

Existence of Temperature on the Nanoscale

Michael Hartmann,^{1,2,*} Günter Mahler,² and Ortwin Hess³

¹*Institute of Technical Physics, DLR Stuttgart, D-70569 Stuttgart, Germany*

²*Institute of Theoretical Physics I, University of Stuttgart, D-70550 Stuttgart, Germany*

³*Advanced Technology Institute, University of Surrey, Guildford GU2 7XH, United Kingdom*

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We consider a regular chain of quantum particles with nearest neighbor interactions in a canonical state with temperature T . We analyze the conditions under which the state factors into a product of canonical density matrices with respect to groups of n particles each and under which these groups have the same temperature T . In quantum mechanics the minimum group size n_{\min} depends on the temperature T , contrary to the classical case. We apply our analysis to a harmonic chain and find that $n_{\min} = \text{const}$ for temperatures above the Debye temperature and $n_{\min} \propto T^{-3}$ below.

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Recent progress in the synthesis and processing of materials with structures on nanometer length scales calls for better understanding of thermal properties of nanoscale devices, individual nanostructures, and nanostructured materials. Experimental techniques have improved to such an extent that the measurement of thermodynamic quantities like temperature with a spatial resolution on the nanometer scale seems within reach [1–4]. These techniques have already been applied for a new type of scanning microscopy, using a temperature sensor [5] that shows resolutions below 100 nm.

To provide a basis for the interpretation of present day and future experiments in this field, it is indispensable to clarify the applicability of the concepts of thermodynamics to systems on small length scales. In this context, one question appears to be particularly important and interesting: Can temperature be meaningfully defined on nanometer length scales?

The standard procedure to show that the thermodynamical limit, and therefore temperature, exists is based on the idea that, as the spatial extension increases, the surface of a region in space grows slower than its volume [6]. If the coupling potential is short ranged enough, the interactions between one region and another become negligible in the limit of infinite size.

However, the full scaling behavior of these interactions with respect to the size of the parts has, to our knowledge, not been studied in detail yet [7–9].

For standard applications of thermodynamics this might not be very important since the number of particles is typically so large that deviations from infinite systems may safely be neglected. Nevertheless, these differences could become significant as the considered systems approach nanoscopic scales. Here it is of special interest to determine the “grain size” needed to ensure the existence of local temperature.

Since a quantum description becomes imperative at nanoscopic scales, the following approach appears to be reasonable: Consider a large quantum system, brought into a thermal state via interaction with its environment,

divide this system into subgroups, and analyze for what subgroup size the concept of temperature is applicable.

We adopt here the convention that a local temperature exists if the considered part of the system is in a canonical state; i.e., the distribution is an exponentially decaying function of energy characterized by one single parameter. This implies that there is a one-to-one mapping between temperature and the expectation values of those observables, by which temperature is usually measured. After proper calibration, such measurements thus all yield the same temperature, contrary to distributions with several parameters. If the distribution were not exponentially decaying, physical quantities like energy would not have “sharp” values.

Our results are thus obtained from calculations with canonical ensembles. Approaches based on different ensembles (e.g., microcanonical ones), which are being discussed [10], may yield significantly different results.

In this Letter we study a chain of identical particles with next neighbor interactions which decomposes into N_G identical subgroups of n particles each. Assuming that the total system is in a thermal (canonical) state, we derive conditions on the interaction strength between the groups and the global temperature which ensure that the state of each group is approximately canonical. Finally, we apply these conditions to a harmonic chain and calculate the minimal group size n_{\min} , which is found to depend on the global temperature and the desired accuracy of the local thermodynamical description.

We start by defining the Hamiltonian of our chain in the form

$$H = \sum_i H_i \quad \text{with} \quad H_i = \frac{p_i^2}{2m} + U(q_i) + V(q_i, q_{i+1}), \quad (1)$$

where the index i labels the particles of mass m , and q_i and p_i are their positions and momenta, respectively. We assume periodic boundary conditions.

We now form N_G groups of n subsystems each [index $i \rightarrow (\mu - 1)n + j$; $\mu = 1, \dots, N_G$; $j = 1, \dots, n$] and split

this Hamiltonian into two parts,

$$H = H_0 + I, \quad (2)$$

where H_0 is the sum of the Hamiltonians of the isolated groups and I contains the interaction terms of each group with its neighbor group:

$$H_0 = \sum_{\mu=1}^{N_G} [\mathcal{H}_\mu - V(q_{\mu n}, q_{\mu n+1})]; \quad (3)$$

$$\mathcal{H}_\mu = \sum_{j=1}^n H_{n(\mu-1)+j}; \quad I = \sum_{\mu=1}^{N_G} V(q_{\mu n}, q_{\mu n+1}).$$

We label the eigenstates of the total Hamiltonian H and their energies with the greek indices (φ, ψ) and eigenstates and energies of the group Hamiltonian H_0 with latin indices (a, b),

$$H|\varphi\rangle = E_\varphi|\varphi\rangle \quad \text{and} \quad H_0|a\rangle = E_a|a\rangle. \quad (4)$$

Here, the states $|a\rangle$ are products of group eigenstates, with $E_a = \sum_{\mu=1}^{N_G} E_\mu$, where E_μ is the energy of one subgroup only, $[\mathcal{H}_\mu - V(q_{\mu n}, q_{\mu n+1})]|a\rangle = E_\mu|a\rangle$.

We assume that the total system is in a thermal state with a density matrix, which reads

$$\langle\varphi|\hat{\rho}|\psi\rangle = \frac{e^{-\beta E_\varphi}}{Z} \delta_{\varphi\psi} \quad (5)$$

in the eigenbasis of H . Here, Z is the partition sum and $\beta = (k_B T)^{-1}$ the inverse temperature. Transforming the density matrix (5) into the eigenbasis of H_0 we obtain

$$\langle a|\hat{\rho}|a\rangle = \int_{E_0}^{\infty} w_a(E) \frac{e^{-\beta E}}{Z} dE \quad (6)$$

for the diagonal elements. Here, the sum over all states $|a\rangle$ has been replaced by an integral over the energy. The conditional probabilities $w_a(E)$ are given by $w_a(E_\varphi) = \eta(E_\varphi) \sum_{\{H|\varphi\rangle = E_\varphi|\varphi\rangle} |\langle a|\varphi\rangle|^2$ with $\eta(E_\varphi)$ denoting the density of energy levels and the sum running over all states $|\varphi\rangle$ with $H|\varphi\rangle = E_\varphi|\varphi\rangle$. To compute the integral of Eq. (6) we need to know the distribution of the conditional probabilities $w_a(E)$.

In the limit of infinite number of groups N_G , $w_a(E_\varphi)$ converges to a Gaussian normal distribution,

$$\lim_{N_G \rightarrow \infty} w_a(E) = \frac{1}{\sqrt{2\pi}\sigma_a} \exp\left(-\frac{(E - E_a - \varepsilon_a)^2}{2\sigma_a^2}\right), \quad (7)$$

where the quantities ε_a and σ_a are defined by

$$\varepsilon_a \equiv \langle a|H|a\rangle - \langle a|H_0|a\rangle, \quad (8)$$

$$\sigma_a^2 \equiv \langle a|H^2|a\rangle - \langle a|H|a\rangle^2. \quad (9)$$

Note that ε_a has a classical counterpart while σ_a is purely quantum mechanical. It appears because the commutator

$[H, H_0]$ is nonzero, and the distribution $w_a(E)$ therefore has nonzero width.

The rigorous proof of Eq. (7) is given in [11] and is based on two assumptions: The energy of each group \mathcal{H}_μ as defined in Eq. (3) has to be bounded, i.e.,

$$\langle\chi|\mathcal{H}_\mu|\chi\rangle \leq C \quad (10)$$

for all normalized states $|\chi\rangle$ and some arbitrary constant C , and

$$\sigma_a^2 \geq N_G C' \quad (11)$$

for some constant $C' > 0$.

If these conditions are met, Eq. (6) can be computed for $N_G \gg 1$:

$$\langle a|\hat{\rho}|a\rangle = \frac{\exp(-\beta y_a + \frac{1}{2}\beta^2\sigma_a^2)}{2Z} \operatorname{erfc}\left(\frac{E_0 - y_a + \beta\sigma_a^2}{\sqrt{2}\sigma_a}\right), \quad (12)$$

where $y_a = E_a + \varepsilon_a$ and $\operatorname{erfc}(x)$ is the conjugate Gaussian error function. The second term appears because the energy is bounded from below and the integration extends from E_0 to ∞ .

If the argument of the error function divided by $\sqrt{N_G}$ is finite (different from zero), the conjugate error function can be approximated by its asymptotic expansion for $N_G \gg 1$ [12]: $\operatorname{erfc}(x) \approx \exp(-x^2)/\sqrt{\pi}x$ for $x \rightarrow \infty$ and $\operatorname{erfc}(x) \approx 2 + \exp(-x^2)/\sqrt{\pi}x$ for $x \rightarrow -\infty$.

The off diagonal elements $\langle a|\hat{\rho}|b\rangle$ vanish for $|E_a - E_b| > \sigma_a + \sigma_b$ because the overlap of the two distributions of conditional probabilities becomes negligible. For $|E_a - E_b| < \sigma_a + \sigma_b$, the transformation involves an integral over frequencies, and thus these terms are significantly smaller than the entries on the diagonal.

We now test under what conditions the density matrix $\hat{\rho}$ may be approximated by a product of canonical density matrices with temperature β_{loc} for each subgroup $\mu = 1, 2, \dots, N_G$. If we assume periodic boundary conditions, all reduced density matrices are equal and their product is of the form $\langle a|\hat{\rho}|a\rangle \propto \exp(-\beta_{\text{loc}} E_a)$. Since the trace of a matrix is invariant under basis transformations, it is sufficient to verify the correct energy dependence of the density matrix in the product basis. Thus the logarithm of the right hand side of Eq. (12) must be a linear function of E_a plus a possible constant. It follows from the asymptotic expansion of the conjugate error function that this can be the case only for

$$\frac{1}{\sqrt{N_G}} \frac{E_a + \varepsilon_a - E_0 - \beta\sigma_a^2}{\sqrt{2}\sigma_a} > 0, \quad (13)$$

meaning the left hand side (lhs) should have a finite positive value, and

$$-\varepsilon_a + \frac{\beta}{2}\sigma_a^2 \approx c_1 E_a + c_2, \quad (14)$$

where c_1 and c_2 are constants.

If $|c_1| \ll 1$, temperature becomes intensive:

$$\beta_{\text{loc}} = \beta. \quad (15)$$

Furthermore, to ensure that the density matrix of each subgroup μ is approximately canonical, it must hold that

$$-\frac{\varepsilon_{\mu-1} + \varepsilon_{\mu}}{2} + \frac{\beta}{4}(\sigma_{\mu-1}^2 + \sigma_{\mu}^2) + \frac{\beta}{6}\tilde{\sigma}_{\mu}^2 \approx c_1 E_{\mu} + c_2, \quad (16)$$

where $\varepsilon_{\mu} = \langle a|V(q_{\mu n}, q_{\mu n+1})|a\rangle$, $\sigma_{\mu}^2 = \langle a|\mathcal{H}_{\mu}^2|a\rangle - \langle a|\mathcal{H}_{\mu}|a\rangle^2$ and $\tilde{\sigma}_{\mu}^2 = \sum_{\nu=\mu-1}^{\mu+1} \langle a|\mathcal{H}_{\nu-1}\mathcal{H}_{\nu}|a\rangle + \langle a|\mathcal{H}_{\nu}\mathcal{H}_{\nu-1}|a\rangle - 2\langle a|\mathcal{H}_{\nu-1}|a\rangle\langle a|\mathcal{H}_{\nu}|a\rangle$.

For a model obeying Eqs. (10) and (11), the two conditions (13) and (16), which constitute the general result of this Letter, must both be satisfied. These fundamental criteria are now applied to a concrete example.

Thermal properties of insulating solids are quite successfully described by harmonic lattice models. We therefore consider as an example a harmonic chain of $N_G \cdot n$ sites with periodic boundary conditions. In this case, the potentials read

$$U(q_i) = \frac{m}{2}\omega_0^2 q_i^2 \quad \text{and} \quad V(q_i, q_{i+1}) = -m\omega_0^2 q_i q_{i+1}, \quad (17)$$

where q_i is the displacement of the particle at site i from its equilibrium position $i \cdot a_0$ with a_0 being the distance between neighboring particles at equilibrium. We divide the chain into N_G groups of n particles each and thus get a partition of the type considered above. The Hamiltonian of one group is diagonalized by a Fourier transformation and reads in terms of creation and annihilation operators a_k^{\dagger} and a_k [13],

$$\mathcal{H}_{\mu} - V(q_{\mu n}, q_{\mu n+1}) = \sum_k \omega_k \left(a_k^{\dagger} a_k + \frac{1}{2} \right) \quad (18)$$

with $k = \pi l / (a_0(n+1))$ ($l = 1, 2, \dots, n$) and $\omega_k^2 = 4\omega_0^2 \sin^2(ka_0/2)$. We chose $\hbar = 1$.

We first check condition (11). Expressing the group interaction $V(q_{\mu n}, q_{\mu n+1})$ also in terms of a_k^{\dagger} and a_k , one sees that $\tilde{\sigma}_{\mu} = 0$ for all μ and therefore $\sigma_a^2 = \sum_{\mu=1}^{N_G} \sigma_{\mu}^2$, where σ_{μ} has a minimum value since $[a_k, a_p^{\dagger}] = \delta_{kp}$ ($\sigma_{\mu}^2 \geq 4\omega_0 n / 3\pi$). σ_a^2 thus fulfills condition (11).

To satisfy condition (10) we consider only states where the energy of every group, including the interactions with its neighbors, is bounded. Thus, our considerations do not apply to product states $|a\rangle$, for which all the energy was located in only one group or only a small number of groups. For $N_G \gg 1$, the number of such states is vanishingly small compared to the number of all product states.

To analyze conditions (13) and (16), we make use of the continuum or Debye approximation [14], requiring $n \gg 1$

and $a_0 \ll l$, where $l = na_0$, the length of the chain, is finite. In this case we have $\omega_k \approx vk$ with the constant velocity of sound $v = \omega_0 a_0$ and $\sigma_{\mu}^2 = 4n^{-2} E_{\mu} E_{\mu+1}$.

It is sufficient to satisfy conditions (13) and (16) for some adequate energy range $E_{\min} \leq E_{\mu} \leq E_{\max}$. We therefore need to estimate E_{\min} and E_{\max} . The total chain is in a thermal state. Let \bar{E} be the expectation value of its energy without the ground state energy,

$$\bar{E} = N_G n k_B \Theta \left(\frac{T}{\Theta} \right)^2 \int_0^{\Theta/T} \frac{x}{e^x - 1} dx. \quad (19)$$

Here, Θ is the Debye temperature, which is a characteristic constant of the material chosen and can be found tabulated [14]. We then choose

$$\frac{1}{\alpha} \frac{\bar{E}}{N_G} + \frac{E_0}{N_G} \leq E_{\mu} \leq \alpha \frac{\bar{E}}{N_G} + \frac{E_0}{N_G} \quad (20)$$

with $\alpha \gg 1$. The product of the strongly growing density of states and the exponentially decaying occupation probability forms a sharp peak around \bar{E} . The above energy range has been chosen to be centered at this peak and to be significantly larger than its width.

We now analyze conditions (13) and (16) for the harmonic chain in Debye approximation. In this case, condition (13) translates into

$$\frac{1}{\sqrt{N_G}} \frac{\sum_{\mu=1}^{N_G} E_{\mu} - E_0 - 4\beta n^{-2} \sum_{\mu=1}^{N_G} E_{\mu} E_{\mu+1}}{\sqrt{2} \sqrt{4n^{-2} \sum_{\mu=1}^{N_G} E_{\mu} E_{\mu+1}}} > 0, \quad (21)$$

where $\varepsilon_{\mu} = 0$, $\tilde{\sigma}_{\mu} = 0$, $n+1 \approx n$ has been used. For $\bar{E} > E_0$, condition (16) turns out to be stronger and (21) becomes irrelevant. For $\bar{E} < E_0$, Eq. (21) is hardest to satisfy if all E_{μ} are equal to the lower boundary of the energy range (20). For n one thus gets

$$n > 4 \frac{\Theta}{T} \frac{\alpha}{\bar{e}} \left(\frac{\bar{e}}{\alpha} + \frac{1}{4} \right)^2, \quad (22)$$

where $\bar{e} = \bar{E} / (n N_G k_B \Theta)$ and we have used $E_0 = n N_G k_B \Theta / 4$.

To investigate condition (16) we take the derivative with respect to E_{μ} on both sides,

$$\frac{\beta}{n^2} \left(E_{\mu-1} + E_{\mu+1} - 2 \frac{E_0}{N_G} \right) + \frac{2\beta}{n^2} \frac{E_0}{N_G} \approx c_1, \quad (23)$$

where we have separated the energy dependent and the constant part on the lhs. Equation (23) is satisfied if the energy dependent part, the first term, is much smaller than 1. Taking $E_{\mu-1}$ and $E_{\mu+1}$ equal to the upper bound in Eq. (20), this yields

$$n > \frac{2\alpha}{\delta} \frac{\Theta}{T} \bar{e}, \quad (24)$$

where the ‘‘accuracy’’ parameter $\delta \ll 1$ quantifies the value of the energy dependent part in (23).

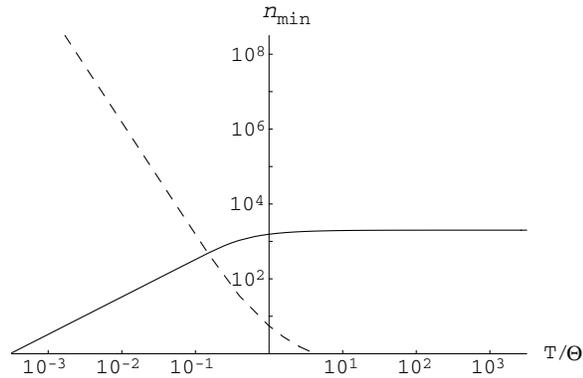


FIG. 1. Log-log plot of n_{\min} from Eq. (22) (dashed line) and n_{\min} from Eq. (24) (solid line) for $\alpha = 10$ and $\delta = 0.01$ as a function of T/Θ for a harmonic chain. δ and α are defined in Eqs. (24) and (20), respectively.

Since, by virtue of Eqs. (22) and (24), the constant part in the lhs of (23) satisfies $(2\beta/n^2)(E_0/N_G) < \sqrt{\delta}/(\sqrt{2}\alpha) - \delta/\alpha^2 \ll 1$, temperature is intensive.

Inserting Eq. (19) into Eq. (22) and (24) one can now calculate the minimal n for given δ , α , Θ , and T . Figure 1 shows n_{\min} for $\alpha = 10$ and $\delta = 0.01$ given by criterion (22) and (24), respectively, as a function of T/Θ .

For high (low) temperatures n_{\min} can thus be estimated by

$$n_{\min} \approx \begin{cases} 2\alpha/\delta & \text{for } T > \Theta, \\ (3\alpha/2\pi^2)(\Theta/T)^3 & \text{for } T < \Theta. \end{cases} \quad (25)$$

The characteristics of Fig. 1 are determined by the energy dependence of σ_a . The low temperature behavior, in particular, is related to the fact that σ_a has a nonzero minimal value. This fact does not only appear in the harmonic chain but is a general feature of interacting quantum particles. The commutator $[H, H_0]$ is nonzero and the ground state of the total system is energetically lower than the lowest product state; therefore, σ_a is nonzero, even at zero temperature [8,15].

Finally, the minimal length scale on which temperature exists according to our approach is given by

$$l_{\min} = n_{\min} a_0, \quad (26)$$

where a_0 is the lattice constant. Temperature measurements with a higher resolution should no longer be interpreted in a standard way.

Let us conclude with some numerical estimates: Choosing the ‘‘accuracy parameters’’ to be $\alpha = 10$ and $\delta = 0.01$, we get for hot iron ($T \gg \Theta \approx 470$ K, $a_0 \approx 2.5$ Å) $l_{\min} \approx 50$ μm, while for carbon ($\Theta \approx 2230$ K, $a_0 \approx 1.5$ Å) at room temperature (270 K) $l_{\min} \approx 10$ μm. The coarse graining will experimentally be most relevant at very low temperatures, where l_{\min} may even become macroscopic. A pertinent example is silicon ($\Theta \approx 645$ K, $a_0 \approx 2.4$ Å), which has $l_{\min} \approx 10$ cm at $T \approx 1$ K (again with $\alpha = 10$ and $\delta = 0.01$).

In summary, we have considered a linear chain of particles interacting with their nearest neighbors. We have partitioned the chain into identical groups of n adjoining particles each. Taking the number of such groups to be very large and assuming the total system to be in a thermal state with temperature T we have found conditions [Eqs. (13) and (16)], which ensure that each group is approximately in a thermal state with the same temperature T , implying intensivity. In the quantum regime, these conditions depend on the temperature T , contrary to the classical case.

We have then applied our general method to a harmonic chain. Equations (25) and (26) provide a first estimate of the minimal length scale on which intensive temperatures exist. This length scale should also constrain the way one can meaningfully define temperature profiles in nonequilibrium scenarios [16].

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*Electronic address: michael.hartmann@dlr.de

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