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Periodic thermodynamics of laser-driven molecular motor*

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Operation of a laser-driven nano-motor inevitably generates a non-trivial amount of heat, which can possibly lead to instability or even hinder the motor's continual running. This work quantitatively examines the overheating problem for a recently proposed laser-operated molecular locomotive. We present a single-molecule cooling theory, in which molecular details of the locomotive system are explicitly treated. This theory is able to quantitatively predict cooling efficiency for various candidates of molecular systems for the locomotive, and also suggests concrete strategies for improving the locomotive's cooling. It is found that water environment is able to cool the hot locomotive down to room temperature within 100 picoseconds after photon absorption. This cooling time is a few orders of magnitude shorter than the typical time for laser operation, effectively preventing any overheating for the nano-locomotive. However, when the cooling is less effective in non-aqueous environment, residual heat may build up. A continuous running of the motor will then lead to a periodic thermodynamics, which is a common character of many laser-operated nano-devices.

Keywords: molecular motor, vibrational relaxation, photoisomerization
PACC: 8116, 8220R, 8250

1. Introduction

As physicist Richard P. Feynman pointed out in a famous talk in 1959, there is indeed plenty of room for making functional devices even down to the bottom of the molecular scale.[1] More than forty years of vigorous development in nanoscience and technology since then have proved many of his visionary remarks. Particularly noteworthy is the recent fascinating progress in molecule-level motors.[2−12] For example, controlled intramolecular rotation and translocation, mostly powered by light or chemical stimuli, have been realized in lab by a number of groups over the world.[2−7] Remarkable achievements of this kind are leading us to a new field of molecular machinery.

While a chemically pumped motor generally requires a liquid environment due to diffusive supply of molecular fuels, light driving has the merit of delivering energy to a motor from a distance, thus allowing for motor operation in a variety of microenvironments. Recently we have proposed a fully laser-operated molecular locomotive,[13−15] which, made of a photoisomerizable polymer chain, may achieve directional motion on a linear track under the driving of a multistep optomechanical work-cycle.[13,14] Absorption of a single photon of the visible spectrum instantaneously injects into the motor a few electron volts of energy, only a portion of which is converted into mechanical work with the rest being redistributed into many vibrational degrees of freedom of the motor molecule. This internal heat is subsequently dissipated into the track and the surrounding microenvironment. However, before the cooling process is completed, the heat trapped in the motor-track system may cause some problems. Trapping of a nontrivial portion of the heat may possibly reduce light absorption efficiency, lead to instability at the motor–track interface or affect motor operation through other currently unknown effects.

The problem of overheating, though rarely studied to date, is a rather general concern for many optically responding molecular devices. In fact, Feynman[1] argued in his famous speech that a really tiny machine 'would not run hot because the heat escapes away from such a small device very, very rapidly'. A series of state-of-art studies[16−18] provide growing evidence that nanoscale heat transfer is es-

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sentially a molecular phenomenon, much subtler than suggested by a simple extrapolation of the classical heat conduction theory for bulk materials. As far as a molecular device is concerned, the key question is whether or not the heat escapes sufficiently rapidly. The answer is not merely related to the heat transfer mechanism, but also subject to the extent of robustness of the device's functioning against internal thermal fluctuations.

Heating and cooling of a laser-excited molecular motor essentially forms a topic of single-molecule thermodynamics in the unique content of nano-machinery. Intramolecular vibrational relaxation and solute-to-solvent heat transfer have long been studied experimentally and theoretically, albeit mostly for an ensemble of a large number of molecules.[19−27] Recent studies increasingly focus on nanoscale heat transfer phenomena.[16−18,28] The issue of heating and cooling for the molecular locomotive has been addressed rudimentarily in our previous study,[13] largely based on the classical theory of heat diffusion. Lacking in molecular details the former estimate is scientifically inadequate, and more importantly, it is unable to tell how to reduce the possibility of overheating by adjusting molecular modules or laser operations of the motor–track system. In the present work we shall reformulate the heating–cooling issue in terms of detailed molecular mechanisms for heat generation and transfer at the nanoscale. This molecular theory allows of determination of its major parameters from experimental data of nanoscale heat transfer, thus leading to a sound evaluation of the cooling rate for the molecular locomotive. Some routes towards a higher cooling efficiency for the locomotive in particular and for functional molecular devices in general shall be discussed within the framework of the molecular theory. Combining the cooling theory with a single-molecule laser heating theory, we shall present a complete framework for the thermodynamics of the nano-locomotive under periodic laser driving.

This paper is organized as follows. In Section 2 we shall present details of the molecular theory for the locomotive's heating and cooling. In Section 3 the key parameters of the theory will be determined by a comparison with experimental data. The theory will then be applied to the molecular locomotive. Possible means of improving motor cooling will also be discussed. In Section 4 a full theory for the heating–cooling dynamics of the laser-driven nano-motor will be constructed. Finally we conclude the present work in Section 5.

2. A Single-molecule cooling theory

Molecular photoisomerization has been the basis of optically responding molecular switch for many functional devices. From the perspective of nanomachinery, a photoisomerizable molecule naturally serves as a molecular engine for optomechanical energy conversion, as was nicely demonstrated in a recent experiment by Gaub *et al.*[29] The molecular locomotive is simply a linear polymer with identical isomerizable units. The locomotive chain extends or contracts its contour length as the units undergo cis–trans transition. The length change of the locomotive and its interaction with the track are coupled by a properly designed sequence of laser operations, making possible a directed nano-locomotion. After absorbing a photon a locomotive unit is electronically excited. An ultrafast process called internal conversion (IC) deposits the electronic energy into the nuclear degrees of freedom, driving the unit into a bifurcate pathway that leads to both isomer states usually with almost equal possibility for either. Intramolecular vibrational redistribution (IVR) then occurs that is believed to be sufficiently fast to create an almost thermalized state of the locomotive unit itself as it constantly interacts with the environment. For polyatomic molecules, vibrational densities of states are high and a quasicontinuum of vibrational levels occurs.[19] This gives rise to many possible pathways for fast redistribution of excitation energy among vibrational levels. Previous experimental studies[21,30,31] found that the IVR process is likely completed within a time of less than 1 ps. Experimental evidence of such quasi-equilibrium states in a molecule having a non trivial number of vibrational degrees of freedom underpins the use of effective temperature in analysis of molecular vibrational relaxation.[19,20] Eventually the unit cools down by its interactions with the track and the environment.

The effective temperature of the locomotive unit, T, is related to the total energy contained in all of the molecular vibrations, E, via the Bose–Einstein distribution:

$$E(T) = \sum_{i=1}^{N_T} \frac{\hbar\omega_i}{\exp(\hbar\omega_i/kT) - 1}. \qquad (1)$$

The above summation is over all accessible eigenmodes of the molecular vibrations with ω_i being the fre-

quency of the ith mode. The excessive heat may be defined as

$$Q(T) = E\,(T) - E(T_0). \tag{2}$$

Here T_0 is the temperature of the bulk environment, and the total vibrational energy at T_0 is determined by the same Bose–Einstein distribution as Eq.(1). The effective temperature will decrease as the locomotive unit dissipates excessive energy into the surroundings, i.e. the track and the outer environment. The dominant cooling mechanism is heat conduction through the motor–environment and motor–track interface, although other processes such as radiational heat transfer or artificially arranged heat convection may contribute too. Heat loss by conduction through a layer of homogeneous bulk material of width d and heat conductivity κ can be described by the classical Fourier theory

$$\dot{Q} = \kappa S\,(T - T_0)\,/d, \tag{3}$$

where Q is the amount of heat in the heat source and T its temperature. S is the interface area separating the source and T_0 temperature of the heat receptor. The validity of the classical theory is in doubt when the interface layer becomes so thin as to only span a few molecules. In the present case the motor–track interface is nothing but a set of direct contacts between the two molecular objects; and the motor–liquid interface, which is relevant in the case of motor operation in water, is essentially a nanometre-thick layer of water molecules directly hydrogen-bonding or randomly colliding with the motor molecule. The use of the interface width completely loses validity for the motor–track contacts that directly mediate exchange of vibrational energy between both molecular objects. The previous studies of heat transfer from an organic solute molecule to bulk water have encountered difficulties in defining the width of the solute-liquid interlayer due to the extremely dynamic nature of water hydrogen-bonding networks.[21,22] With the meaning of the interlayer blurred, the concept of heat conductivity for the nanoscale objects must be re-considered accordingly.

In the present work we adapt the heat conduction theory into a new form that incorporates molecular mechanisms for the energy dissipation of a single hot molecule. The temperature difference between the hot motor and the cooler neighbours should still be the driving force for the cooling. The interface area S, if counted using atomistic details of the motor molecule, remains meaningful and useful to certain extent, considering the size of the motor and track (e.g. the whole polymer chain making up the motor can be as long as 100 nm with side-groups of several nanometres size). We note that calculation of molecular surface area is a regular practice, e.g. to account for hydrophobic effects in protein folding studies. Both the interface width and heat conductivity are discarded. We instead introduce a parameter to inclusively quantify the motor–surrounding couplings for heat exchange. Thus, we have the following equation to describe the time evolution of the excessive heat of the motor molecule

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -CS(T - T_0), \tag{4}$$

where T is the effective temperature of the motor, T_0 is the temperature of the track or the bulk water, which is taken as the room temperature throughout the paper. C is the coupling strength that measures the energy flow driven by unit temperature difference through unit area of the interlayer of arbitrary thickness. Comparing the new and the classical equations, one immediately recognizes the analogue $C = \kappa/d$. While such an interpretation is physically meaningless in the present situation as already made clear, the analogue argues for regarding the C parameter as a constant independent of temperature. Because of complexity of molecular mechanisms for energy transfer through the interlayer, it is difficult to calculate the C parameter. We shall determine it by fitting to experimental data. The strategy of experimental determination of the C value is not just a choice of convenience, it automatically takes into account the extent of the interlayer extension into the surrounding as such information is contained in the experimental data of temperature decay of a hot molecule. In the same dissolving liquid, the C value for polymers made of an identical basic unit (monomer) should be independent of the polymer length (the number of the monomers), because the size effect has been accounted for by the explicit introduction of S parameter in the above equation. In addition, the effective thickness of the polymer-solvent interlayer should not change with varying length of the polymer.

Using $\dfrac{\mathrm{d}Q}{\mathrm{d}t} = \dfrac{\mathrm{d}T}{\mathrm{d}t}c_\mathrm{m}$, where $c_\mathrm{m} = \mathrm{d}Q/\mathrm{d}T$ is the effective heat capacity of the motor, Eq.(3) can be rewritten as a closed equation in terms of temperature. The solution of the equation yields the cooling dynamics.

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{CS}{c_\mathrm{m}\,(T)}(T - T_0). \tag{5}$$

While the C parameter should be properly extracted from experimental data for the present purpose, the molecular heat capacity $c_{\rm m}$ and the S parameter can be readily calculated from atomistic details of the motor molecule.

Some previous studies[21,22] on cooling of solute molecules in liquid made a more elaborate treatment of the heat transfer process. Because of the high density of liquids, a hot molecule presumably interacts only directly with its immediate neighbours. This so-called first solvent shell[21,22] is a rather stable local network of solvent molecules which form hydrogen bonds with each other. Therefore, the hot solute first deposits its excessive energy into the first solvent shell, leading to a transient rise of its temperature. The heated solvent shell subsequently dissipates energy into the bulk liquid of temperature T_0. Due to the extremely complicated liquid dynamics in the vicinity of a solute molecule, it is difficult, if not impossible, to quantify the extension and thermodynamics of the solvent shell that mediates the energy transfer between the solute and the bulk solvent. Consequently, the former works generally introduced fitting parameters to treat the complicated solvent effects. To avoid uncertainties from this type of treatments, the present theory explicitly deals with only the effective temperature of the hot molecule (T) and the equilibrium temperature of the bulk liquid (T_0), and uses the single parameter C to account in an average sense for the solvent thermodynamics in the solute vicinity. The C value derived from experimental data thus contains a certain amount of information on the solvent effects.

3. Cooling of molecular locomotive

In the following part of the paper, we shall apply the molecular cooling theory to the motor operating in a liquid environment. Thus we shall focus on heat transfer through the motor–liquid interface, and carry out a detailed analysis for a candidate polymer molecule of the motor. The cooling rate will be estimated on the basis of existing experimental data, and the cooling rate thus derived places a lower limit to the actual cooling efficiency of the motor when it is operated in water.

Azobenzene-based chromophores have been popularly used for the purpose of photon-switch in a broad range of scientific and technological fields, mainly because the absorption spectra for their cis and trans configurations are well separated, thus allowing selective excitation and controlled configuration switch. Synthetic poly-azobenzenes are also good candidates for making the molecular locomotive. Of particular interest is a synthetic poly-azobenzene, the optomechanical capacity of which has been examined in a single-molecule experiment[29] and appears to be sufficient for the purpose of the molecular locomotive. The large amount of existing research results on azobenzene and variants, experimental as well as theoretical, provides a solid ground for calibration of our theory and for reliable estimate of the cooling efficiency for a poly-azobenzene-based molecular locomotive.

3.1. Determination of C values from experimental data

Several experimental groups have applied ultrafast laser spectroscopy to probe the cooling dynamics of organic molecules after photo-excitation in a variety of solvents.[21−23,25,27] These experimental studies generally found an exponential decay of effective temperature of the molecules after photo-absorption, i.e. $T - T_0 \propto {\rm e}^{-t/\tau}$. A recent experiment reported the time constant of $\tau \approx 20$ ps for azobenzene in DMSO-d6 solution.[23] We shall use this experimental result to determine the parameter C. All the 66 vibrational eigenmodes of azobenzene are readily available from Ref.[32], yielding the molecular heat capacity by using Eq.(1). The surface area of the azobenzene molecule has been estimated by counting for each constituent atom its sphere of van der Vaals interaction and by properly discarding overlaps using the data of bond lengths. This method has been frequently adopted in atomistic studies of biomolecules. Using the result $S \approx 0.80{\rm nm}^2$, the equation for T evolution has been solved for a number of trivial values of C parameter and the results are shown in Fig.1.

After absorbing a photon of typical visible wavelength 408nm a cis azobenzene molecule is excited to the S_1 excited state and then decays to the ground state via IC process, leading to a hot molecule of $T \approx$1160K (corresponding to excess energy of about $117.6kT_0$ in the vibrational system of the molecule). As can be seen in Fig.1 the subsequent decrease of T can be satisfactorily described by mono-exponential decay for all three trial values of C spanning three orders of magnitude. A best fit of the resultant time constant τ to the experimental value of 20 ps yields a

C value of 4.61×10^{-7} W/(K·m^2).

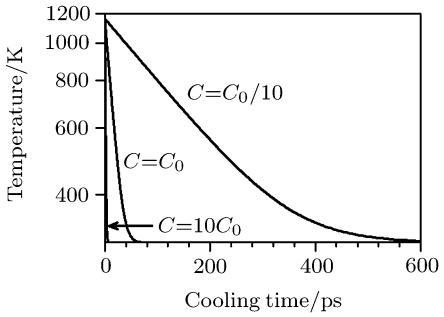


Fig.1. Cooling dynamics of cis azobenzene in DMSO-d6 solution after absorbing a photon of wavelength 408nm. Shown are the predictions of Eq.(4) using three values of C parameter: The middle line is the result for $C = C_0 = 4.61\times10^{-7}$W/(K·m^2), while the other two lines are the results for $C = 10C_0$ and $C_0/10$, respectively. Fitting the lines down to temperature $T = 400$K with a mono-exponential decay function $T \propto e^{-t/\tau}$ yields the time constant τ=2, 20, and 200 ps with increasing value of C.

The single-exponential decay observed in our calculation is consistent with existing experiments. When the temperature is so high that most of the vibrational frequencies of the molecule $\{\omega_i\}$ satisfy the relation $\hbar\omega_i < kT$, the total amount of vibrational energy contained by the molecule depends linearly on temperature, i.e. $E \approx N_T kT$, where N_T is the number of the vibrational modes excited. This amounts to the equipartition of energy, and the molecular heat capacity thus will be independent of temperature, resulting in a mono-exponential decay of T with time. The azobenzene cooling appears to be close to this high T limit. A close look at the heat capacity indeed reveals that it changes by about 61.6% for azobenzene over the range of temperature of interest (see Fig.2).

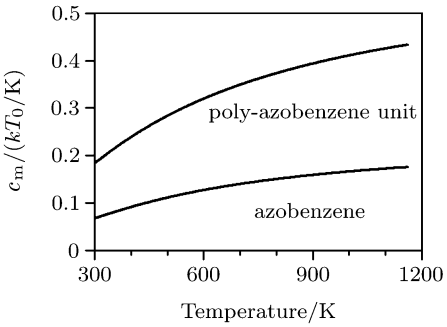


Fig.2. Comparison of heat capacity between azobenzene and the basic unit of a poly-azobenzene that is a potential candidate for the molecular locomotive. Shown are the data over the range of effective temperature relevant to their photoisomerization and subsequent cooling processes in solution.

As a good approximation, Eq.(3) can be rewritten by replacing the slow varying $c_{\rm m}$ with its average $\langle c_{\rm m}\rangle$, and this leads to an approximate relation for the decay constant

$$\tau \approx \frac{\langle c_{\rm m}\rangle}{SC}. \tag{6}$$

On the other hand, if most of the vibrational quanta are energetically larger than the thermal energy, the number of vibrational modes to be excited will strongly depend on the temperature. The molecular heat capacity will approximately follow a Debye T^3 rule, and deviation from the mono-exponential behaviour of the cooling may occur. This high frequency (or low T) limit, however, appears to be inconsistent with the azobenzene cooling studied here.

3.2. Cooling efficiency of a poly-azobenzene candidate for the molecular locomotive

We focus on the synthetic poly-azobenzene studied by Gaub *et al*,[29] as a candidate molecular modulus for the molecular locomotive. We note that azobenzene molecules and their derivatives have been widely used in light-responsive devices.[33] The basic unit of this polymer is made of azobenzene backbone plus a sidechain of catenanes. Considering the high level of similarity between the polymer unit and azobenzene, it should be a good approximation to apply to the candidate polymer the C value derived from the above analysis of the azobenzene data. The additional vibrational modes from the sidechains and the surface area ($S \approx$3.40nm^2) have been obtained by an atomistic analysis of the polymer unit. In Fig.3 we present the time evolution of the effective temperature for a photoexcited polymer unit in DMSO-d6.

Absorption of a photon of wavelength 420nm makes a cis unit into a hot molecule with an initial temperature of about 707.6K, which is considerably lower than that of the azobenzene case due to a larger heat capacity introduced by the side groups. Nevertheless, the time evolution of the temperature can also be fitted well by a mono-exponential function with a time constant of about 8.9ps. It takes about 40ps for the molecule to essentially reach the liquid temperature. The cooling rate is maximum (about $15.4kT_0$/ps) at t=0, and decreases as the temperature difference between the molecule and the liquid is

reduced.

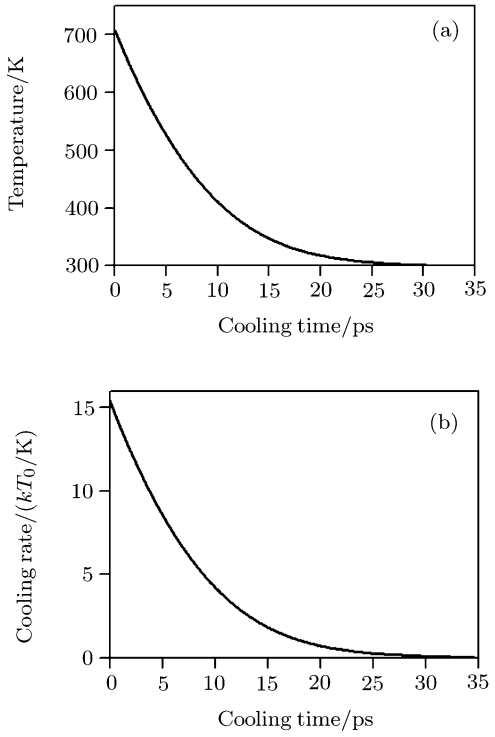


Fig.3. Cooling dynamics of an azobenzene derivative in DMSO-d6 solution after the molecule in its cis configuration is excited by absorption of a photon of wavelength 420 nm. This molecule serves as the basic unit for a poly-azobenzene that can potentially be used to make the molecular locomotive. Shown are the results predicted by Eq.(4) using the C parameter extracted from experimental data ($C = 4.61\times10^{-7}$ W/(K·m^2)). (a) Time evolution of temperature, which can be satisfactorily described by mono-exponential decay with a time constant $\tau = 8.9$ ps. (b) Time evolution of the cooling rate.

The occurrence of the exponential behaviour is understandable. The basic unit of the candidate polymer for the locomotive has about 100 more vibrational modes than azobezene molecule, and the mode density of the former changes with energy more smoothly than that of the latter. Consequently, the poly-azobenzene unit has a heat capacity that is larger and generally less temperature-dependent as has been confirmed by the data from the atomistic calculation for both molecules (see Fig.2).

3.3. Estimate of the minimum cooling rate of a molecular locomotive operating in water

If being operated in liquid, a locomotive can dissipate its internal heat to the surrounding liquid directly, and to the track that in turn passes heat into the liquid environment more efficiently because of its much larger size than the motor polymer. The heat transfer from the motor to the track can be a nontrivial effect because the track, due to its high heat capacity, remains constantly at a lower temperature and plays a role of heat reservoir for the motor. While the contribution of the motor–track interface to the cooling is a question of interest for future study, a sound estimate of the heat loss through the motor–liquid interface alone will set a lower limit for the motor's cooling efficiency. The cooling data obtained in the preceding sections are sufficient for us to derive a minimum cooling rate for in-liquid operation of a molecular locomotive made of a chemically similar poly-azobenzene.

Considering the cooling mechanism from the motor–liquid interface alone, it is clear that in organic solvents, such as DMSO, any basic unit of the motor polymer, once excited by laser, is able to cool down exponentially with a time constant of $\tau \approx 8.9$ps. We note that this estimate is based on the surface area for a free molecule in the liquid. As a locomotive part, the unit, at least its backbone, is constantly bound with the track, and cannot expose completely to the liquid. Therefore, the motor–liquid interface responsible for direct heat loss is smaller than estimated for a free flying locomotive polymer. Taking a reduction factor of 0.5 for the interface area (S), and noting that the decay constant τ is inversely proportional to S for a slow changing $c_{\rm m}$ (see Eq.(3)), which is relevant to the present case, we obtain $\tau \approx$17.8ps for a single unit of the locomotive. A locomotive chain may contain several tens of photoisomerizable units, and the maximum hot state is that all of the units are excited simultaneously. Even in such an extreme case, the whole locomotive is able to essentially cool down within 18 ps by directly depositing energy into the liquid environment. In fact, because of stochastic nature of photon absorption it is extremely rare that all of the units of the locomotive are in the excited state within any period as short as 17.8 ps. Therefore, we may safely take 100ps as an upper limit for the cooling time of the locomotive in liquid. The additional cooling channel via the sizable track will most likely ensure an even shorter cooling time. Turning to motor operation in water, a further rise of cooling efficiency is expected because water has a heat conduction capacity generally superior to organic solvents like DMSO.

A cooling time of 100ps is several orders of magnitude shorter than the average period of the work

cycle of the locomotive ($\sim$ several ms), therefore overheating is unlikely a problem for the locomotive operation in water. Nevertheless, some subtleties concerning nano-machinery may arise. A locomotive unit generally needs absorb more than one photon to ensure a desired configuration change, for example, from cis to trans, because the internal conversion of the electronically excited unit may lead to either cis or trans state usually with almost equal chance. Thus, each unit of the locomotive has to cyclically absorb several photons to successfully realize a mechanical step of the whole locomotive, i.e. its extension or contraction that plays a key role in the work cycle. The extension/contraction time may be as long as several hundreds ns, during which any unit that fails to reach the target isomer state will cool down sufficiently fast to such extent as to resume its ability for a next absorption. Therefore, the estimated cooling efficiency is able to meet the requirements for quickly resetting the locomotive system for a continuous operation. The possible trapping of heat at the locomotive-track interface is another issue of concern because the resultant instability might complicate or even hinder some key operational steps that rely on regulated motor–track interactions. Although it is unclear how the motor–track and water–liquid interfaces share the heat flow, an efficient draining through the latter undoubtedly reduces the possibility of heat trapping at the former. More generally, a sub-nanosecond cooling time might also help minimize heat-related photophysical damage to the locomotive-track system.

3.4. Effects of sidechains on the cooling efficiency

Azobenzene and the basic unit of a candidate polymer, both having been analysed above, shares the same azobenzene backbone but with the latter having additional side groups of catenanes. Therefore, a comparison of their cooling dynamics will shed light on the influence of side chains on the cooling efficiency. A close look of the relevant molecular properties of both molecules as summarized in Table 1, reveals some interesting points.

Table 1. Molecular properties and cooling abilities of azobenzene and an azobenzene derivative with sizable groups. (The latter molecule serves as the basic unit for a poly-azobenzene that is a potential candidate for the molecular locomotive) The data of heat capacity are an average over the T range of 300–1200K. This temperature range is relevant to photoisomerization of the molecules and their subsequent cooling in solution.

	mainbody surface area /nm^2	sidechain surface area /nm^2	total surface area /nm^2	heat capacity /(kT_0/K)	time constant for cooling (τ) /ps
azobenzene	0.80	0	0.80	0.136	20
derivative	0.80	2.60	3.40	0.279	8.9

The side chain enlarges the surface area by more than 4 times, but only doubles the average heat capacity, resulting in a two-fold increase of the time constant for temperature decay. This is in line with Eq.(3), implying a distinctly lower heat capacity for the side groups than for the azobenzene backbone. As also is clear from Eq.(3), increasing the surface area by adding low-heat-capacity sidechains will improve the cooling efficiency. Since engineering chemical groups into a polymer is an established technique, introduction of side chains of large surface area and low heat capacity may serve as a strategy of optimizing the cooling properties of the molecular locomotive of the present interest. The strategy may apply generally to any molecular devices that operate in liquid yet have an overheating problem.

4. Periodic thermodynamics of laser-operated nano-locomotive

Now that the cooling model has been established, we shall combine it with a heat generation theory to develop a complete description of the full thermodynamics of the nano-locomotive under laser operation. As we have mentioned before, the origin of heat is photoabsorption and subsequent internal conversion (IC) of the isomeric units of the locomotive chain. If the absorption rate is very low compared to the ultrafast IC process, which is often the case, the heat generation dynamics will be largely governed by the absorption alone.[13] Then the heat production by the locomotive chain during a laser-driven stretch or contraction oper-

ation may be approximated by the following equation

$$Q_{\rm S} = 2NE_{\rm ph}\left(1 - {\rm e}^{-\gamma_{\rm ab}t/2}\right). \qquad (7)$$

Here $\gamma_{\rm ab}$ is the photoabsorption rate of a locomotive unit, $E_{\rm ph}$ is the photon energy, and N is the total number of the isomeric units of the locomotive chain. Further assuming an exponential cooling of each locomotive unit, we obtain an equation to describe the full process of heating and cooling of the locomotive during a laser operation

$$\frac{{\rm d}Q}{{\rm d}t} = \frac{{\rm d}Q_{\rm S}}{{\rm d}t} - \frac{1}{\tau}Q. \qquad (8)$$

Here Q is the total excessive heat of all of the locomotive units, i.e. $Q = \sum_{i=1}^{N} Q_i$. In the case of motor operation in solution, the time constant for cooling is given by $\tau = \dfrac{\langle c_{\rm m}\rangle}{CS}$ as discussed in the preceding section.

Typical solutions to the nano-motor heating–cooling dynamics are shown in Fig.4 for a laser-driven extension operation of a locomotive chain made of 50 repeated units.

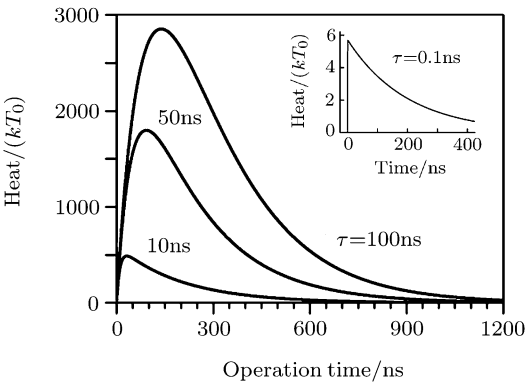


Fig.4. Heat generation and dissipation of the molecular locomotive made of a poly-azobenzene of 50 repeated units during an extension operation of the locomotive chain under irradiation of a laser beam of wavelength 420nm. The results shown were obtained assuming a photo-excitation rate of $0.01{\rm ns}^{-1}$ for individual units of the locomotive. This absorption rate largely determines the heating dynamics. An exponential behaviour for cooling of the units is assumed. The results are presented for three different values for the time constant of the cooling dynamics.

We assume a fixed value for laser excitation rate of $0.01{\rm ns}^{-1}$, which is sufficient to facilitate a nano-locomotion speed of a few micrometres in a second comparable to those of biological motor kinesin. It is clear from the figure that the amount of instantaneous heat residing in the locomotive chain is determined by the competition between photoisomerization dynamics of the multiple units and their cooling dynamics. When the time constant for cooling is short, e.g. τ=100ps for the case of the candidate poly-azobenzene in solution as determined in the preceding section, there is hardly any heat accumulation through the whole laser operation, re-confirming that overheating cannot be any problem for the motor's operation. This is the case of the nano-motor thermodynamics in which cooling overwhelms heat production, since the former is nearly 3 orders of magnitude faster than the latter. However, in less ideal situations such as motor operation in gas–surface interface, the cooling rate can possibly decrease drastically. The nano-motor thermodynamics theory developed here can be used to determine the minimum acceptable cooling efficiency from nano-machinery perspective. As far as the molecular locomotive is concerned, a cooling constant up to τ=10ns seems to be acceptable, keeping the residual heat below $10kT_0$ per unit. When the cooling rate becomes comparable to the laser excitation rate, a nontrivial amount of heat may be trapped within the locomotive. The amount of residual heat quickly reaches a peak during the early stage of the laser irradiation, and decreases subsequently after the saturation of photoisomerization of the locomotive units. Such a temporal pattern of heating and cooling will possibly occur when the nano-motor and its operation are optimized for a maximum nano-locomotion speed. The heating–cooling pattern will appear periodically during continuous running of the nano-locomotive along its track. This unique periodic thermodynamics is a common character of the big category of laser-operated nano-devices.

5. Conclusions

As laser-operated functional nano-devices and nano-motors quickly become a new frontier of nanosciences, there comes the necessity of studying the unique thermodynamics of a nano-system under periodic laser driving. With this regard nanomechanical devices such as molecular motors are particularly interesting, in which optomechanical energy conversion and subsequent vibrational relaxation generate a nontrivial amount of heat during each laser-driven work cycle. If the motor cannot get rid of the heat sufficiently fast, thermal instability may develop within the motor and at the motor–track interface to reduce motor's performance or even hinder its working.

We have investigated the problem of overheating for a model system of a recently proposed, fully laser-operated molecular locomotive. A theory of single-molecule cooling in solution has been constructed that takes into account sufficient molecular details and allows for a determination of remaining parameters from data of femtosecond laser spectroscopy experiments. Integration of a theory for single-molecule heat generation after photoabsorption into the cooling theory has led to a complete framework for quantitative description of the thermodynamics of the nano-locomotive. It has been found that a water environment is able to cool the laser-excited locomotive down to room temperature within a time (∼100ps) a few orders of magnitude shorter than the typical duration of the nano-locomotion work cycle, thus effectively avoiding any overheating problem. However, when the cooling is less effective in a non-aqueous environment, residual heat may build up over the period of laser operation. The nano-locomotive thermodynamics then exhibits a periodic pattern as the motor runs continuously along its track.

Such a periodic thermodynamics is a common feature of laser-pumped nano-devices. This nanothermodynamics phenomenon merits a topic of study, because it bears direct relevance to the emerging field of nano-machinery. The single-molecule cooling theory may be useful in thermodynamic study of laser-driven nano-machine systems in general, due to its attractive feature of separating the influence of computable atomic details from those of only experimentally traceable complex interactions with the environment. Analysis with the molecular cooling theory has suggested using side chains of large surface area and modest heat capacity as a rather general strategy to promote cooling efficiency for laser-operated molecular nano-devices.

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