Evaporative Cooling of Helium Nanodroplets with Angular Momentum Conservation

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We model the evaporative cooling with a statistical rate model that includes, for the first time, angular momentum conservation as a constraint on the accessible droplet states. It is found that while the final temperature of the droplets is almost identical to that previously predicted and later observed, the distribution of total droplet energy and angular momentum states is vastly more excited than a canonical distribution at the same temperature. It is found that the final angular momentum of the droplets is highly correlated with the initial direction, and that a significant fraction of the alignment of the total angular momentum should be transferred to the rotational angular momentum of an embedded molecule.

Evaporative Cooling Model— Consider a helium nanodroplet, D, with initial values of the conserved quantities \( n \) (number of helium atoms), \( E' \) (total internal energy in units of Kelvin), and \( J' \) (the total angular momentum in units of \( \hbar \)). If \( E' \) is sufficiently great, the droplet will cool by helium atom evaporation by the reaction: \( D(n, E', J') \rightarrow D(n-1, E'', J'') + He \) (\( E_{\text{trans}} \)) where \( E_{\text{trans}} \) is the center of mass translational energy in the dissociation and \( L \) is the orbital angular momentum quantum number of the fragments. Conservation of total angular momentum requires that \( J', J'', L \) obey the triangle rule. Based upon the bulk density of helium, the droplet has radius \( R(n) = \sqrt[3]{n/\rho_0} \), with \( \rho_0 = 2.22 \) Å. Conservation of energy, including the change in the surface energy defined by surface tension, \( \sigma = 0.272 \text{KÅ}^{-2} \), requires that

\[
E' = E'' + E_b \cdot \frac{8\pi}{3} r_o^2 \sigma n^{-1/3} + E_{\text{trans}} \tag{1}
\]

where \( E_b = 7.2 \) K is the binding energy of helium to the bulk.\(^\text{1}\) Because of the centrifugal barrier, classically \( E_{\text{trans}} \geq h^2 L(L+1)/(2m_{He}R(n)^2) \), leading to a \( E''_{\text{max}} \) value for each \( L \).

Using statistical reaction rate theory, the rate of helium atom evaporation is given by

\[
k(n, E', J') = \frac{1}{\hbar} \frac{N_o(n, E', J')}{\rho(n, E', J')} \tag{2}
\]

\( \rho(n, E', J') \) is the density of states of the droplet at fixed angular momentum, and \( N_o(n, E', J') \) equals the number of states of the product droplet and departing He atom consistent with total \( E' \) and \( J' \) with the departing He atom having kinetic energy above the centrifugal barrier. If we denote the total number of \( n \) atom droplet states with energy \( \leq E \) and total angular momentum quantum number \( J \) by \( N(n, E, J) \), we can use the triangle rule to write \( N_o(n, E', J') \) as a sum of \( N(n-1, E''_{\text{max}}(L), J'') \) over all allowed values of \( L, J'' \).

For droplets of the size and energy range of interest to experiments, the density of states is dominated by quantized capillary waves on the surface of the droplets (ripples modes). Simple, but highly accurate, analytical approximations for \( N(n, E', J') \) and \( \rho(n, E', J') = (\partial N/\partial E)_p \) have recently been published, allowing calculation of \( k(n, E, J) \).

Using an ensemble that conserves \( n, E, J \), the droplet temperature can be calculated using

\[
( k_B T(n, E, J) )^{-1} = (\partial \ln \rho(n, E, J)/\partial E)_J.
\]
For droplets with only ripplon excitations, the densities of states depends upon \( n \) only through the size of a reduced energy scale which is equal to 3.77 \( n^{-1/2} \) K. Starting with a given initial size, energy, and total angular momentum for the droplet at time zero, we calculate the evaporation rate and advance time by the inverse of this number. We then randomly pick a single open decay channel \((E'', J'', L)\) with probability proportional to \( N(n-1, E'', J'') \). We can treat the product droplet as a new initial condition, and calculate another evaporation event. As the droplet cools, the rate of evaporation falls exponentially. When the cumulative time for the next evaporation event is greater than the assumed free flight time in an experiment, we terminate the evaporation process. We also did evaporative cooling calculations for droplets with an embedded linear rotor with effective rotational constant \( B \), which will typically be several times smaller than the corresponding value in the gas phase due to helium motion induced by the rotation.\(^5,6\)

For these calculations, the integrated density of states, \( N_c(n, E, J) \), for the combined droplet + rotor system is calculated by convolution of the integrated droplet density of states with the spectrum of the rigid rotor: \( N_c(n, E, J) = \sum_j \sum_{j'-j} N(n, E - B j (j + 1), J') \)

These were calculated for various values of \( B \) and the resulting densities fit to the same functional form previously used for \( N(n, E, L) \), but with the fitting constants now expressed as polynomial function of \( B \) and its inverse. Differentiation gives the combined density of states, \( \rho_c(n, E, J) \).

Alignment is defined as \( \langle P_2(\cos \theta) \rangle \), where \( \theta \) is the angle of the angular momentum vector with the quantization axis (chosen to be the velocity vector of the helium droplet beam). In order to track the changes in alignment during cooling, we must propagate the angular momentum projection quantum numbers of droplet \((M)\) and embedded rotor \((m)\). The final alignments are found to be proportional to the initial alignment of the total angular momentum created by the pickup process.

If we have an initial distribution \( P(n, M') \) over angular momentum projection quantum numbers \( M' \), we can use the Wigner-Eckart theorem to calculate the product distribution of the projection quantum number populations\(^1\): \( P(n - 1, M'') = \sum_{M''} \sum_{M'''} (J'', M'', L, M'' - M'') (J', M', M'')^2 P(n, M') \). The assumption of equal probability of all states consistent with total \( E \) and \( J \) leads to a similar expression for the probability of populating a rotor quantum state \( j, m \). This allows the calculation of the alignment of the rotor angular momentum, which is an experimental observable.

**Results**—We did evaporative cooling calculations with initial values of \( n = 10^4 \), \( E = 1700 \) K, and \( J = 10, 1000, 2000, \ldots 5000 \), computing 2500 Monte Carlo ‘trajectories’ in each case. These values where selected as likely initial conditions following the pickup of a tetracene molecule.\(^2,13\) These conditions correspond to an initial droplet temperature of 2.61 K independent of \( J \). We also assumed that the initial condition for the total angular momentum is \( P(M) = \delta_{0,M} \) (initial alignment = \(-1/2\)). A cooling time of 100 \( \mu s \) was used.

We can first make some qualitative predictions. We expect that on average the evaporated helium atoms will reduce droplet energy by \( E_b + (3/2)k_B T \) where \( T \) is the average temperature during evaporation, which would imply an energy loss of \( \approx 10 \) K per He evaporated. Thus, we would expect \( \approx 170 \) helium atoms to be evaporated. A helium atom evaporated at \( T \) will carry root mean squared (rms) angular momentum of \( \sqrt{2m_H c_k B T R} \approx 23h \). If the departing atom’s angular momentum is parallel to the initial angular momentum (as for water droplets leaving a wet, spinning tennis ball), we can expect the droplet to lose about 4000\( h \) while cooling. Alternatively, if the orbital angular momenta of the evaporated atoms are random, the droplet angular momentum would undergo a 3D random walk, and the mean squared angular momentum of the droplets would be expected to increase by the number of evaporated atoms times the square of the angular momentum per evaporation event. The form for \( \rho(n, E, J) \) for fixed \( n, E \) is that of a thermal distribution of a spherical rotor with a mean value of \( J(J+1) \) that grows as \( E^{8/7} \). For the initial values of \( n, E, R \), the rms of the distribution of \( \rho(n, E, J) \) occurs for \( J = 345 \), an order of magnitude below the mean value of the angular momentum deposited in pickup of a large molecule, such as pentacene. It can be expected that during evaporation, the density of states will bias evaporation such that the \( J \) moves towards the rms value, which will result in the average angular momentum being reduced during evaporation. For a canonical distribution at 0.38 K, the mean terminal value of \( \langle E \rangle = 18.5 \) K and \( \sqrt{J(J+1)} = 39 \) are predicted for droplets of \( n = 10^4 \).

Figure 1 shows a plot of droplet energy, angular momentum quantum number, temperature, and number of evaporated helium atoms as a function of time for five representatative trajectories with initial condition \( E_{int} = 1700 \) K and \( J_{int} = 3000 \). It is found that most of the evaporation takes place in the first \( \approx 1 \) ns, but that the temperature slowly drops even for long times. The final temperatures of each trajectory is similar to that observed experimentally for molecules inside helium droplets and also to that predicted by evaporative cooling calculations without angular momentum constraints. The remarkable difference from those previous calculations is that the final energies and angular momenta are vastly higher than that found in the previous work.

Table I gives a summary of the numerical results for a range of initial angular momentum values. For calculations with a shorter cooling time \( (10 \mu s) \), the results were almost identical, except that the final temperatures were systematically \( \approx 50 \) mK higher. It is seen that droplet cooling gives a mean residual energy and angular momentum vastly higher than that of a canonical ensemble at the same final temperature, and this energy and angu-
lar momentum rises quickly with initial angular momentum value. Notice that the ‘trapping’ of angular momentum is found even for initial values considerably smaller than the ‘maximum’ value predicted above that can be shed by evaporation. It is also evident from the table that most of the initial alignment of the total angular momentum is maintained which indicates that the final angular momentum is nearly parallel to the initial angular momentum. While for each initial condition, a broad distribution of final \( E \) and \( L \) values are found, these are distributed in a narrow band of energy width \( \approx 8 \text{ K} \), following a line corresponding to constant temperature. For fixed \( J \), the final \( E \) values are \( \approx 45\% \) larger than the lowest possible droplet energy for that \( J \), which corresponds to \( J/2 \) quanta in the lowest, \( L = 2 \) ripplon mode.

While a systematic study of the final distributions upon the full range of likely droplet initial conditions is beyond the scope of the present report, we would like to indicate the trends. If the initial energy and total angular momentum quantum number are kept constant at 1700 K and 1000 respectively, and the initial size of the droplet is decreased from \( n = 10^4 \) to \( 3 \times 10^3 \), the initial temperature rises from 2.61 to 3.69 K. As expected, the higher initial temperature rises the average kinetic energy carried away by the He atoms (3.53 \( \rightarrow \) 4.88 K), resulting in a modest decrease (164 \( \rightarrow \) 149) in the average number of evaporated He atoms. Because of decreased droplet size, the rms orbital angular momentum carried away by the He atoms decreases (25.7 \( \rightarrow \) 20.4). Despite this, the final average angular momentum decreases (401 \( \rightarrow \) 355), due to an increased correlation in the emission direction (average cosine of angle between \( L \) and \( J \) increases from 0.156 to 0.23). The final average energies and temperatures are almost unchanged. If we keep the initial angular momentum at \( J = 1000 \) and the size at \( n = 10^5 \) but decrease the initial energy from \( E = 1700 \) to 1000 K, we find that the initial temperature (2.61 \( \rightarrow \) 2.08 K), and number of evaporated helium atoms (164 \( \rightarrow \) 101) both decrease as expected. The He atoms mean kinetic energy (3.53 \( \rightarrow \) 2.87 K) and rms orbital angular momentum (25.7 \( \rightarrow \) 23.0) both decrease as expected for lower initial temperature. Unexpectedly, the average final droplet energy (44.2 \( \rightarrow \) 49.8) and angular momentum (401 \( \rightarrow \) 475) increase when the initial energy is decreased.

We performed evaporative cooling calculations for \( B = 0.6 \) and 1.2 GHz. These values were selected as they represent typical values for “heavy rotors” that have been studied in helium nanodroplets with rotational resolution. As expected, the presence of the rotor has little effect upon the final distribution of \( E \) and \( J \) of the droplets. Figure 2 shows the calculated ratio of alignment of the rotor angular momentum to that of the total angular momentum for droplets with the average final values of \( E \) and \( J \) for initial states corresponding to the \( J_{\text{initial}} = 10, 1000, 2000 \ldots 5000 \). It can be seen that the degree of rotor alignment increases with both \( j \) and the initial angular momentum, though the alignment ratio appears to saturate at higher \( J_{\text{initial}} \) values. The level of alignment found in this work is certainly within the range that should be detectable by experiments of the type reported for pentacene (\( \approx 10 \rightarrow 20\% \)).

**Experimental Consequences**—This work has demonstrated that the distribution of the internal excitations of helium nanodroplets should be vastly more excited than had been previously predicted, based solely upon the low temperature of the droplets. The present results support the interpretation of Pörtner et al., that a remnant of the initial pick up angular momentum survives evaporative cooling and provides a bias that partially aligns embedded molecules. The present work predicts that this should be a common phenomenon. It also provides a rationalization for the failure of a previous attempt to predict the rovibrational lineshapes of embed-


Table I: Evaporative Cooling of Helium Nanodroplets initially with 10000 helium atoms and initial internal energy equal to 1700. K. “±” after each entry gives the standard deviation of the ensemble of 2300 cooling trajectories.

| Initial | 10 | 100 | 1000 | 2000 | 3000 | 4000 | 5000 |
|---------|----|-----|------|------|------|------|------|
| $\langle \Delta n \rangle$ | 166.05 ± 3.15 | 164.39 ± 3.09 | 160.75 ± 2.86 | 157.24 ± 2.83 | 153.63 ± 2.68 | 150.05 ± 2.46 |
| $\langle E_{\text{final}} \rangle$ | 25.88 ± 5.66 | 44.45 ± 8.56 | 81.06 ± 9.96 | 125.0 ± 10.1 | 174.98 ± 10.30 | 229.2 ± 9.9 | K |
| $\langle J_{\text{final}} \rangle$ | 170. ± 6.4 | 404 ± 107. | 897 ± 135. | 1528 ± 145. | 2273 ± 152. | 3108 ± 151. |
| $\langle T_{\text{final}} \rangle$ | 354.7 ± 21.9 | 347.1 ± 17.2 | 343.4 ± 11.4 | 342.8 ± 8.2 | 344.4 ± 6.2 | 346.1 ± 5.0 | nK |
| $\langle E_{\text{trans}} \rangle$ | 3.53 ± 2.79 | 3.52 ± 2.75 | 3.53 ± 2.71 | 3.47 ± 2.65 | 3.39 ± 2.56 | 3.26 ± 2.44 | K |
| $\sqrt{(L(L+1))}$ | 25.6 ± 26.2 | 25.7 ± 26.0 | 26.1 ± 26.1 | 26.5 ± 26.1 | 26.6 ± 25.9 | 26.6 ± 25.6 |
| $\langle \cos(\theta_{J, L}) \rangle$ | 0.03 ± 0.58 | 0.156 ± 0.572 | 0.267 ± 0.554 | 0.357 ± 0.530 | 0.426 ± 0.504 | 0.480 ± 0.480 |
| $\langle J_{\text{final}} \rangle$ | 0.002 ± 0.020 | 0.829 ± 0.053 | 0.958 ± 0.007 | 0.983 ± 0.002 | 0.992 ± 0.001 | 0.995 ± 0.0004 |

Many of the predictions of the present calculations could be directly experimentally tested. The trapping of increasing energy in the droplets with increasing initial angular momentum will reduce the expected amount of helium atom evaporation as the collision energy is changed. However, it is not clear if this could be disentangled from other effects, including a collision and impact parameter dependence of the pickup probability and the possibility of coherent ejection of helium atoms during the pickup process, i.e. the early evaporation events could be strongly nonstatistical and thus poorly predicted by the present model. Measurement of the spatial distribution of helium atoms evaporated from a droplet would be very revealing, as the present calculations predict that the atomic velocity distribution is highly anisotropic in the center of mass frame. Since the orbital angular momentum of the evaporated atoms is on average parallel to the initial angular momentum, which itself is largely perpendicular to the droplet velocity, one expects to find the evaporated helium atoms peaked ahead and behind the droplets in the center of mass frame. Measurement of the radial distribution of atoms or molecules embedded in helium nanodroplets would also reveal the expected increased translational angular momentum of the dopant. It is possible that high energy electron or X-Ray scattering experiments could reveal the radial distribution function of atoms or molecules solvated by helium nanodroplets. The most direct test of the present model would be to measure the trapped internal energy and/or angular momentum of the droplets. One way that could be done in principle is to measure the Stokes and antistokes Raman spectrum from the lowest, $L = 2$ ripplon mode. It should be noted that excitation of the $L = 2$ mode should dominate in the trapped states, which have nearly the lowest possible internal energy for a given total angular momentum.

This work was supported by the National Science Foundation.

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