction [45,46], we have reanalyzed fullerene-fullerene collisions with the help of the \( ab \) \initio nonadiabatic quantum molecular (NA-QMD) method [47–50]. For systems as large as we are investigating here, NA-QMD is numerically more efficient than its \( ab \) \initio approximation [48–50]. In extension to previous studies [3,27–29,31] we include a normal mode analysis [51] of the vibrational kinetic energy. This method decomposes the total kinetic vibrational excitation energy \( E_{\text{vib}} \) into the individual contributions of all 174 eigen-modes of \( C_{60} \) as a function of time \( t \) according to

\[
E_{\text{vib}}(t) = \sum_{i=1}^{60} \frac{m_c}{2} \dot{r}_i^2 + \sum_{i=1}^{174} \frac{m_v}{2} \left( \sum_{i=1}^{60} \dot{r}_i \mathbf{b}_\nu \right)^2
\]

with the atomic carbon mass \( m_c \), the atomic velocities \( \dot{r}_i \) (in the molecular center-of-mass system without rotational components) and the normal mode eigenvectors \( \mathbf{b}_\nu \).

In fig. 1, such an analysis is shown for two central \( C_{60} + C_{60} \) collisions with the same impact energy of \( E_{\text{c.m.}} = 104 \text{ eV} \) but for different initial orientations of the clusters, leading in one case to scattering (fig. 1(a)) and, in the other, to fusion (fig. 1(b)). In both cases, the extraordinary dominance of the \( H_g(1) \) mode is obvious.

During the approach, this mode is very strongly excited to a much higher degree than any other vibrational mode. Its excitation energy of several eV is huge as compared to a single quantum of this mode of \( \hbar \omega_{\text{mode}} \sim 34 \text{ meV} \) [52] and, thus, its amplitude is extremely large, as compared to a typical displacement of the elementary excitation (“giant” \( H_g(1) \) mode). Consequently at the distance of the closest approach \( R_{\text{ret}} \), a highly deformed \textit{oblate-oblate} configuration of the double-cluster system is formed (see above illustrations in fig. 1). This clearly distinguishable state accommodates practically the whole impact energy into deformation (potential) energy, which is quantitatively shown in fig. 2(a), also for other impact energies. Up to this stage of the collision, there is no appreciable difference to the other collision systems (nuclei, droplets), where at this “critical distance” the system loses immediately its memory and the energy is dissipated into internal degrees of freedom (DOF) leading to a hot compound.

The fundamental difference to the other systems consists in the specific properties of the oblate-prolate mode in fullerenes and its special role in collisions. First of all, among all vibrational modes, the \( H_g(1) \) mode in \( C_{60} \) has the largest oscillation period of \( T = 122 \text{ fs} \) [52]. This is comparable with a typical collision time and therefore, once excited, this mode will \textit{not} lose immediately its memory, as clearly seen in figs. 1(a) and (b). Second, the oblate-prolate mode is the only eigenmode which can couple directly to the relative motion via its elongated \textit{prolate-prolate} configuration, provided it survives the dissipative coupling to all the other internal modes. This is exactly what happens in \( C_{60} + C_{60} \) collisions and results in the majority of cases in scattering, like a \textit{fission} process with the \textit{prolate-prolate} configuration at the scission point [42] (note the pronounced excitation of the mode in fig. 1(a) at \( t \sim 165 \text{ fs} \)). Only strong coupling to the internal DOF can prevent this mechanism, allowing for fusion (note the strongly damped prolate oscillation of the mode in fig. 1(b) at \( t \sim 165 \text{ fs} \)). Thus, the competitive coupling of the oblate-prolate mode to the relative motion and to all the other (bath-like) vibrational DOF determines the reaction channel!

The strength of the bath coupling is solely determined by the amount of energy stored in the mode at \( R_{\text{ret}} \). This coupling dominates, if the energy exceeds a certain limit which generally can occur only at appropriate large impact energies. This explains (at least preliminarily and qualitatively) the high fusion barriers. At a fixed impact energy just above the barrier \( E_{\text{c.m.}} \gtrsim V_B \) (as in fig. 1), only very rare and specific initial orientations of the clusters can lead
to high $H_g(1)$ excitation energies, namely, those with the principal axes of the $H_g(1)$ mode aligned to the collision axis, ensuring maximal energy transfer, which is the case in the example shown in fig. 1(b) (note that $E_{cin}$ of the mode during the approach in the case of fusion (fig. 1(b)) is twice as large as compared to scattering (fig. 1(a))). This finally, explains the low fusion cross-sections and completes the present, new picture of the fusion mechanism.

It modifies also the hitherto existing interpretation of scattering, as a “bouncing off” mechanism \cite{3,4,22,28,31}, like in collisions between two soccer balls. Instead, “fusion” via the prolate-prolate configuration strongly suggests, that the final kinetic energy of the fragments is largely independent of the impact energy. This is nicely confirmed in the calculations and shown in fig. 2(b).

The collision scenario presented in figs. 1 and 2 is characteristic for fullerene-fullerene reactions and qualitatively observed in our NA-QMD calculations also for the other combinations and finite, small impact parameters. Despite its microscopic complexity, the mechanism is nevertheless simple and can be understood and described by ordinary macroscopic concepts, as will be shown in the following.

**Collision model.** – The basic idea is to reduce drastically the 360-dimensional scattering problem to a one-dimensional one with only two, but relevant collective DOF, treated explicitly in a time-dependent fashion: the distance between the centers $R(t)$ and the diameter $D(t)$ of the fullerenes: two collinear colliding springs (with spring constants $k_{mode}$ and masses $m$) interact during the approach via a third, massless spring (spring constant $k$ and initial length $R^0_c$) located at the collision center.

\[
\mu R = -\frac{dU}{dR_c}\bigg|_{R_c = R - D},
\]

\[
\mu_{mode} \ddot{D} = -\frac{dV_{mode}}{dD} + \frac{1}{2} \frac{dU}{dR_c}\bigg|_{R_c = R - D}
\]

with the reduced masses $\mu = \frac{M}{2}$ and the mass constant $\mu_{mode} = \frac{M}{2}$. The harmonic potentials are given by $U(r_c) = \frac{1}{2}(r_c - R_0^2)^2$ with $k = 0.12$ a.u. (see fig. 2(a)) and $V_{mode}(D) = \frac{k_{mode}}{2}(D - D^0)^2$ with the spring constant $k_{mode} = \mu_{mode} \omega_{mode}^2 = 0.51$ a.u., obtained from the experimental frequency of the $H_g(1)$ mode in C$_{60}$ ($\omega_{mode} = 273 \text{cm}^{-1}$ \cite{52}). The equations of motion (EOM) (2) can be solved analytically (see appendix). They describe the collision up to the distance of the closest approach, i.e., the classical returning point $R_c^{ret}$. At this point the potential $U(R_c)$ for $R_c > R_c^{ret}$ is replaced by the “dissipative” one $U_d(R_c)$ which, in dependence on $E_{c.m.}$, controls the outcome. It is therefore repulsive (leading in any case to scattering) or attractive (leading usually to fusion, but not necessarily always). Thus, it has the general form

\[
U_d(R_c) = (E^{ret} - E_d(\infty)) f(R_c - R_c^{ret}) + E_d(\infty),
\]

where the form factor $f$ must fulfill the conditions, $f(0) = 1$ (ensuring the continuity of the potential at $R_c^{ret}$) and $f(\infty) = 0$ (making sure that the maximal amount of dissipated energy cannot exceed $E_d(\infty)$, in the case of scattering). In fact, the concrete radial dependence of...
Fig. 5: Comparison between NA-QMD (dashed lines) and model calculations (solid lines) for central C_{60} + C_{60} collisions at three impact energies $E_{c.m.}$: distance between the centers $R$ in a.u. (top), kinetic energy of the relative motion $E_{\text{kin}}$ (middle), and vibrational kinetic energy of the $H_g(1)$ mode $E_{\text{vib}}$ (bottom) in eV as a function of time $t$.

The potential (3) is not relevant, and thus, we choose a simple exponential form of $f(x) = \exp(-\frac{x}{\kappa})$ with

$$
\Delta = \left[ \frac{R_{\text{c.m.}}^2 - R_i^2}{2} \right] \left( 1 - \phi_{\text{d}}(\infty) \right),
$$

which guarantees also continuity of the force at $R_{\text{c.m.}}^2$ in the case of scattering.

With this, all model parameters ($\kappa$, $k_{\text{mode}}$, $\Delta E$) are fixed and the EOM (2) can be easily solved numerically. The results are shown in fig. 5 and compared with NA-QMD calculations (for movies see www.dynol.org).

The model reproduces nearly precisely the microscopic calculations for both scattering ($E_{\text{c.m.}} = 40, 60\text{ eV}$) and fusion ($E_{\text{c.m.}} = 150\text{ eV}$). The ongoing oscillations of some quantities in the exit channel are the natural consequence of the absence of a damping mechanism for the $H_g(1)$ mode in the spring model. The most impressive result, however, concerns the fusion barrier predicted by the model of $V_B = 85\text{ eV}$, which is in excellent agreement with former (extremely expensive) QMD calculations [28] of $V_B = 80\text{ eV}$.

**Analytical solution for the fusion barrier.** – The simplicity of the EOM (2) and the transparency of the ansatz (3) encouraged us to further elaborate the model and to demonstrate its predictive power. As mentioned already, the EOM (2) can be solved analytically, and, from this solution one can derive an approximate expression for the energy stored during the approach $E_{\text{ret}}$ (see fig 4(a)), resulting in a linear dependence on the impact energy of $E_{\text{ret}} = \alpha(\kappa) E_{\text{c.m.}}$ with $\kappa$ the ratio of the spring constants

$$
\kappa = \frac{k_0}{k_{\text{mode}}} = \frac{M}{4} \frac{c_{\text{mode}}^2}{k},
$$

and the universal function $\alpha(\kappa)$ of

$$
\alpha(\kappa) = \frac{1}{4(\kappa^2 + 1)^2} \left[ (\kappa - 1 + \sqrt{\kappa^2 + 1})^2 + (\kappa - 1 + \sqrt{\kappa^2 + 1})^{-2} \right] \times \sin \left( \frac{\pi \kappa + 1 + \sqrt{\kappa^2 + 1}}{2} \right) \frac{1}{\sqrt{2\kappa}}
$$

(see appendix). The difference ($E_{\text{ret}} - E_d(\infty)$) determines the (positive or negative) slope of the potential $U_d$ (3) at the returning point $R_{\text{c.m.}}^2$. Taking an idealized trajectory as shown in fig. 4 (i.e., neglecting the acceleration of the mode near the barrier), the fusion condition simply reads $E_{\text{ret}} = E_d(\infty)$ at $E_{\text{c.m.}} = V_B$. With $E_d(\infty) = E_{\text{c.m.}} - \Delta E$ (see fig 2(b)), the fusion barrier becomes

$$
V_B = \frac{\Delta E}{1 - \alpha(\kappa)}.
$$

Table 1: Fusion barriers $V_B$ in eV for various fullerene-fullerene combinations as predicted by our former QMD calculations [28] (first and third columns) and the present analytical model (second and fourth columns). The experimental values [29] are presented in the last column.

|                  | $T = 0\text{ K}$        | $T = 2000\text{ K}$ |
|------------------|--------------------------|----------------------|
|                  | QMD model | QMD model | exp. |
| C_{60} + C_{60}  | 80  82     | 60  65     | 60 ± 1 |
| C_{60} + C_{70}  | 94  87     | 70  69     | 70 ± 6.5 |
| C_{70} + C_{70}  | 104 93     | 75  73     | 76 ± 4 |

For $C_{60} + C_{60}$ collisions, this approximate expression gives $V_B = 82\text{ eV}$, which is very close to the exact model value ($V_B = 85\text{ eV}$) obtained in the upper dynamical calculations. To obtain a first insight about the qualitative trends for the other combinations ($C_{60} + C_{70}, C_{70} + C_{70}$), we ignore subtleties and use the same $\kappa$ and $\Delta E$ values as obtained already for $C_{60} + C_{60}$ by NA-QMD fine tuning. The internal spring constant for $C_{70}$, however, is carefully chosen and fixed again by experiment. From the (partly) non-degenerate five $H_g(1)$ modes in $C_{70}$ ($E_g', E_{g''}, A_1$) an experimental mean value of $\omega_{\text{mode}}(C_{70}) = 261\text{ cm}^{-1}$ has been reported [53] giving the spring constant $k_{\text{mode}}(C_{70}) = 0.55\text{ a.u.}$ For the (slightly) asymmetric $C_{60} + C_{70}$ collision a reasonable mean value of $k_{\text{mode}}(C_{60})$ and $k_{\text{mode}}(C_{70})$ of $k_{\text{mode}}(C_{60}/C_{70}) = 0.53\text{ a.u.}$ is used.

With these parameters, the predicted fusion barriers from (6) are compared with high-precision QMD values [28], in table 1 (first two columns). The analytical model reproduces the right trend and delivers absolute values within 10% accuracy. Obviously, the $H_g(1)$ frequencies $\omega_{\text{mode}}$ and fullerene masses $M$, eq. (4), determine the fusion barriers in fullerene-fullerene collisions.

This is strongly supported by comparing the predictions with experimental data. In this case, the finite temperature ($T \approx 2000\text{ K}$) of the colliding fullerenes has to be taken into account [29]. This has been done in the former QMD calculations [28] and led to the (well-known) perfect agreement with the experimental data (cf. third and fifth columns in table 1). In the present model, a finite temperature can be naturally taken into account by reducing the mode frequencies $\omega_{\text{mode}}$. Using an arbitrary common scaling factor for $k_{\text{mode}}$ of 0.85, the predicted fusion barriers by eq. (6) are in beautiful agreement with the experiment (fourth and fifth columns in table 1).
Conclusion. — To summarize, ab initio NA-QMD studies have finally cleared up the fusion mechanism in fullerene-fullerene collisions. The excitation of a “giant” $H_g(1)$ mode explains both large fusion barriers and small fusion cross-sections. This microscopic picture is non-ambiguously confirmed by a macroscopic spring model which depicts clearly the physics, reproduces the NA-QMD results and the experimental fusion barriers quantitatively.

We note finally, that a “giant” vibrational excitation of the $A_g(1)$ breathing mode in $C_{60}$ has been found recently in a time-resolved laser experiment \cite{45}. The general investigation of large amplitude motion in fullerenes, including laser-induced fission \cite{46}, could become an interesting new field of research.

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Appendix: analytical solution in the entrance channel. — Inserting the harmonic potentials $U(R_c)$ and $V(D)$, the EOM (2) can be written as

$$
\mu \ddot{R} = -k (R_c - R^0_c)|_{R_c = R} - D ,
$$

$$
\mu \ddot{D} = -k_{\text{mode}} (D - D^0) + \frac{k}{2} (R_c - R^0_c)|_{R_c = R} - D
$$

(A.1)

which can be solved by making an exponential ansatz $e^{i\omega t}$. Doing so, the fundamental eigenfrequencies $\Omega_{1/2}$ of the system read

$$
\Omega_{1/2} = \omega \sqrt{\kappa + 1 \pm \sqrt{\kappa^2 + 1}} \left/ f_{1/2}(\kappa) \right.
$$

(A.2)

with the frequency $\omega = \sqrt{k/\mu}$ and the force constant ratio $\kappa$ as defined in eq. (4).

With the initial conditions

$$
R(0) \equiv R^0 = D^0 + R^0_c , \quad \dot{R}(0) = v_{\text{c.m.}},
$$

\noindent

$$
D(0) = D^0 , \quad \dot{D}(0) = 0
$$

the solution of (A.1) is given by

$$
R(t) = \frac{v_{\text{c.m.}}}{\omega} \sum_{i=1,2} a_i \sin(\Omega_i t) + R^0_c ,
$$

(A.3)

$$
D(t) = \frac{v_{\text{c.m.}}}{\omega} \sum_{i=1,2} b_i \sin(\Omega_i t) + D^0
$$

(A.4)

with the amplitudes $a_{1/2} = \frac{1}{2 f_{1/2}(\kappa)} (1 \mp \frac{\kappa}{\sqrt{\kappa^2 + 1}})$ and $b_{1/2} = \frac{1}{2 f_{1/2}(\kappa)} \frac{1}{\sqrt{\kappa^2 + 1}}$.

With the analytical solution (A.3), (A.4), the potential energy at the returning point $E_{\text{ret}}$ can be calculated. $E_{\text{ret}}$ is given by

$$
E_{\text{ret}} \equiv U(R_{\text{ret}}^0) = \frac{k}{2} (R_c - R^0_c)^2
$$

(A.5)

with $R_{\text{ret}}^0 \equiv R_c(t_{\text{ret}}) = R(t_{\text{ret}}) - D(t_{\text{ret}})$.

The returning time $t_{\text{ret}}$ defined by $R(t_{\text{ret}}) = 0$ is approximated by $t_{\text{ret}} \approx \frac{\pi}{2 \Omega_{1/2}}$. The approximation is justified since the second term of the sum in eq. (A.3) dominates for the parameter range of $\kappa$ used here ($\frac{\omega}{v_0} \ll 1$).

Inserting the analytical solution (A.3), (A.4) in the definition (A.5) and using the relation (A.2) we find

$$
E_{\text{ret}} = \alpha(\kappa) E_{\text{c.m.}}
$$

with the impact energy $E_{\text{c.m.}} = \frac{\alpha}{2} v^2_{\text{c.m.}}$ and the coefficient $\alpha(\kappa)$ as defined before in eq. (5).

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