

Communication

On the Sign of Local Temperature in Molecules

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Abstract *Lin* proposed earlier based on qualitative considerations that electronic motion was associated with negative absolute temperature. Here, a local temperature formula is proposed for electronic motion in atoms and molecules, which allows the existence of negative absolute temperature in a local sense in thermodynamic equilibrium. The proposed temperature formula is a function of total energy density $e(\mathbf{r})$, entropy density $s(\mathbf{r})$, and electron density $r(\mathbf{r})$.

Keywords: Negative absolute temperature, local temperature, entropy density, energy density, electron density.

What is heat? — A paramount question of thermodynamics is echoed in the title of *Dyson's* popular paper some forty-five years ago [1]. The answer is given by only two words: “Heat is disordered energy”. Quantitative analysis of this definition gives rise to the well-known thermodynamic relation between temperature T , entropy S , and total energy E :

$$T = \left. \frac{\partial E}{\partial S} \right|_{X=\text{const}} \quad (1)$$

where X represents all of the additional, independent thermodynamic variables that appear in the thermodynamic equations relating TdS and dE .

The sign of the temperature is determined by the sign of the derivative in eq. 1. The existence of negative temperature is, therefore, possible in a thermodynamic system where the entropy is not restricted to a monotonically increasing function of the total energy, or, in other words where there is a state of maximum entropy [2].

For the movements of atoms in a body of matter, or for the movements of electrons in a molecule, there is no state of maximum entropy. Excitation by supplying more and more energy will result in ever increasing entropy as the atoms and electrons jump to higher and higher-energy quantum states. Therefore, negative absolute temperature would have no place in chemistry so far as we know [3].

It should be noted, however, that there exists at least one magnetic system, the LiF crystal which was used, for the first time, to produce and detect a negative absolute temperature by *Purcell* and *Pound* in 1950 [4]. The nuclear spin has only two states which means that a finite number of nuclear spins have a minimum energy state with all the spins being parallel to an external magnetic field, and, a maximum energy state with all the spins pointing in the opposite direction. Thus, the minimum energy state and the maximum energy state are both associated with zero entropy (maximum order) with the trivial consequence of a maximum entropy state at some intermediate energy. According to eq. 1 the maximum entropy state corresponds to infinite temperature, states toward the minimum energy state are in the positive temperature range, and states toward the maximum energy state are in the negative temperature range. The minimum and maximum energy states are both at absolute zero temperature. The extremely slow spin lattice relaxation time of LiF with respect to spin-spin relaxation time allows for jumping from positive temperature territory to negative temperature territory by quickly reversing the magnetic field and, then, measuring negative temperatures for a finite time interval.

We want to argue in this short communication that, locally, the sign of the temperature within the three-dimensional space of a molecule may vary. *Ghosh et al.* have given a transcription of ground-state density-functional theory into a local thermodynamics by introducing the concept of a local temperature corresponding to the electronic motion and also an entropy associated with the electron distribution [5]. Local thermodynamics utilizes a density function of thermodynamic quantities related to the electron distribution in terms of the electron density function $r(\mathbf{r})$. In particular, local temperature, *i.e.*, temperature density is defined in terms of the kinetic energy density $k(\mathbf{r})$ [5]:

$$k(\mathbf{r}) = \frac{3}{2} r(\mathbf{r}) R t(\mathbf{r}) \quad (2)$$

where $t(\mathbf{r})$ is the temperature density and R is the gas constant.

Note that integration of eq. 2 over three-dimensional space results in the ideal gas expression of (total) kinetic energy $K=3/2RT$. $k(\mathbf{r})$ is always positive and so is $r(\mathbf{r})$, therefore, eq. 2 renders $t(\mathbf{r})$ to be

also positive. We want to argue that $t(\mathbf{r})$ should be replaced by $|t(\mathbf{r})|$ in eq. 2 and, the sign of $t(\mathbf{r})$ should be determined by some local form of eq. 1. Replacing $t(\mathbf{r})$ by $|t(\mathbf{r})|$ in eq. 2 will not change anything in the Ghosh *et al.* local thermodynamics, but explicit definition of the sign of $t(\mathbf{r})$ may provide additional insight about electronic motion in molecules.

Here we propose a local form of eq. 1. For isolated molecules, X in eq. 1 represents two thermodynamic variables, the number of particles N and the volume V . In fact, it is only N that counts since the change in volume would require a change in the relative energies of the quantum energy levels, which in turn would require external energy in terms of an external field, but our focus here is on isolated molecules in vacuum. The local definition of $N=\text{const}$ in eq. 1 involves the concept of isocontour surfaces (A_{r_r}) of the electron density. Isocontour surfaces are two-dimensional surfaces where $r(\mathbf{r})=\text{const}$. Isocontour surfaces fill the three-dimensional space of the molecule very much like onion shells make up the onion. For our definition of a local differential in eq. 1 at a particular point $\mathbf{r}$, the isocontour surface with a constant electron density $r_r=r(\mathbf{r})$ is considered, in the sufficiently small vicinity of that point. We want to calculate the change of E with respect to the change of S in the vicinity of $\mathbf{r}$, moving on the isocontour surface A_{r_r} . Of course, the value of the proposed differential depends on the path we take on A_{r_r} . A rigorous definition leads to a variational problem.

Let us consider total energy density $e(\mathbf{r})$, entropy density $s(\mathbf{r})$, and electron density $r(\mathbf{r})$ at a particular point $\mathbf{r}=(x, y, z)$ where x, y, z are three-dimensional Cartesian coordinates. The total energy density $e(\mathbf{r})$ can be calculated at various levels of quantum theory as the sum of the kinetic energy density $k(\mathbf{r})$ and the potential energy density $v(\mathbf{r})$. The entropy density $s(\mathbf{r})$ can be calculated by a Sackur-Tetrode equation, which is an expression of $k(\mathbf{r})$ and $r(\mathbf{r})$ only [5]. The value of the electron density at $\mathbf{r}$ is $r_r=r(\mathbf{r})$. The constraint of a constant electron density defines a two-dimensional isocontour surface $A_{r_r}(u, v)$ where u, v are two-dimensional curvilinear coordinates on the surface ($A_{r_r}(u, v) = x(u, v)\mathbf{i} + y(u, v)\mathbf{j} + z(u, v)\mathbf{k}$). On this surface, an appropriate $(x, y, z) \rightarrow (u, v)$ coordinate transformation gives rise to $e^A(u, v)$ and $s^A(u, v)$, respectively. Let us further define a parametric curve $C(u(t), v(t))$ on A_{r_r} , passing through $\mathbf{r}$. Along this curve, the energy density and the entropy density is defined by $e^C(u(t), v(t)) \equiv e^C(t)$ and $s^C(u(t), v(t)) \equiv s^C(t)$, respectively. Let us finally consider the following implicit function system with two equations and three variables, viz., energy density e , entropy density s , and the curve parameter t :

$$\begin{aligned} s - s^C(t) &= 0 \Rightarrow & t &= [s^C]^{-1}(s) \\ e - e^C(t) &= 0 \Rightarrow & e &= e^C([s^C]^{-1}(s)) \end{aligned} \quad (3)$$

Now the one-dimensional differential de/ds along C on A_{r_r} , at $\mathbf{r}$, is given by application of the chain rule:

$$\left. \frac{de}{ds} \right|_{\mathbf{r}} = \frac{de^C}{d[s^C]^{-1}} \frac{d[s^C]^{-1}}{ds} = \frac{de^C}{dt} \frac{dt}{ds} \quad (4)$$

Subject to regularity conditions (existence and continuous differentiability of $e^C(s)$ and $t(s)$ in the sufficiently small vicinity of $\mathbf{r}$ on A_{r_r}), de^C/dt is trivial and dt/ds can be calculated utilizing the inverse function theorem:

$$\frac{ds}{dt} = \left(\frac{ds^C}{du}, \frac{ds^C}{dv} \right)^T \left(\frac{du}{dt}, \frac{dv}{dt} \right) \Rightarrow \frac{dt}{ds} = \left(\left(\frac{ds^C}{du}, \frac{ds^C}{dv} \right)^T \left(\frac{du}{dt}, \frac{dv}{dt} \right) \right)^{-1} \quad (5)$$

Thus, a typical variational problem would be finding a curve C on A_{r_r} that maximizes eq. 4. This problem maybe of some interest, but our definition of the sign of $t(\mathbf{r})$ should conform with eq. 2. Therefore, we propose the following definition for the sign of $t(\mathbf{r})$. The sign of $t(\mathbf{r})$, at $\mathbf{r}$, is defined as the sign of eq. 4 for such C on A_{r_r} , for which the absolute value of eq. 4 is equal to:

$$\left| \frac{de}{ds} \right| = \frac{2}{3R} \frac{k(\mathbf{r})}{r(\mathbf{r})} \quad (6)$$

for non-vanishing $r(\mathbf{r})$. For zero electron density, $t(\mathbf{r})=0$. Of course, the proposed definition can break down in two different ways. On the one hand, eq. 6 may not have a unique solution, or, it may have multiple solutions. Moreover, in the latter case, the multiple solutions may have different signs. We hope that numerical calculations will resolve this ambiguity.

It should be noted that although analytical solution of eqs. 3-6 seems prohibitive for molecules, a numerical approximation via finite differences is straightforward. The numerical procedure involves calculating $\Delta e/\Delta s$ along small displacement vectors lying in the tangent plane of A_{r_r} . The displacement vectors can be envisioned as arrows radiating from $\mathbf{r}$ and sweeping a small circle on A_{r_r} with some finite angle increment. Note that e and s can readily be calculated from the wavefunction and the gradient of r , which defines the tangent plane, is also available in quantum chemistry program packages [6,7].

Concluding Remarks

We have demonstrated that a local temperature formula can be constructed for electronic motion in atoms and molecules, which allows the existence of negative absolute temperature in a local sense in thermodynamic equilibrium. The proposed temperature formula is a function of total energy density $e(\mathbf{r})$, entropy density $s(\mathbf{r})$, and electron density $r(\mathbf{r})$. Numerical tests will be conducted to test the proposed theory.

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References and Notes

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