

## COMMUNICATIONS

## Bias in the temperature of helium nanodroplets measured by an embedded rotor

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The rovibrational spectra of molecules dissolved in liquid  $^4\text{He}$  nanodroplets display rotational structure. Where resolved, this structure has been used to determine a temperature that has been assumed to equal that of the intrinsic excitations of the helium droplets containing the molecules. Consideration of the density of states as a function of energy and total angular momentum demonstrates that there is a small but significant bias of the rotor populations that make the temperature extracted from a fit to its rotational level populations slightly higher than the temperature of the ripples of the droplet. This bias grows with both the total angular momentum of the droplet and with the moment of inertia of the solute molecule. © 2004 American Institute of Physics. [DOI: 10.1063/1.1638991]

## INTRODUCTION

A hallmark of rovibrational spectroscopy of molecules in liquid  $^4\text{He}$  nanodroplets has been the observation of rotational structure, as in the gas phase.<sup>1,2</sup> The distribution of intensity of transitions in this structure has allowed the determination of the rotational temperature of these molecules, and it has been assumed that this provides a measure of the temperature of the droplets themselves.<sup>1,3</sup> This assumption has been supported by the close similarity of the temperatures determined for a wide range of molecules and by the assumption that on the long time scales between pickup of solutes and spectroscopic interrogation, the entire system will come to equilibrium as the droplets cool by evaporation.

Adriaan Dockter and I have modeled the evaporative cooling of pure and doped helium nanodroplets using an angular momentum conserving statistical rate model.<sup>4</sup> These calculations have predicted that the droplets cool to a temperature close to those inferred from experiments and previous evaporative cooling calculations, but with a vastly broader distribution of energy and total angular momentum than for a canonical distribution at the same temperature. We also found, much to our initial surprise, that while the populations of the rotational levels of a solvated rotor follow a thermal distribution, the fitted temperature of the rotor populations is higher than that of the droplet itself. While this would seem to violate a fundamental principle of thermodynamics, as will be demonstrated below, this divergence of the two temperatures is in fact a consequence of the constraints imposed by conservation of angular momentum. The temperature of the helium is defined by the inverse of the derivative of the log of the density of states with respect to energy at fixed total angular momentum. However, when a rotor is excited to a state with rotor angular momentum

quantum number  $j$ , the internal degrees of freedom of the droplet can have angular momentum values between  $|J-j|$  and  $J+j$ , where  $J$  is the total angular momentum quantum number, which is treated as a conserved quantity. Thus the derivatives of the droplet density of droplet states with respect to  $J$  contributes to the rotor population.

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At the temperature of helium nanodroplets, 0.38 K, the only intrinsic droplet excitations are surface ripplon modes.<sup>5</sup> The density of states and other thermodynamic quantities can be written as a function of a reduced energy,  $\bar{E} = E/E_R$  where  $E_R = 3.77k_B K/\sqrt{N}$  and  $N$  is the number of helium atoms in the droplet.<sup>5</sup> We denote the density of states as a function of reduced energy and total angular momentum as  $\rho_{RJ}(\bar{E}, J)$ , and the density states summed over angular momentum states as  $\rho_R(\bar{E}) = \sum_J (2J+1)\rho_{RJ}(\bar{E}, J)$ . Using methods recently described,<sup>6</sup> these can be well approximated by the analytical expressions

$$\rho_R(\bar{E}) = \exp(a\bar{E}^{4/7} + b\bar{E}^{1/7}), \quad (1)$$

$$\rho_{RJ}(\bar{E}, J) = \rho_R(\bar{E})(2J+1) \sqrt{\frac{\beta(\bar{E})^3}{\pi}} \times \exp(-\beta(\bar{E})(J+1/2)^2), \quad (2)$$

$$\beta(\bar{E}) = c\bar{E}^{-8/7} + d\bar{E}^{-13/7}, \quad (3)$$

if the values  $a = 2.5088$ ,  $b = -4.3180$ ,  $c = 0.8642$ , and  $d = -0.3524$  are used.<sup>7</sup> Note that for fixed  $J$ , the density is the number of distinct states, i.e., does not include the  $(2J+1)$  spatial quantization degeneracy of each such state. We define the ripplon microcanonical temperature,  $T_R(\bar{E})$ , and with fixed total energy and angular momentum,  $T_{RJ}(\bar{E}, J)$ , by

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$$\frac{1}{T_R(\bar{E})} = \frac{d \ln(\rho_R(\bar{E}))}{d\bar{E}} = \frac{4}{7} a \bar{E}^{-3/7} + \frac{1}{7} b \bar{E}^{-6/7}, \quad (4)$$

$$\begin{aligned} \frac{1}{T_{RJ}(\bar{E}, J)} &= \frac{d \ln(\rho_{RJ}(\bar{E}))}{d\bar{E}} \\ &= \frac{1}{T_R(\bar{E})} + \left( \frac{3}{2\beta(\bar{E})} - (J+1/2)^2 \right) \left( \frac{d\beta}{d\bar{E}} \right), \end{aligned} \quad (5)$$

where in both cases, temperature is measured in units of reduced ripplon energy,  $E_R$ , divided by Boltzmann's constant.

We now consider a droplet that has a solvated rigid linear rotor, with effective rotational constant  $B$ , given again in units of  $E_R$ . Let  $j$  be the rotational quantum number of the rotor,  $J_R$  the rotational quantum number of the ripples, and  $J$  the total rotational quantum number. The total density of states for fixed values of  $\bar{E}$ ,  $J$  is given by

$$\rho(\bar{E}, J) = \sum_j \sum_{J_R=|J-j|}^{J+j} \rho_{RJ}(\bar{E} - Bj(j+1), J_R). \quad (6)$$

$P(j)$ , the fraction of states with rotor quantum number  $j$ , is given by

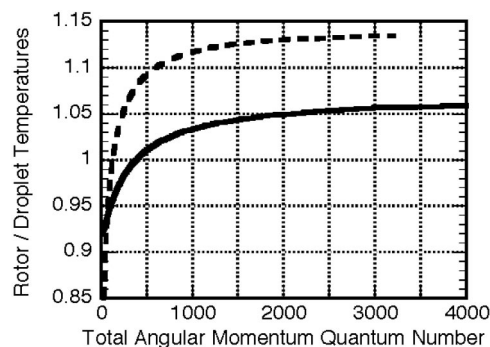


FIG. 1. Plot of the ratio of the rotor temperature,  $T_r(\bar{E}, J)$  to the droplet temperature,  $T(\bar{E}, J)$  for droplets of 3000 (dashed curve) and 10 000 (solid curve) helium atoms and a solvated rotor with  $B = 1$  GHz as a function of the total angular momentum quantum number,  $J$ . For each value of  $J$ ,  $\bar{E}$  has been fixed by the condition that  $T_{RJ} = 0.35$  K.

$$P(j) = \frac{\sum_{J_R=|J-j|}^{J+j} \rho_{RJ}(\bar{E} - Bj(j+1), J_R)}{\rho(\bar{E}, J)}. \quad (7)$$

The temperature,  $T(\bar{E}, J)$ , of the coupled system, at fixed  $\bar{E}$  and  $J$  is given by

$$\frac{1}{T(\bar{E}, J)} = \frac{d \ln(\rho(\bar{E}, J))}{d\bar{E}} = \frac{\sum_j \sum_{J_R=|J-j|}^{J+j} \rho_{RJ}(\bar{E} - Bj(j+1), J_R) / T_{RJ}(\bar{E} - Bj(j+1), J_R)}{\rho(\bar{E}, J)}. \quad (8)$$

A rotor temperature,  $T_j(\bar{E}, J)$ , can be defined from a Boltzmann fit to the rotor level populations  $P(j)$ . This latter corresponds to the “droplet temperature” that has been reported in numerous experiments. This assignment of the rotor temperature to that of entire system, i.e., that  $T_j(\bar{E}, J) = T(\bar{E}, J)$ , is natural assumption for a system in microcanonical equilibrium, i.e., by equating  $P(j)$  to the ratio of density of states. If we ignore angular momentum conservation and sum over all values of  $J$ , then the above identification would be exact as long as the mean energy in the rotor,  $T_r$ , is much less than the total energy in the droplet,  $\bar{E}$ , so that the “heat bath” of ripplon states does not change temperature significantly over the range of significantly populated rotor states. Equivalently, we expect  $T_j(\bar{E}, J) = T(\bar{E}, J)$  if  $\rho_{RJ}(\bar{E})$  can be approximated by  $\rho_{RJ}(\bar{E} - Bj(j+1)) = \rho_R(\bar{E}) \exp(-Bj(j+1)/T_R(\bar{E}))$ . Note that if the finite heat capacity of the droplet heat bath is considered, then we would expect the population in higher rotational levels to fall off faster than predicted by the Boltzmann distribution, and thus the effective temperature determined by a fit to the rotor populations to be lower than the droplet temperature.

When we look at the  $J$  conserving ensemble, we must consider the fact that the average value of  $J_R(J_R + 1)$  equals to  $J(J+1) - j(j+1)$  for fixed  $J, j$ . Thus the population of

different rotor levels will be influenced not only by  $T_R$ , but also by the  $J$  dependent factor in  $\rho_{RJ}$ , which has the same form as the rotational distribution function of a spherical top in a canonical ensemble. In order to test the size of the expected bias in the estimate of  $T(\bar{E})$  by  $T_j$ , we will examine numerical results for droplet of  $N = 3000$  and 10 000 helium atoms, for which  $E_R = 0.069$  and 0.0377 K, respectively. Based upon our evaporative cooling calculations,<sup>4</sup> we will assume that the droplets cool to a final temperature of 0.35 K, but have a wide range of final angular momentum values,  $J$ . This condition allows calculation of an isothermal curve  $\bar{E}(J)$  for each droplet size. We further assume that  $B = 1$  GHz, which equals 0.70 (1.27) in reduced units for droplets of 3000 (10 000) helium atoms. This is the effective  $B$  constant for SF<sub>6</sub> dissolved in helium, from which the temperature of helium nanodroplets was first measured.<sup>1</sup> It is found that  $T(\bar{E}(J), J) = T_{RJ}(\bar{E}(J), J)$  to better than 1 % for all values of  $J$  over the range from 0–4000. It is found that the values of  $P(j)$  fit a Boltzmann distribution to high accuracy, so that values of  $T_r$  are well defined. However, over this range of  $J$ , we find a small systematic difference in the values between  $T_j(\bar{E}(J), J)$  and  $T(\bar{E}(J), J)$ , as demonstrated in Fig. 1. The ratio of  $T_j(\bar{E}(J), J)$  to  $T(\bar{E}(J), J)$  is found to be approximately proportional to  $B^{-1}$ , i.e., is linearly pro-

portional to the effective rotational moment of inertia of the rotor in helium (including the contribution due to motion of the helium). As is evident from the figure, the size of the bias decreases for larger droplets, though less than linearly with number of helium atoms in the droplet.

The present results demonstrate that for, helium droplets with significant trapped angular momentum, the population of rotational levels of rotors will be biased from that predicted by a Boltzmann distribution at the temperature of either the droplet excitation modes or the temperature of the entire system. The size of the bias is on the order that should be detectable by careful measurement of the droplet rotational constant as the temperature of the pickup gas (and thus the initial collisional angular momentum) is increased. Previous experiments have reported a range of rotational temperatures, but up to now these do not appear to have been considered physically significant. For example, in a study of the cluster size dependence of the spectrum of SF<sub>6</sub>, the temperature was found to be constant to within statistical noise (0.36–0.40 K) for droplets of more than a few thousand He atoms, but to systematically increase for smaller droplets, down to a value of 0.48(20) K for droplets of a few hundred He atoms.<sup>8</sup> The authors concluded that the temperature of smaller droplets was higher, but the present result suggest that another possibility is that the effect they observed could be, at least in part, due to the bias effect predicted by the present work. Nauta and Miller found that, for the spectrum of HF dimer, the rotational temperature was 0.34(1) K,<sup>9</sup> below the expected droplet temperature of 0.38(2) K. It should be pointed out that the rotational constant of HF dimer in helium is three times larger than that of SF<sub>6</sub>, and that the pickup of two HF molecules should deposit considerably less angular momentum than the pickup of SF<sub>6</sub>. It should be noted that the size of the bias is a function only of the total rotational quantum number, and thus the effect should be essentially unchanged for a symmetric top or spherical top

molecule. For an asymmetric top, this effect should lead to a failure of the transition intensities to follow that expected for a gas in thermal equilibrium if this bias effect is ignored. Stimulated by the present analysis, Miller and collaborators have made an attempt to look in a systematic way at the temperature extracted from fits to rotor populations for different molecules. Unfortunately, the asymmetries of the lineshapes often observed for the lowest rovibrational transitions lead to model dependent biases in the fitted rotational temperatures that could not be disentangled from the expected effects.<sup>10</sup> This gives yet one more reason for the need to address this problem of lineshapes of rovibrational transitions in helium nanodroplets beyond the one previous attempt.<sup>11</sup> That previous work assumed a canonical ensemble of internal states which the recent evaporative cooling work has now shown to be a poor assumption.

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<sup>1</sup>M. Hartmann, R. E. Miller, J. P. Toennies, and A. F. Vilesov, *Phys. Rev. Lett.* **95**, 1566 (1995).

<sup>2</sup>C. Callegari, K. K. Lehmann, R. Schmied, and G. Scoles, *J. Chem. Phys.* **115**, 10090 (2001).

<sup>3</sup>S. Grebenev, J. P. Toennies, and A. F. Vilesov, *Science* **279**, 2083 (1998).

<sup>4</sup>A. Dokter and K. K. Lehmann, *Phys. Rev. Lett.* (submitted).

<sup>5</sup>D. M. Brink and S. Stringari, *Z. Phys. D: At., Mol. Clusters* **15**, 257 (1990).

<sup>6</sup>K. K. Lehmann, *J. Chem. Phys.* **119**, 3336 (2003).

<sup>7</sup>In Ref. 6, the integrated density of states was fit to the form used here for the density of states. However, with a slight change in the constants, to the values given here, this form also accurately fits the density of states for reduced energy greater than  $\approx 50$ .

<sup>8</sup>M. Hartmann, N. Portner, B. Sartakov *et al.*, *J. Chem. Phys.* **110**, 5109 (1999).

<sup>9</sup>K. Nauta and R. E. Miller, *J. Chem. Phys.* **113**, 10158 (2000).

<sup>10</sup>R. E. Miller (unpublished).

<sup>11</sup>K. K. Lehmann, *Mol. Phys.* **97**, 645 (1999).