Kinetic and thermodynamic temperatures in quantum systems

Alessio Gagliardi, Alessandro Pecchia, Aldo Di Carlo

Dipartimento di Ingegneria Elettronica, Università' of Roma "Tor Vergata", Via del Politecnico 1, 00133, Rome, Italy
gagliardi@ing.uniroma2.it, Tel: (+39) 06 7259-7367, Fax: (+39) 06 7259-7939.
† CNR-ISMN, Via Salaria km 29.600, 00017 Monterotondo, Roma
(Dated: July 23, 2013)

In this work we present a formalism to describe non equilibrium conditions in systems with a discretized energy spectrum, such as quantum systems. We develop a formalism based on a combination of Gibbs-Shannon entropy and information thermodynamics that arrives to a generalization of the De-Brujin identity applicable to discrete and non-symmetric distributions. This allows to define the concept of a thermodynamic temperature with a different, albeit complementary meaning to the equilibrium kinetic temperature of a system. The theory is applied to Bosonic and Fermionic cases represented by a harmonic oscillator and a single energy state, respectively. We show that the formalism correctly recovers known results at equilibrium, then we demonstrate an application to a genuine non equilibrium state: a coherent quantum oscillator.

PACS numbers: May be entered using the \pacs{#1} command.

Non equilibrium thermodynamics is intimately linked to the concept of non-equilibrium temperature which in turn tightens to the concept of non-equilibrium entropy. Several attempts have been made in the past in order to provide a consistent definition of all these concepts and the field is still reach of fruitful debates. One of such attempts can be called informational thermodynamics, resting on the extension of the Gibbs-Shannon entropy to non-equilibrium conditions. This encounters the difficulty of assigning probabilities to microstates which is solved, for instance, using the debated postulate of maximal entropy or maximal entropy production rate. However, for many nonequilibrium systems, maximal entropy principle fails, signifying that fast evolving dynamics prevent any meaningful definition of such probabilities. Nonetheless, in non-equilibrium systems under steady-state conditions the concept of a probability distribution is meaningful. Such systems are characterized by steady-state fluxes of energy, mass or charges driven by non-equilibrium distributions of phase-space degrees of freedom. To this class belong a broad range of interesting physical systems ranging from electronic devices, electrochemical cells, catalytic systems, photochemical steady state reactions. Especially brought under attention by the advent of nanotechnology are extremely miniaturized devices comprising a small number of atoms or molecules, usually kept under strong non-equilibrium steady-state conditions. Many examples can be easily found in the literature, such as nano-mosfets or, at the extreme, molecular electronic devices. Many assumptions widely used in the simulation of macroscopic or mesoscopic scales often assume local quasi-equilibrium, with a well defined local electrochemical potential controlling state occupancy and densities and a local equilibrium temperature. However, this approximation fails when the perturbation cannot be considered small with respect to the characteristic length scale. On the other hand, in a non-equilibrium theory, it would be useful to retain as much as possible those concepts that have provided so deep insights in systems close to equilibrium, such as the concept of temperature, that can be viewed as a parameter controlling thermodynamics heat fluxes.

A central quantity in statistical mechanics is the Shannon-Gibbs classical entropy, defined as

$$S = -k_B \int p(\vec{x}) \log(p(\vec{x}))d^d\vec{x},$$

where $k_B$ is the Boltzmann constant and $p(\vec{x})$ the probability of the system to occupy the $\vec{x}$ microstate of the phase space. The microstate can be expressed in terms of generalized coordinates representing the degrees of freedom (DOF) of the system. Under Gibbs definition, $S$ is a special way of measuring the phase-space available to the system. We note that equation (1) is well-defined when the integration is actually interpreted as a dense sum.

In information theory (Shannon entropy), the state $\vec{x}$ represents a set of symbols (word) emitted by an information source and $k_B = 1$. Despite this formal identity, the connection between thermodynamics and information theory is not obvious but it has been established. Theorems and formalisms derived in the context of information theory can be readapted to statistical mechanics.

Entropy and average energy, $\bar{E} = \int p(\vec{x})E(\vec{x})d^d\vec{x}$, define two concepts of temperature. The thermodynamic temperature is defined as

$$T_{th} = \partial \bar{E}/\partial S,$$

and it is related to the statistics in the phase space. The kinetic temperature, on the other hand, is connected to the energy stored in the dynamical DOFs. In equilibrium it is directly connected to the equipartition theorem, giving for a classical gas of $N$ particles,

$$T_{kin} = \frac{2\bar{E}}{3NK_B}.$$

Finally, for systems in contact with a bath, it is possible to define the temperature of the external environment reservoir, $T_{th}$. 
Under equilibrium conditions $T_{kin} = T_0 = T_{th}$. For systems under non-equilibrium these three temperatures assume different values with different meaning. We present here a formalism that extends thermodynamics and temperature to non-equilibrium conditions, at least under steady state, making extensive use of informational theory concepts. The formalism is first introduced and applied to an ensemble of quantum harmonic oscillators following bosonic statistics (BS) and a single state ensemble following Fermi statistics (FS), for which the equilibrium probability distributions (PD) are well known. Then, we consider the non-equilibrium distribution represented by the coherent states of a bosonic oscillator, for which we demonstrate that the thermodynamic, kinetic and bath temperatures depart from each others with different meanings.

Before moving forward we point out that the quantum extension of the Von Neuman entropy based on the density matrix (DM), $S = -k_B \text{Tr} [\hat{\rho} \ln \hat{\rho}]$. The theory we discuss here is valid for systems in a mixed state with diagonal DM, reducing the Von Neuman entropy to a classical sum over the probability distribution.

An incoherent ensemble of harmonic oscillators in equilibrium follow the geometric distribution,

$$
p_n = e^{-\frac{E_n}{kT_0}} \left(1 - e^{-\frac{E_n}{kT_0}}\right) = \Delta^n (1 - \Delta),
$$

Similarly, we can define the equilibrium occupation probability of a single energy state following Fermi statistics,

$$
p_1 = \frac{1}{e^{\frac{E_1}{kT_0}} + 1},
$$

and $p_0 = 1 - p_1$. From these expressions of $p_n$, we can easily verify that in equilibrium in both cases $T_{th} = T_0$.

In a recent work, we have made an extensive discussion concerning the generalization of entropy for system under steady-state non equilibrium conditions. In essence, the DOF of a system driven out of equilibrium correlate to external variables, $\vec{y}$. An example we can think of an external field that induces fluxes of particles or energy, inducing correlations between particle motions. The non-equilibrium form of the energy spectrum and the PD will also be different from equilibrium. Assuming the form of the Gibbs-Shannon entropy still applicable, non equilibrium (NE) entropy is actually a conditional entropy,

$$
S(\vec{x}|\vec{y}) = S^{eq}(\vec{x}) - kI(\vec{x} \wedge \vec{y}),
$$

where $S^{eq}$ is the equilibrium entropy and the last term is the mutual information. The same equation also implies a reduction of the available phase space, associated with a reduction of entropy and increase of available free energy, according to:

$$
F_{NE} = \bar{E}_{NE} - T_{th} S^{eq} + k_B T_{th} I,
$$

where $\bar{E}_{NE}$ is the average non-equilibrium energy (depending on the NE PD).

We turn now our attention to discrete PDs, $p_n$, defined on a generally finite support, $n \in [\alpha, \beta]$, that may represent a discrete energy spectrum. For discrete distributions the integrals of equations (1) and (7) become summation over the index $n$. In order to evaluate (7) we need to construct a functional perturbation to the PD, $p_n$, that induces an infinitesimal increase of entropy, $\delta S$, and mean energy, $\delta \bar{E}$. In making such a mathematical construction we assume that the energies of the microstates, $E_n$, are left unchanged. This is consistent with taking the derivative of eq. (9) at constant volume and particle number. In a way that resembles the original de Bruijn scheme for continuous PD, we consider a perturbation obtained as a discrete convolution $p_n^\varepsilon = \sum_m p_{m+n} q_m(n, \varepsilon)$, where $q_m(\varepsilon)$ is generally defined in the interval $\alpha < n < \beta$ and

$$
\begin{align*}
q_1 &= \varepsilon \\
q_0 &= 1 - 2\varepsilon \\
q_1 &= \varepsilon
\end{align*}
$$

and $q_m = 0$ for $m > 1$ and $m < -1$. However the perturbation needs to be modified at the two boundaries such that for $n = \alpha$, $q_1 = 0$, $q_0 = 1 - \varepsilon$, $q_1 = \varepsilon$ and for $n = \beta$, $q_1 = \varepsilon$, $q_0 = 1 - \varepsilon$, $q_1 = 0$. It follows that the perturbed PD, $p_n^\varepsilon$, is

$$
\begin{align*}
p_n^\varepsilon &= p_\alpha + \varepsilon(p_{\alpha+1} - p_\alpha) \\
p_n^\varepsilon &= p_n + \varepsilon(p_{n+1} - 2p_n + p_{n-1}), \quad \alpha < n < \beta \\
p_\beta &= p_\beta + \varepsilon(p_\beta - p_\beta).
\end{align*}
$$

The modifications at the boundaries are just needed for preserving the normalization of the PD to unity. For a Fermi statistics the perturbed probability reduces to $p_n^\varepsilon = (1 - \varepsilon)p_\varepsilon + \varepsilon p_\varepsilon$ and $p_\beta^\varepsilon = (1 - \varepsilon)p_\varepsilon + \varepsilon p_\varepsilon$. We note that the original de Bruijn identity is demonstrated for continuous PDs defined on an infinite support. In this context $\varepsilon p_\varepsilon$ becomes a normal distribution with mean 0 and variance $\varepsilon$.

**Theorem 1:** Given a perturbation of PD as in equations (10), in the limit $\varepsilon \to 0^+$, the entropy variation can be written as

$$
\frac{1}{k} \frac{\delta S}{\varepsilon} = D[p_{n+1}||p_n] + D[p_{n-1}||p_n],
$$

where $D[p_{n+1}||p_n]$ is the Kullblak-Leibler divergence (KLD), a well-known concept in information theory, defined as

$$
D[p_n||q_n] = \sum_n p_n \ln \left( \frac{p_n}{q_n} \right),
$$
representing a pseudo-distance between two PDs, which has the property of being always non negative and equal to zero iff \( p_n = q_n, \forall n \). The demonstration of this theorem is given in the appendix.

Observing that \( D[p_n\|p_n] = 0 \), the r.h.s. of equation (11) can be rewritten as \( D[p_{n+1}\|p_n] + D[p_{n-1}\|p_n] - 2D[p_n\|p_n] \), which has the suggestive form of a discrete curvature measure of the PD. This geometrical concept has interesting implications developed by Amari and coworkers.\(^{20}\) The perturbed PD also gives a perturbation to the average energy according to

\[
\frac{\delta E}{\varepsilon} = \sum_n E_n \frac{p_n^2 - p_n}{\varepsilon}.
\]

(13)

Combining eq. (11) and (13) we can rewrite \( \frac{dS}{dE} = \frac{\delta S}{\varepsilon} \) giving,

\[
\frac{1}{kT_{th}} \frac{\delta E}{\varepsilon} = D[p_{n+1}\|p_n] + D[p_{n-1}\|p_n].
\]

(14)

A similar expression was obtained in,\(^{18,21}\) but in those derivations the PD is always assumed defined on an infinite support \( n \in (-\infty, \infty) \) and completely symmetric with respect to the origin. Under the more restrictive assumptions stated above, equation (14) leads to the well-known De Bruijn identity,\(^{12}\) usually derived in the context of continuous and differentiable PDs. In such a context \( T_{th} \) is also known as the Fisher temperature of the system. Our theorem can be considered a generalization to non symmetric and discrete PDs. The generality of Theorem 1 makes it valid to any arbitrary PD, including non equilibrium conditions. Indeed, no specific assumptions have been made. In the case of distributions defined on semi-infinite supports, i.e. \( n \in [0, + \infty) \), the form (19) need to be corrected only at the lowest boundary.

An obvious sanity check is to show that under an equilibrium PD the relationship (14) leads to the correct equilibrium temperature. This can be shown for the Bose-Einstein and Fermi statistics using the detailed-balance relationships, \( p_{n+1} = p_n \Delta \). Substituting in eq. (13) we get \( \frac{\delta E}{\varepsilon} = h\omega (1 - \Delta) \) from which follows, from eq. (14), \( h\omega (1 - \Delta)/T_{th} = h\omega (1 - \Delta)/T_0 \), therefore \( T_{th} = T_{kin} = T_0 \). A similar proof can also be carried out for the equilibrium Fermionic PD of eq. (19).

Under non equilibrium conditions the three temperatures \( (T_0, T_{th} \text{ and } T_{kin}) \) are generally different. The kinetic temperature is in fact obtained from \( E_{NE} \) alone, while the thermodynamic temperature is related to the statistics of the PD. The meaning of these temperatures is still debated but could be generally linked to the heat and mechanical work exchanged between reservoir and system\(^{12}\). Limited to the assumption of Langivin dynamics, Sanistrava and coworkers demonstrate the relationships,

\[
\Delta Q \propto T_0 - T_{th}, \quad (15)
\]

\[
\Delta W \propto T_{th} - T_{kin}, \quad (16)
\]

where \( \Delta Q \) and \( \Delta W \) are, respectively, the net heat and mechanical work exchanged. A positive sign corresponds to a system absorbing energy (heat or work) from the reservoir. The relevant result of the relations above is that \( T_{th} \) and \( T_{kin} \) could be used to understand fluxes of work and heat in non-equilibrium systems, simply based on the non-equilibrium PD.

**Laser Field.** As an example of our formalism we consider the non-equilibrium \( T_{th} \) and \( T_{kin} \) for a cavity laser. This can be described as a mixed state given by a superposition of coherent states with a distribution of all possible phases,

\[
\hat{\rho} = \frac{1}{2\pi} \int d\phi |\alpha e^{i\phi}\rangle \langle \alpha e^{i\phi}| = \sum_n e^{i|\alpha|^2} \frac{n!}{n!} |n\rangle \langle n|,
\]

(17)

in which the coherent or Glauber states are defined as

\[
|\alpha\rangle = e^{-\frac{|\alpha|^2}{2}} \sum_n \frac{\alpha^n}{\sqrt{n!}} |n\rangle.
\]

(18)

From (17) it follows that the non-equilibrium laser field can be described by an ensemble following a Poissonian distribution,

\[
r_n = \frac{|\alpha|^{2n}}{n!} e^{-|\alpha|^2},
\]

(19)

from which the averaged occupation number is \( \langle n \rangle = |\alpha|^2 \) and the averaged energy is \( \bar{E} = h\omega (|\alpha|^2 + \frac{1}{2}) \). Due to this particular relation, the kinetic temperature can be obtained by inverting the equilibrium Bose-Einstein distribution,

\[
T_{kin} = \frac{h\omega}{k_B \ln (1 + |\alpha|^2)},
\]

(20)

Applying eq. (11) to the Poissonian distribution it is possible to compute the thermodynamic temperature for the cavity field. The calculation of the KLD divergences is made simple by using the relationship \( (n+1)r_{n+1} = \langle n \rangle r_n \), that after some manipulations, leads to

\[
T_{th} = \frac{h\omega r_0}{k \left[ \sum_{k=1}^{\infty} \frac{1}{r_k} \ln \left( \frac{2k+1}{2k} \right) - r_0 \ln (|\alpha|^2) \right]},
\]

(21)

with \( r_0 = \exp(-|\alpha|^2) \). There is no closed analytical form for this \( T_{th} \), however the series in the denominator converges very quickly and can be numerically evaluated. The thermodynamic and kinetic temperatures for different \( \langle n \rangle \) are shown in Figure 1 where we can observe that for low values of \( \langle n \rangle \) the two temperatures are essentially equivalent, but then the kinetic temperature increases with the average energy, while the thermodynamic temperature goes asymptotically to zero. This shows that the intuitive concept of temperature is related to \( T_{kin} \), whereas \( T_{th} \) measures in fact something quite different, related to the statistics of the PD. For a laser field, even
if the average energy is increasing with \( \langle n \rangle \), the 'disorder' associated with the distribution decreases and with it the thermodynamic temperature. As shown in Figure 2 the non-equilibrium entropy is strictly lower than the entropy in equilibrium, as expected from the relationships \([6,8]\), for the same average energy or average occupation, \( \langle n \rangle \). We also notice that the mutual information, \( k_B I = S^{eq} - S \), increases with \( \langle n \rangle \), reflecting the fact that the system free energy increases. Indeed, manipulating equation (8) we get

\[
F - F^{eq} = (T_0 - T) S^{eq} + k_B T I.
\]

The fact that this difference increases with \( \langle n \rangle \) reflects the high degree of order of the energy stored in a coherent state as opposed to a thermalized equilibrium energy. From this follows that, without external constrains, the coherent state will evolve towards an equilibrium state of maximal entropy. Concluding, we have developed a formalism to treat non-equilibrium conditions for discrete distributions based on a new generalized relation between the Kullback-Leibler curvature and the thermodynamic temperature. The formalism has been applied to the equilibrium case of Bose and Fermi distributions to show its validity and then to a real non equilibrium case represented by a quantum harmonic oscillator in a coherent state. The generality of our approach paves the way to a new simple approach to compute non-equilibrium thermodynamical properties, that can be applied to more complex systems and nanoscale quantum devices under non-equilibrium conditions.

**I. APPENDIX A: THEOREM DEMONSTRATION**

We want to compute the entropy variation of equation (11),

\[
\frac{\delta S}{\varepsilon} = \frac{S(p^\varepsilon) - S(p)}{\varepsilon},
\]

where the difference is respect the entropy computed with the perturbed probability distribution \( p^\varepsilon \) of equation (10), and the reference entropy. In appendix of ref.\(^{18}\) a demonstration of equation (11) is presented, but the reference PD is assumed symmetric and with infinite support. We extend their results for a general discrete non-symmetric PD with arbitrary support.

Using the perturbation form of equation (10), we can write

\[
S[p^\varepsilon] = -k_B \sum_{n=\alpha+1}^{\beta-1} [(1 - \varepsilon)p_n + \varepsilon p_{n+1} + \varepsilon p_{n-1}] \ln(p_n) - k_B[(1 - \varepsilon)p_\alpha + \varepsilon p_{\alpha+1}] \ln(p_\alpha) - k_B[(1 - \varepsilon)p_\beta + \varepsilon p_{\beta-1}] \ln(p_\beta).
\]

From this follows, rearranging terms,

\[
\delta S = k_B D[p_n||p^\varepsilon_n] + k_B \varepsilon \sum_{n=\alpha+1}^{\beta-1} (p_n - p_{n-1}) \ln(p_n) + k_B \varepsilon \sum_{n=\alpha}^{\beta-1} (p_n - p_{n+1}) \ln(p_n)
\]

where we have used the discrete form of the KLD and that \( p^\varepsilon_n = p_n + O(\varepsilon) \). The first term can be expanded in
series as

\[ D[p\|p^\varepsilon] = D[p\|p] + \frac{\partial D[p\|p^\varepsilon]}{\partial \varepsilon}\varepsilon + O(\varepsilon^2), \quad (25) \]

where \( D[p\|p] = 0 \) by definition. Thanks to the normalization of \( p^\varepsilon_n \) the term \( \frac{\partial D[p\|p^\varepsilon]}{\partial \varepsilon} = 0 \) in the limit \( \varepsilon \to 0^+ \). It follows that \( D[p\|p^\varepsilon] = o(\varepsilon^2) \). The following two terms can be expressed once more using the KLD, as

\[ \lim_{\varepsilon \to 0^+} \frac{\delta S}{\varepsilon} = k_B D[p_{n+1}\|p_n] + k_B D[p_{n-1}\|p_n], \quad (26) \]

with the understanding

\[ D(p_{n+1}\|p_n) = \sum_{n=\alpha+1}^{\beta} p_n \ln \left( \frac{p_{n+1}}{p_n} \right), \quad (27) \]

\[ D(p_{n-1}\|p_n) = \sum_{n=\alpha}^{\beta-1} p_{n+1} \ln \left( \frac{p_{n-1}}{p_n} \right). \quad (28) \]

The last results demonstrate the theorem.

1. J. C. Vasquez and D. Jou, Rep. Prog. Phys., vol. 66, 1937 (2004).
2. D. A. Sivak, G. E. Crooks, Phys. Rev. Lett., vol. 108, 150601 (2012).
3. G. E. Crooks, Phys. Rev. E, vol. 60, 2721 (1999).
4. C. Jarzynski, The European Phys. Journal B, vol. 64, 331 (2008).
5. C. Jarzynski, Ann. Rev. Condens. Matter Phys., vol. 2, 329 (2011).
6. T. Sagawa and M. Ueda, Phys. Rev. E, 85, 021104 (2012).
7. T. Sagawa and M. Ueda, Phys. Rev. Lett., 109, 180602 (2012).
8. E. T. Jaynes, Phys. Rev. A, vol. 106, 620 (1957).
9. E. T. Jaynes, Phys. Rev. A, vol. 108, 171 (1957).
10. G. Schulze, K. J. Franke, A. Gagliardi, G. Romano, C. S. Lin, A. L. Rosa, T. A. Niehaus, Th. Frauenheim, A. Di Carlo, A. Pecchia and J. I. Pascual, Phys. Rev. Lett., vol. 100, 136801 (2008).
11. Y. Dubi, M. Di Ventra, Rev. Mod. Phys., vol. 83, 131 (2011).
12. S. Toyabe, T. Sagawa, M. Ueda, E. Muneyuki and M. Sano, Nature Physics, 6, 988 (2010).
13. M. Auf der Maur, G. Penazzi, G. Romano, F. Sacconi, A. Pecchia and A. Di Carlo, IEEE Transactions on Electron Devices, vol. 58, 1425 (2011).
14. N. Merhav, Foundation and Trends in Communication and Information Theory, vol. 6, 1-212 (2009).
15. K. R. Narayanan and A. R. Sanistrava, Phys. Rev. E, vol. 85, 031151 (2012).
16. A. Gagliardi and A. Di Carlo, arXiv:submit/0713552 [cond-mat.stat-mech], (2013).
17. T. M. Cover and J. A. Thomas, “Elements of information theory”, Wyley (2006).
18. K. R. Narayanan and A. R. Sanistrava, arXiv:0711.1460 v2 [cond-mat.stat-mech] (2007).
19. A. Gagliardi and A. Di Carlo, Phys. A, vol. 391, 6337 (2012).
20. S.-I. Amari, Ann. Inst. Statist. Math. Vol. 41, No. 4, 623-648 (1989).
21. R. S. Ingarden, Int. J Engng Sci. Vol. 19, No 12, 1609 (1981).
22. R. J. Glauber, ”Quantum theory of optical coherence”, Wyley-VHC (2007).