Maximum Efficiency of Ideal Heat Engines Based on a Small System: Correction to the Carnot Efficiency at the Nanoscale

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We study the maximum efficiency of a heat engine based on a small system. It is revealed that due to the finiteness of the system, irreversibility may arise when the working substance contacts with a heat reservoir. As a result, there is a working-substance-dependent correction to the Carnot efficiency. We derive a general and simple expression for the maximum efficiency of a Carnot cycle heat engine in terms of the relative entropy. This maximum efficiency approaches the Carnot efficiency asymptotically when the size of the working substance increases to the thermodynamic limit. Our study extends Carnot’s result of the maximum efficiency to an arbitrary working substance and demonstrates the subtlety of thermodynamic laws in small systems.

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Introduction: Carnot conceived an ideal thermodynamic cycle, which consists of two isothermal and two adiabatic processes [1]. This cycle, now known as Carnot cycle, has the highest efficiency among all thermodynamic cycles. The Carnot cycle is of great importance in the development of the principles of thermodynamics, especially the second law of thermodynamics. For a Carnot cycle, its efficiency is given by \( \eta_C = 1 - \frac{T_C}{T_H} \), where \( T_C \) and \( T_H \) describe the temperatures of the cold and the hot heat reservoirs respectively. Since Carnot’s era it has been widely accepted that the maximum efficiency (the Carnot efficiency) does not depend on the details of the working substance [1] (when the working substance is in the thermodynamic limit, the Carnot efficiency is synonymous to the maximum efficiency of a heat engine). In most textbooks the Carnot efficiency is derived by utilizing thermodynamic methods, such as using the thermodynamic (or absolute) temperature scale (see Ref [2] for example), in which it was assumed implicitly that the working substance is in the thermodynamic limit. One exception, however, is Gibbs’ book [3], where the Carnot efficiency is derived from the first principle. In obtaining the result, it has been assumed implicitly that the system is always in a canonical distribution in all the four thermodynamic processes [4]. In the isothermal processes, this is certainly true. In the adiabatic processes, however, this assumption is not obviously consistent with classical mechanics [5] (or quantum mechanics [6]), because Hamiltonian dynamics (or quantum mechanics) does not necessarily maintain the canonical distribution. The subtlety is that for the working substance in the thermodynamic limit, the above assumption is always valid. Nevertheless, for the working substance in the opposite limit, i.e., for a small system consisting of a few molecules, this assumption usually does not hold true [5] and it may lead to a non-negligible correction to the Carnot efficiency [5] (see also [7]), or alternatively, in a small system, the Carnot efficiency is no longer synonymous to the maximum efficiency of an ideal heat engine.

In recent years, thermodynamics of small systems has attracted a lot of attention [8,9]. Some theorems concerning far from equilibrium processes have been discovered [10–12], and have been verified experimentally in small systems, for example, in a single RNA molecular chain [13]. In the field of thermodynamics in small systems an important question is the validity of the thermodynamic laws when the system is in the opposite regime of the thermodynamic limit - only a few particles are involved. In recent years some investigations have been carried out to reexamine the validity of the laws and principles of thermodynamics in small systems. For example in Ref. [14,15], it has been pointed out that irreversibility may arise when the system contacts with a heat reservoir due to the finiteness of the system. In Ref. [5] it has been pointed out that the Carnot efficiency may not be achieved in a small system. In the study of its quantum analogue, it has been emphasized in Refs. [6] (see also [5,14,16]) that two conditions (i) the process must be quasi-static and (ii) all energy levels change in the same ratio in the adiabatic process must be satisfied in order to achieve the Carnot efficiency. When either condition is not satisfied, the maximum efficiency of the heat engine will be lower than the Carnot efficiency. Despite of the rapid progress in this research field in the last few years, a key question remains to be answered: What is the maximum efficiency of an ideal heat engine when the working substance is much less than the thermodynamic limit? and if the maximum efficiency is lower than the Carnot efficiency, how does the result reconcile with the Carnot’s theorem in the thermodynamic limit?

In this letter we address this question and derive a simple and general expression for the maximum efficiency of an ideal heat engine based on an arbitrary system. For macroscopic system, the maximum efficiency reproduces the Carnot efficiency. For a microscopic system, the maximum efficiency approaches the Carnot efficiency only in special cases, i.e., when the all energy levels of the system change in the same ratio in the adiabatic process. Otherwise a correction to the Carnot efficiency occurs. We would like to mention that the efficiency of a Carnot cycle at the maximum power [17] has been extensively studied in recent years, but our emphasis is different. We only consider the quasi-static process or zero power case. Instead of focusing on the maximum power, our emphasis is put on the correction to the Carnot efficiency due to the finite size effect. For simplicity, we
will focus on the classical system. The extension of our current study to quantum systems \[18\] is straightforward.

**Carnot cycle at the nanoscale:** As is known a Carnot cycle consists of two isothermal and two adiabatic processes. When all the processes proceed quasi-statically or reversibly, the efficiency approaches its maximum value, \(\eta = 1 - \frac{T_C}{T_H}\) which depends only on the temperatures of the two heat reservoirs, and has nothing to do with the details of the working substance \[14\]. Let us recall that a Carnot cycle consists of four processes (See Fig. 1). It starts from an isothermal process \((A \rightarrow B)\). In order to achieve the maximum efficiency, this process proceeds quasi-statically, so that the system is always in a canonical distribution at every instant of the process and its temperature is always equal to the temperature of the heat reservoir \(T_H\). After this process, the system of interest is taken out of the heat reservoir at instant \(B\). Some external parameters are manipulated quasi-statically and adiabatically in the following process \((B \rightarrow C')\). This is an adiabatic process. In order to achieve the maximum efficiency, this process also needs to proceed slow enough, or quasi-statically. At the end of this adiabatic process \((B \rightarrow C')\), the system may or may not be in a canonical distribution even though at the beginning of the process (at instant \(B\)) the system is. Hence, in general one cannot use an effective temperature to describe the system after the adiabatic process \[5,14\] unless the system satisfies certain conditions or its size is large enough (We will clarify later that for a system in the thermodynamic limit, it is very close to a canonical distribution at instant \(C'\), so that one can still assign an effective temperature to it). When the system is not in a canonical distribution after the adiabatic process, there is an irreversible relaxation process of the system soon after it is put into contact with a heat reservoir (we have carefully chosen the parameter \(\lambda_C\) such that the average energy of the system does not change after the relaxation process.) \[14\].

We use \(C'\) and \(C\) to denote the states of the system before and after the relaxation. After the relaxation the system reaches a canonical distribution and the temperature of the system is equal to that of the lower temperature heat reservoir. We will see that in the thermodynamic limit, the effect of the relaxation process can be ignored, because the entropy increases in the relaxation process is negligibly small in comparison with the entropy of the system. Following the relaxation process there is another isothermal compression process \((C \rightarrow D)\). This is similar to the isothermal expansion process in which the system is always in equilibrium with the lower temperature heat reservoir (it is always in a canonical distribution during this process). After the isothermal compression process another adiabatic compression process \((D \rightarrow A')\) follows. Similar to the adiabatic expansion process \((B \rightarrow C')\), the small system may not be in a canonical distribution during the adiabatic process even though it proceeds quasi-statically. In order to restore the working substance to its original state, we need to put the system into contact with the heat reservoir at temperature \(T_H\) again. The process is irreversible, because the system will relax from a non-canonical distribution \(A'\) to a canonical one \(A\). In the relaxation process, although the average energy does not change, the statistical entropy of the ensemble increases in this relaxation process. The reason is that for a given average energy, the distribution which maximizes the entropy is the canonical distribution.

In order to describe the whole thermodynamic cycle, we use a parameter \(\lambda\) to describe the cycle (See Fig. 1). The thermody-
The adiabatic processes.

Entropy is a widely used quantity in the studies of (quantum) information theory [20] and non-equilibrium thermodynamics [14, 21–23]. This quantity is non-negative, and is equal to zero only when the two distributions are identical.

D-sman's constant. The efficiency of the thermodynamic cycle can be expressed as the parameter \( \lambda \) and the temperature \( T \) can be determined by the conditions of the average energy during the relaxation process

\[
\langle E_l \rangle = \int d\Gamma_l \rho^{eq}(\lambda_l, \Gamma_l) H(\lambda_l, \Gamma_l)
\]

\[
= \int d\Gamma \rho(\lambda, \Gamma) H(\lambda, \Gamma) \equiv \langle E_l \rangle, (l = A, C).
\]

We consider \( l = C \) as an example. Here \( \Gamma_C \) represents a point in the phase space with the parameter \( \lambda_C \): \( \rho^{eq}(\lambda_C, \Gamma_C) \propto \exp \left[ -\beta H(\lambda_C, \Gamma_C) \right] \) describes the equilibrium (canonical) distribution of the microscopic states in the phase space with the parameter \( \lambda_C \) and the temperature \( T_C \) (point \( C \) in Fig. 1); \( H(\lambda_C, \Gamma_C) \) describes the energy of the system; \( \rho(\lambda_C', \Gamma_C') \) describes the density distribution of the states of the system in the phase space evolving from an equilibrium (canonical) distribution \( \rho^{eq}(\lambda_B, \Gamma_B) \propto \exp \left[ -\beta H(\lambda_B, \Gamma_B) \right] \), and \( \rho(\lambda_C', \Gamma_C') \) is not necessarily to be in an equilibrium (canonical) distribution [5].

The heat absorbed \( dQ_H \) in the isothermal expansion process \( (A \rightarrow B) \) and released \( dQ_C \) in the isothermal contraction process \( (C \rightarrow D) \) can be expressed as

\[
dQ_H = T_H(S_B - S_A),
\]

\[
dQ_C = T_C(S_C - S_D),
\]

where \( S_i = -k_B \int d\Gamma_i \rho^{eq}(\lambda_i, \Gamma_i) \ln \rho^{eq}(\lambda_i, \Gamma_i), (i = A, B, C, D) \) is the equilibrium thermodynamic entropy; \( k_B \) is the Boltzmann's constant. The efficiency of the thermodynamic cycle can be expressed as the \( \eta_{max} \equiv \frac{dW}{dQ_H} = 1 - \frac{dQ_C}{dQ_H} \). Substituting Eq. 1 into the expression of the efficiency we obtain

\[
\eta_{max} = 1 - \frac{T_C[(S_{C'} - S_D) + (S_C - S_{C'})]}{T_H[(S_B - S_A) - (S_A - S_{A'})]},
\]

where \( S_j = -k_B \int d\Gamma_j \rho(\lambda_j, \Gamma_j) \ln \rho(\lambda_j, \Gamma_j), (j = A', C') \) is the statistical entropy of the ensemble after the adiabatic evolution \( D \rightarrow A' \) and \( B \rightarrow C' \). Because of the Liouville theorem, the statistical entropy of the working substance remains a constant in the adiabatic processes \( S_B = S_{C'}, S_D = S_A' \). In addition, the change of the entropy of the system in the relaxation process can be expressed as a relative entropy [14] due to the conditions of the average energy [1]

\[
S_l - S_{l'} = D[\rho_{l'}^{eq}|\rho_l^{eq}]
\]

\[
\equiv \int d\Gamma \rho(\lambda, \Gamma) \ln \frac{\rho(\lambda, \Gamma)}{\rho^{eq}(\lambda, \Gamma)}(l = A, C),
\]

where \( D[\rho_{l'}^{eq}|\rho_l^{eq}], (l = A, C) \) is the relative entropy [19] of the two distributions of ensembles in the phase space. Relative entropy is a widely used quantity in the studies of (quantum) information theory [20] and non-equilibrium thermodynamics [14, 21–23]. This quantity is non-negative, and is equal to zero only when the two distributions are identical \( \rho_l^{eq} = \rho_{l'}^{eq} \).
or in our case the system changes from one canonical distribution to another. Substituting the above equation into Eq. (3), the maximum efficiency can be expressed in terms of the relative entropy 

$$\eta_{\text{max}} = 1 - \frac{T_C \{ (S_B - S_D) + D[\rho_C \| \rho_C^0] \}}{T_H \{ (S_B - S_D) - D[\rho_A \| \rho_A^0] \}}.$$  

(4)

This is the main result of our letter. Because of the facts $S_B - S_D > 0$ and both relative entropies $D[\rho_C \| \rho_C^0]$ and $D[\rho_A \| \rho_A^0]$ are nonnegative, from the expression of the efficiency (3) we immediately obtain the relation $\eta_{\text{max}} \leq \eta_C = 1 - \frac{4}{\pi^2}$. Here, the equality holds only when both $D[\rho_C \| \rho_C^0]$ and $D[\rho_A \| \rho_A^0]$ are equal to zero. We emphasize that the efficiency obtained here is universal, because it holds irrespective of the working substance. From the Carnot theorem, one would naturally expect that when the working substance is in the thermodynamic limit $N \to \infty$ (here $N$ is the number of the particles of the system) the above maximum efficiency (4) approaches the Carnot efficiency so that our result can reconcile with Carnot’s theorem. That is, in the thermodynamic limit, the relative entropy $D[\rho_C \| \rho_C^0]$ and $D[\rho_A \| \rho_A^0]$ should be negligibly small in comparison with $S_B - S_D$. Because both $S_B$ and $S_D$ are thermodynamic entropy, and hence are extensive quantities $S_B \propto N$, $S_D \propto N$, we expect that in the thermodynamic limit, the relative entropy increases slower than $N$:

$$\lim_{N \to \infty} \frac{D[\rho_V \| \rho_V^0]}{N} \to 0, (l = A, C).$$  

(5)

A rigorous proof of this result is given in the supplemental material. In the following we use a simple example to demonstrate our main result. We will show that in the extreme limit of a few particles the correction is non-negligible. The correction to the Carnot efficiency decreases with the increase of the number of the particles involved. In the thermodynamic limit, our result reproduces the Carnot efficiency. Hence, our result of the maximum efficiency (equation (4)) includes the Carnot efficiency as a special case.

**Example:** In order to achieve the Carnot efficiency, the key requirement is that the system always be in a canonical distribution (at a varying temperature) in the two adiabatic processes $B \to C'$ and $D \to A'$ [5, 16, 17]. For classical systems this is equivalent to the requirement that the energy of the system changes in the same ratio in the adiabatic process. Let us consider a system consisting of $N$ weakly coupled particles described by the following Hamiltonian

$$H = \sum_{\alpha=x,y,z} \sum_{i=1}^N \frac{\lambda^2_i \mathbf{q}_i^2}{2m} + |a(t)q_{i,\alpha}|^{\alpha(t)} + V,$$

(6)

where $m$ is the mass of a particle; $a(t)$ and $\lambda(t)$ are two controlling parameters; $q_{i,\alpha}$ and $p_{i,\alpha}$ denote the position and the momentum of the $\alpha$ ($\alpha = x, y, z$) degree of freedom of the $i$th particle. The interactions among these particles $V$ are so weak that they can be ignored in comparison with the kinetic and potential energy of the particles, but they are strong enough to make the $N$-particle system to be ergodic. When one fixes $\lambda = 2$ and varies $a(t)$, this is a forced harmonic oscillator. It can be easily checked that when $\lambda$ is fixed, and $a(t)$ is varied quasistatically and adiabatically, we obtain

$$D[\rho_C \| \rho_C^0] = 3Nk_B \frac{2 - \frac{\lambda C}{2\lambda C}}{2\lambda C} + k_B \ln \left[ \frac{\Gamma \left( \frac{3N + 2 + \frac{\lambda C}{2\lambda C}}{2\lambda C} + 1 \right)}{\Gamma \left( \frac{3N + 1}{2\lambda C} \right)} \right] + \frac{3Nk_B}{2 - \frac{\lambda C}{2\lambda C}} \left\{ \ln \left[ \frac{\Gamma \left( \frac{3N + 2 + \frac{\lambda C}{2\lambda C}}{2\lambda C} \right)}{\Gamma \left( \frac{3N}{2\lambda C} \right)} \right] - \ln \left[ \frac{\Gamma \left( \frac{3N + \lambda C}{2\lambda C} \right)}{\Gamma \left( \frac{3N}{2\lambda C} \right)} \right] \right\},$$  

(7)

where $\alpha = x, y, z$ is the mass of a particle; $a(t)$ and $\lambda(t)$ are two controlling parameters; $q_{i,\alpha}$ and $p_{i,\alpha}$ denote the position and the momentum of the $\alpha$ ($\alpha = x, y, z$) degree of freedom of the $i$th particle. The interactions among these particles $V$ are so weak that they can be ignored in comparison with the kinetic and potential energy of the particles, but they are strong enough to make the $N$-particle system to be ergodic. When one fixes $\lambda = 2$ and varies $a(t)$, this is a forced harmonic oscillator. It can be easily checked that when $\lambda$ is fixed, and $a(t)$ is varied quasistatically and adiabatically, we obtain

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(7)
where $\Gamma(x)$ is the Gamma function. Similarly we obtain an expression for $D[\rho_A || \rho_A^{eq}]$. Substituting them into Eq. 4 we obtain the maximum efficiency and the correction to the Carnot efficiency (see Fig. 3). Meanwhile, from Eq. (7) one can see that $\lim_{N \to \infty} D[\rho_v || \rho_v^{eq}]/N \to 0$ is satisfied. This means when the particle number is large, not necessarily to be close to $N \sim 10^{23}$, the correction is already vanishingly small in comparison with $S_B - S_D$, which is proportional to $N$. Hence, in the thermodynamic limit the maximum efficiency reproduces the Carnot efficiency $\eta_{max} \to \eta_C = 1 - \frac{C}{T_H}$. Nevertheless, when the particle number is in the opposite limit $N \to 1$, the correction to the Carnot efficiency may have observable consequence in experiments. In Fig. 3 we plot the maximum efficiency as a function of the particle number. It can be seen that this correction to the Carnot efficiency is less prominent when the particle number is larger than 20. Although the deviation from the Carnot efficiency in our example is tiny (less than two percent), it well serves the purpose to demonstrate our main results.

One can understand the correction to the Carnot efficiency through the following fact: the canonical ensemble and the microcanonical ensemble are equivalent in the thermodynamic limit. However, these two ensembles are not equivalent when the system is in the extremely small limit.

![FIG. 3: Relative efficiency of a Carnot cycle as a function of the particle number $N$. Here we choose the Boltzmann constant $k_B = 1$, the temperatures $T_H = 4.6$, $T_C = 2.3$, and the parameters of the cycle $\lambda_B = 2$, and $\lambda_D = 4$.](image)

**Discussion and conclusion:** The Carnot efficiency is a milestone in the development of the principles of traditional thermodynamics. Since Carnot’s seminal work [1] in 1820s it has been widely accepted that the maximum efficiency of an ideal heat engine depends only on the temperatures of the two heat reservoirs, and does not depend on the details of the working substance. In this letter we reexamine the maximum efficiency of a heat engine based on a small system. We find, however, this statement may not hold true when the working substance consists of only a few particles (at the nanoscale). The Carnot efficiency is not synonymous to the maximum efficiency of an ideal heat engine based on a small system if the variation of the potential is fixed. By utilizing the Liouville theorem and the adiabatic invariant, we derive a universal and simple expression for the maximum efficiency and the correction to the Carnot efficiency (see Fig. 3). Meanwhile, from Eq. (7) one can see that $\lim_{N \to \infty} D[\rho_v || \rho_v^{eq}]/N \to 0$ is satisfied. This means when the particle number is large, not necessarily to be close to $N \sim 10^{23}$, the correction is already vanishingly small in comparison with $S_B - S_D$, which is proportional to $N$. Hence, in the thermodynamic limit the maximum efficiency reproduces the Carnot efficiency $\eta_{max} \to \eta_C = 1 - \frac{C}{T_H}$. Nevertheless, when the particle number is in the opposite limit $N \to 1$, the correction to the Carnot efficiency may have observable consequence in experiments. In Fig. 3 we plot the maximum efficiency as a function of the particle number. It can be seen that this correction to the Carnot efficiency is less prominent when the particle number is larger than 20. Although the deviation from the Carnot efficiency in our example is tiny (less than two percent), it well serves the purpose to demonstrate our main results.

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Combining Eq. (9) and Eq. (10) we obtain the following relation.

**A: PROOF OF EQUATION (5) OF THE MAIN BODY**

Equation (5) in the main body is

\[
\lim_{N \to \infty} \frac{D[\rho_{l}||\rho_{l}^{\text{eq}}]}{N} \to 0, (l = A, C).
\]  

We will prove the case of \(l = C\). The case of \(l = A\) can be proved in a similar way. The sketch of the proof of this equation can be outlined as follows: The system consists of \(N\) particles. At instant \(B\), the canonical ensemble \(\rho_{B}^{\text{eq}}\) is indistinguishable from a microcanonical ensemble of the \(N\)-particle system when \(N\) approaches infinity (\(N \to \infty\)). After the quasistatic process, at instant \(C'\), the ensemble \(\rho_{C'}\) is also very close to a microcanonical ensemble if \(N\) approaches infinity (\(N \to \infty\)). Let us consider the subsystem of a single particle, and denote its density distribution function with \(\rho_{\text{sub}}\). At point \(C'\), the subsystem is exactly a canonical ensemble if \(N \to \infty\)

\[
\lim_{N \to \infty} D[\rho_{\text{sub}}||\rho_{\text{sub}}^{\text{eq}}] \to 0,
\]

where \(\rho_{\text{sub}}^{\text{eq}}\) is the equilibrium (canonical) distribution function of a single particle. It can be obtained from the equilibrium density distribution function of \(N\) particle \(\rho_{C'}^{\text{eq}}\). For a system of \(N\) particles (weakly coupled and decomposable), we have

\[
D[\rho_{C'}||\rho_{C'}^{\text{eq}}] = ND[\rho_{\text{sub}}||\rho_{\text{sub}}^{\text{eq}}].
\]

Combining Eq. (9) and Eq. (10) we obtain the following relation

\[
\lim_{N \to \infty} \frac{D[\rho_{C'}||\rho_{C'}^{\text{eq}}]}{N} \to 0.
\]
**B: CALCULATION OF THE RELATIVE ENTROPY**

Number of states in the phase space enclosed by the energy shell for a $N$-particle system in a $d$-dimensional potential:

Let us consider a system consisting of $N$ particles in $d$ dimension. The Hamiltonian of the system can be written as

$$ H = \sum_{\alpha=1}^{d} \sum_{i=1}^{N} \frac{p_{i,\alpha}^2}{2m} + |a q_{i,\alpha}|^{\lambda(t)} + V. \quad (12) $$

Here $q_{i,\alpha}$ and $p_{i,\alpha}$ denote the position and the momentum of the $\alpha$th degree of freedom of the $i$th particle. The interactions among particles $V$ are so weak that they can be ignored in comparison with the kinetic and potential energy of the particles. Meanwhile they are strong enough to ensure the $N$-particle system to be ergodic. In the following we will derive Eq. (7) of the main body.

Let us start from calculating the volume of the phase space as a function of the total energy $E$. The partition function of the $N$-particle system is

$$ Z_N = \frac{1}{N!} \left[ \frac{1}{h} \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dq \exp \left[ -\beta \left( \frac{p^2}{2m} + |a q|^{\lambda} \right) \right] \right]^{dN} $$

$$ = \frac{1}{N!} \left[ \frac{1}{h} \sqrt{2\pi m} \frac{2}{\Gamma} \left( 1 + \frac{1}{\lambda} \right) \right]^{dN} \beta^{-\frac{dN}{2}} - dN, \quad (13) $$

where $h$ is Planck’s constant, $\Gamma(x)$ is the Gamma function and we have used the following relation

$$ \int_0^{\infty} dx \exp \left[ -ax^b \right] = a^{-\frac{1}{b}} \Gamma \left( 1 + \frac{1}{b} \right). \quad (14) $$

The density of states of the $N$-particle system

$$ \frac{\partial \Phi(E)}{\partial E} = g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Z_N d\beta, (\beta' > 0), $$

$$ Z_N = \int_0^{\infty} g(E) e^{-\beta E} dE, \quad (15) $$

where $\Phi(E)$ is the number of states in the phase space enclosed by the energy shell characterized by the total energy $E$. The density of state for the $N$-particle system in a power law potential is

$$ g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} \frac{1}{N!} \left[ \frac{1}{h} \sqrt{2\pi m} \frac{2}{\Gamma} \left( 1 + \frac{1}{\lambda} \right) \right]^{dN} \beta^{-\frac{dN}{2}} - dN d\beta. \quad (16) $$

By utilizing the relation

$$ \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} \exp (sx) \frac{ds}{s^{n+1}} = \begin{cases} \frac{x^n}{n!} & (x > 0) \\ 0 & (x < 0) \end{cases}, \quad (17) $$

we have

$$ g(E) = \frac{1}{N!} \left[ \frac{1}{h} \sqrt{2\pi m} \frac{2}{\Gamma} \left( 1 + \frac{1}{\lambda} \right) \right]^{dN} \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} \beta^{-\frac{dN}{2}} - dN d\beta $$

$$ = \frac{1}{N!} \left[ \frac{1}{h} \sqrt{2\pi m} \frac{2}{\Gamma} \left( 1 + \frac{1}{\lambda} \right) \right]^{dN} E^{\frac{dN}{2} + \frac{dN}{\lambda} - 1} \frac{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda} \right)}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda} + 1 \right)}. \quad (18) $$

The number of states in the phase space enclosed by the energy shell is then given by

$$ \Phi(E, \beta) = \int_0^{E} g(E') dE' $$

$$ = \frac{1}{N!} \left[ \frac{1}{h} \sqrt{2\pi m} \frac{2}{\Gamma} \left( 1 + \frac{1}{\lambda} \right) \right]^{dN} \frac{E^{\frac{dN}{2} + \frac{dN}{\lambda}}}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda} + 1 \right)}. \quad (19) $$
Determining parameters of the thermodynamic cycle of the heat engine: We assume the particles are weakly coupled, so the N-particle system is ergodic and the adiabatic invariant of the system can be used to determine the final energy of the system from its initial energy. The system is initially prepared in a microcanonical ensemble with energy \( E = E_0 \) and the potential is characterized by \( \lambda = \lambda(0) \). When the parameter is adiabatically ramped to \( \lambda(\tau) \), the ensemble remains in a microcanonical ensemble due to the ergodicity of the system. The final energy of the system can be calculated from the adiabatic invariant \( \Phi[\lambda(0), E_0] = \Phi[\lambda(\tau), E_1] \). That is

\[
\frac{1}{N!} \left[ \frac{1}{\hbar} \sqrt{2\pi m \tau} \right] \Gamma \left( 1 + \frac{1}{\lambda(0)} \right) \frac{dN}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda(0)} + 1 \right)} = \frac{1}{N!} \left[ \frac{1}{\hbar} \sqrt{2\pi m \tau} \right] \Gamma \left( 1 + \frac{1}{\lambda(\tau)} \right) \frac{dN}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda(\tau)} + 1 \right)}
\]

or

\[
E_1 = \left[ \Gamma \left( 1 + \frac{1}{\lambda(\tau)} \right) \right]^{2\lambda(\tau)} \left[ \Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda(\tau)} + 1 \right) \right]^{\frac{2\lambda(\tau)}{\lambda(\tau)}} \frac{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda(\tau)} + 1 \right)}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda(0)} + 1 \right)} \frac{n_{\lambda(\tau)}^N}{n_{\lambda(\tau)}^{\lambda(\tau) + 1}}.
\]

The Carnot cycle can be uniquely determined if the following parameters are fixed: Boltzmann constant \( k_B = 1 \), at instant \( B \), \( \lambda_B = 2 \), and at instant \( D \), \( \lambda_D = 4 \). The temperatures of the two heat reservoirs are \( T_H = 4.6 \), and \( T_C = 2.3 \).

In the following we will try to determine \( \lambda_C \) and \( \lambda_A \). The energy of the system at point \( C' \)

\[
E_\lambda = \frac{\Gamma \left( 1 + \frac{1}{\lambda_B} \right) \Gamma \left( 1 + \frac{1}{\lambda_C} \right)}{\Gamma \left( 1 + \frac{1}{\lambda_C} \right) \Gamma \left( 1 + \frac{1}{\lambda_C} \right)} \frac{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_C} + 1 \right)}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_C} + 1 \right)} \frac{n_{\lambda_C}^N}{n_{\lambda_C}^{\lambda_C + 1}} \frac{\lambda_C^2}{\lambda_C \lambda_C}.
\]

The probability distribution of energy at point \( C' \)

\[
P(E_\lambda, \beta_H) = \frac{1}{Z_N} \rho(E_\lambda) e^{-\beta_H E_\lambda}
\]

\[
= \beta_H \frac{(\beta_H E_\lambda)^{\frac{dN}{\lambda_B}} + \frac{dN}{\lambda_B} - 1}{\frac{dN}{\lambda_B} + \frac{dN}{\lambda_B}} e^{-\beta_H E_\lambda}.
\]

The average energy of the ensemble after the adiabatic evolution from \( B \) to \( C' \) is

\[
\langle E_{C'} \rangle = \int_0^\infty dE_\lambda P(E_\lambda, \beta_H) \left[ \Gamma \left( 1 + \frac{1}{\lambda_B} \right) \Gamma \left( 1 + \frac{1}{\lambda_B} \right) \right]^{\frac{2\lambda_B}{\lambda_B}} \frac{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_C} + 1 \right)}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_C} + 1 \right)} \frac{n_{\lambda_C}^N}{n_{\lambda_C}^{\lambda_C + 1}} \frac{\lambda_C^2}{\lambda_C \lambda_C}.
\]

By utilizing Eq (23), we obtain

\[
\langle E_{C'} \rangle = \left[ \Gamma \left( 1 + \frac{1}{\lambda_B} \right) \Gamma \left( 1 + \frac{1}{\lambda_C} \right) \right]^{\frac{2\lambda_B}{\lambda_B}} \frac{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_C} + 1 \right)}{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_C} + 1 \right)} \frac{n_{\lambda_C}^N}{n_{\lambda_C}^{\lambda_C + 1}} \frac{\lambda_C^2}{\lambda_C \lambda_C} \beta_H^{-\frac{2\lambda_B}{\lambda_B} \lambda_C}.
\]

The average energy of the ensemble after the relaxation is

\[
\langle E_C \rangle = \int dE_1 P(E_1, \beta_C, \lambda_C) E_1
\]

\[
= \int dE_1 \beta_C \left( \beta_C E_1 \right)^{\frac{dN}{\lambda_C}} \frac{e^{-\beta_C E_1}}{\frac{dN}{\lambda_C} + \frac{dN}{\lambda_C}} \exp \left[ -\beta_C E_1 \right] E_1
\]

\[
= \frac{1}{\beta_C} \left( \frac{dN}{\lambda_C} + \frac{dN}{\lambda_C} \right).
\]
The parameter $\lambda_C$ at point $C$ can be determined by the equation $\langle E_{C'} \rangle = \langle E_C \rangle$. That is

$$\frac{1}{\beta_C} \left( \frac{dN}{2} + \frac{dN}{\lambda_C} \right) = \frac{\Gamma \left( 1 + \frac{1}{\lambda_B} \right)}{\sqrt{\pi N}} \left[ \frac{1}{\sqrt{N}} \right] \left[ \frac{2 + \lambda_C}{2 + \lambda_D} \right] \frac{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_B} + (2 + \lambda_B)\lambda_C \lambda_B(2 + \lambda_C) \beta_H^{2 + (2 + \lambda_B)\lambda_C}}{\lambda_B(2 + \lambda_C)} \right].$$

(27)

Substituting $\lambda_B = 2$, $T_C = 2.3$, and $T_H = 4.6$ into the above formula we obtain the value of $\lambda_C$. It is worth mentioning that $\lambda_C$ is a function of $N$, $\lambda_C = \lambda_C(N)$. We can also determine $\lambda_A$ at point $A$ in a similar way. At point $D$, $\lambda_D = 4$, we have the energy of the system at point $A'$

$$\frac{1}{\beta_H} \left( \frac{dN}{2} + \frac{dN}{\lambda_A} \right) = \frac{\Gamma \left( 1 + \frac{1}{\lambda_B} \right)}{\sqrt{\pi N}} \left[ \frac{1}{\sqrt{N}} \right] \left[ \frac{2 + \lambda_A}{2 + \lambda_D} \right] \frac{\Gamma \left( \frac{dN}{2} + \frac{dN}{\lambda_B} + (2 + \lambda_B)\lambda_A \lambda_B(2 + \lambda_A) \beta_C^{2 + (2 + \lambda_B)\lambda_A}}{\lambda_B(2 + \lambda_C)} \right].$$

(28)

Through a similar procedure, we obtain the value of $\lambda_A$ at point $A'$. Thus the parameters of the Carnot cycle are completely determined.

**Relative entropy and the efficiency of the Carnot cycle:** In order to calculate the efficiency as a function of the particle number $N$, we need to obtain the thermodynamic entropy of the system $S_B$, $S_D$ and the relative entropy $D[\rho_{C'}||\rho_{C'}^g] = S_C - S_{C'}$ and $D[\rho_A||\rho_{A'}^g] = S_A - S_{A'}$. The entropy of the $N$ particle system at point $B$ is

$$S_B = -k_B \int_0^\infty dE_0 g(E_0, \lambda_B) \left( \frac{\exp[-\beta_H E_0]}{Z_N(\lambda_B, \beta_H)} \ln \frac{\exp[-\beta_H E_0]}{Z_N(\lambda_B, \beta_H)} \right) = \left( \frac{dN}{\lambda_B} + \frac{dN}{2} \right) k_B + N k_B \ln \left( \frac{1}{\lambda_B} \right) \left( \frac{2 + \lambda_B}{2 + \lambda_B} \right) k_B \ln (1 + \lambda_B) N!$$

(29)

$$S_D = \left( \frac{dN}{\lambda_D} + \frac{dN}{2} \right) k_B + N k_B \ln \left[ \frac{1}{N} \left( \frac{2}{a} \right)^d \left( \frac{2 \pi m}{h} \right)^d \Gamma(1 + \frac{1}{\lambda_D} \right) - \left( \frac{dN}{\lambda_D} + \frac{dN}{2} \right) k_B \ln (1 + \lambda_D) N!$$

(30)

Hence we have

$$S_B - S_D = \left( \frac{dN}{\lambda_B} - \frac{dN}{\lambda_D} \right) k_B + N k_B \ln \left( \frac{1}{\lambda_B} \right) \left( \frac{2 + \lambda_B}{2 + \lambda_B} \right) k_B \ln (1 + \lambda_B) N!$$

(31)

This entropy is extensive, or proportional to $N$ when both $N$ and $2/a$ increase by the same ratio. The entropy at point $C$ is

$$S_C = \left( \frac{dN}{\lambda_C} + \frac{dN}{2} \right) k_B + N k_B \ln \left[ \frac{1}{N} \left( \frac{2}{a} \right)^d \left( \frac{2 \pi m}{h} \right)^d \Gamma(1 + \frac{1}{\lambda_C} \right) \left( \frac{2 + \lambda_C}{2 + \lambda_C} \right) k_B \ln (1 + \lambda_C) N!$$

(32)

Because of the Liouville theorem, we have $S_C' = S_B$. Hence the entropy increase in the relaxation process can be expressed as

$$D[\rho_{C'}||\rho_{C'}^g] = S_C - S_B$$

(33)

From Eq. (27) we have

$$\frac{2 + \lambda_C}{2\lambda_C} \ln (1 + \lambda_C) + \frac{2 + \lambda_C}{2\lambda_C} \ln \left( \frac{dN}{\lambda_C} + \frac{dN}{2} \right) = \frac{2 + \lambda_C}{2\lambda_C} \ln \left( \frac{dN}{\lambda_C} + \frac{dN}{2} \right) \ln \left( \frac{1}{\lambda_B} \right) \left( \frac{2 + \lambda_B}{2 + \lambda_B} \right) k_B \ln (1 + \lambda_B) N!$$

(34)
Substituting them into Eq. (33) we obtain

\[
D[\rho_C'||\rho_C^{eq}] = \left( \frac{dN}{\lambda_C} - \frac{dN}{\lambda_B} \right) k_B + k_B \ln \left[ \frac{\left( \frac{dN}{\lambda_C} + \frac{dN}{\lambda_C} + 1 \right)}{\left( \frac{dN}{\lambda_B} + \frac{dN}{\lambda_B} + 1 \right)} \right] + dN k_B \frac{2 + \lambda_C}{2\lambda_C} \ln \left( \frac{\left( \frac{dN}{\lambda_C} + \frac{dN}{\lambda_B} \right)}{\left( \frac{dN}{\lambda_B} + \frac{dN}{\lambda_B} \right)} \right) - dN k_B \frac{2 + \lambda_C}{2\lambda_C} \ln \left[ \frac{dN}{\lambda_C} \right].
\]  

(35)

Interestingly this relative entropy is independent of the temperatures. The relative entropy \(D[\rho_C'||\rho_C^{eq}]\) can be obtained when \(\lambda_B\), and \(\lambda_C\) are fixed. If we choose \(d = 3\) the relative entropy can be further simplified to

\[
D[\rho_C'||\rho_C^{eq}] = 3N k_B \frac{2 - \lambda_C}{2\lambda_C} + k_B \ln \left[ \frac{\left( \frac{3N}{2} + \frac{3N}{\lambda_C} + 1 \right)}{\Gamma \left( \frac{3N}{2} + 1 \right)} \right] + 3N k_B \frac{2 + \lambda_C}{2\lambda_C} \left\{ \ln \left( \frac{3N + 2\lambda_C}{\Gamma \left( 3N \right)} \right) - \ln \left[ \frac{3N}{2} + \frac{3N}{\lambda_C} \right] \right\},
\]  

(36)

where \(\lambda_C(N)\) is determined by Eq. (27). One can further simplify the relative entropy when taking the limit of \(N \to \infty\)

\[
\lim_{N \to \infty} D[\rho_C'||\rho_C^{eq}] \approx k_B \frac{2\lambda_C}{2 + \lambda_C}.
\]  

(37)

The relative entropy \(D[\rho_A'||\rho_A^{eq}]\) can also be obtained in a similar way when \(\lambda_D\) and \(\lambda_A\) are fixed.