Periodic heating amplifies the efficiency of a thermoelectric energy conversion

Supplementary Information

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The steady state analytical solution to the efficiency of a thermoelectric power generator (TPG)

For the steady state case a constant heat flux q_0 is applied to the left boundary. The heat conduction equation in 1D is,

$$\frac{\partial^2 T(x)}{\partial x^2}+\frac{q'''}{k}=0 \tag{1}$$

where k is thermal conductivity and $q'''=I^2R/AL=I^2/\sigma A^2$ is the volumetric internal joule heating due to a current I flowing through the TPG with resistance R (cross sectional area A, thickness L, and electrical conductivity σ). The Peltier effect results in a cooling on the hot side and heating on the cold side, captured by q_{p1} and q_{p2} in Figure 2. Accordingly, the boundary condition on the hot side at $x=0$ is,

$$-k\left.\frac{dT}{dx}\right|_{x=0}=q_0-q_{p1}-h_1\left[T(0)-T_\infty\right] \tag{2}$$

where q_0 is the imposed heat flux and h_1 is the heat transfer coefficient on the hot side. The Peltier heat flux is $q_{p1}=T(0)SI/A$, where S is the Seebeck coefficient. The boundary condition on the cold side at $x=L$ is

$$-k\left.\frac{dT}{dx}\right|_{x=L} = h_2\left[T(L) - T_\infty\right] - q_{p2} \tag{3}$$

where h_2 is the heat transfer coefficient on the cold side and q_{p2} is the Peltier heat flux $q_{p2} = T(L)SI/A$ on the cold side. The resultant temperature distribution is,

$$T(x) = \frac{q'''x^2}{2k}\left(\frac{L}{x} - 1\right) - \frac{x}{L}\left(T_h - T_c\right) + T_h \tag{4}$$

Where T_h and T_c are the hot side and cold side temperatures. The power delivered to the load with resistance R_l is,

$$W = I^2 R_l = \left[\frac{S\left(T_h - T_c\right)}{R + R_l}\right]^2 R_l \tag{5}$$

The total rate of heat flow from the source Q_0 is

$$q_0 A = Q_0 = SIT_h + \frac{kA}{L}\left(T_h - T_c\right) - \frac{I^2 R}{2} + h_1 A\left(T_h - T_\infty\right) \tag{6}$$

where the final term is zero if the hot side is insulated (i.e., h_1 is very low). The efficiency is maximized when the ratio of the resistance of the load to that of the generator is given by[1]

$$R_l / R = \sqrt{1 + Z\bar{T}} \tag{7}$$

where $Z = \sigma S^2/k$ and $\bar{T} = \left(T_h + T_c\right)/2$. With this substitution, the efficiency of the thermoelectric device can be derived in terms of $Z\bar{T}$ as,

$$\eta_{SS} = \frac{W}{Q_0} = \frac{\left(T_h - T_c\right)\left(\sqrt{1 + Z\bar{T}} - 1\right)}{T_h\left(\sqrt{1 + Z\bar{T}} + T_c/T_h\right)} \tag{8}$$

Eqn. (8) yields η_{SS}=4.8% with the TPG properties defined in Table 1, T_h=400, and T_c=300K.

Analytical solution to quasi-steady periodic heating of a TPG

The transient heat conduction equation in one dimension is,

$$\frac{\partial^2 T(x,t)}{\partial x^2}+\frac{q'''(t)}{k}=\frac{1}{\alpha}\frac{\partial T(x,t)}{\partial t} \tag{9}$$

where volumetric heat generation term is $q'''(t)=I(t)^2/\sigma A^2$. A periodic heat flux with Peltier cooling $q_{p1}(t)=T(0,t)SI(t)/A$ and convective heat loss are assumed at the left boundary,

$$-k\left.\frac{dT}{dx}\right|_{x=0}=q_0+q_1e^{i\omega t}-q_{p1}(t)-h_1\left[T(0,t)-T_\infty\right] \tag{10}$$

and Peltier heating $q_{p2}(t)=T(L,t)SI(t)/A$ and convective heat loss are assumed at the right boundary.

$$-k\left.\frac{dT}{dx}\right|_{x=L}=h_2\left[T(L,t)-T_\infty\right]-q_{p2}(t) \tag{11}$$

To reach an approximate analytical solution the temperature will be represented as the superposition of a steady state term $T_{ss}(x)$, and periodic terms $\varphi(x,t)$ where we focus on the periodic term at *1ω*. In what follows steady state terms are distinguished from the total variable by the subscript *ss*.

$$T(x,t)=T_{ss}(x)+\varphi(x,t) \tag{12}$$

Hence the temperature at $x=0$ (hot side) is,

$$T(0,t)=T_{hss}+\varphi(0,t) \tag{13}$$

and at $x=L$ (cold side) is,

$$T(L,t)=T_{css}+\varphi(L,t) \tag{14}$$

In the quasi-steady low frequency regime, it is reasonable to use I_{ss} as an estimate of the amplitude of $I(t)$,

$$I(t)=I_{ss}+I_{ss}e^{i\omega t} \tag{15}$$

which leads to the following expression for $I(t)^2$

$$I(t)^2 = I_{ss}^2 + 2I_{ss}^2 e^{i\omega t} + I_{ss}^2 e^{2i\omega t} \tag{16}$$

where the final term is at a frequency 2ω, and will be ignored for our solution at 1ω. Given the expressions in eqns. (12)-(16), q_{p1}, q_{p2}, and q''' can be explicitly defined, and the periodic component of eqn. (9) at a frequency 1ω is specified by,

$$\frac{\partial^2 \varphi(x,t)}{\partial x^2} + \frac{2I_{ss}^2 R}{kLA} e^{i\omega t} = \frac{1}{\alpha}\frac{\partial \varphi(x,t)}{\partial t} \tag{17}$$

The boundary condition at $x=0$ from eqn. (10) becomes,

$$-k\left.\frac{d\varphi}{dx}\right|_{x=0} = \frac{\left(q_1 - ST_{hss}I_{ss}\right)}{A} e^{i\omega t} - \left(\frac{SI_{ss}}{A} + h_1\right)\varphi(0,t) \tag{18}$$

and the boundary condition at $x=L$ from eqn. (11) becomes,

$$-k\left.\frac{d\varphi}{dx}\right|_{x=L} = -\frac{ST_{css}I_{ss}}{A} e^{i\omega t} - \left(\frac{SI_{ss}}{A} - h_2\right)\varphi(L,t) \tag{19}$$

The periodic solution to this problem is

$$\varphi(x,t) = \left[C_1 e^{(1+i)\sqrt{\frac{\omega}{2\alpha}}x} + C_2 e^{-(1+i)\sqrt{\frac{\omega}{2\alpha}}x} + \frac{2I_{ss}^2 R\alpha i}{AkL\omega}\right] e^{i\omega t} \tag{20}$$

Where C_1 and C_2 are constants defined by substituting eqn. (20) into boundary conditions. We can see that the periodic temperature response is at a frequency 1ω and exponentially decays with a length scale $L_p = \sqrt{\alpha/\pi f}$.

Quasi-steady TPG efficiency

To determine the TPG efficiency the instantaneous temperature difference between the hot and cold side ($\Delta\varphi$) must be specified from eqn. (20) as,

$$\Delta\varphi = \varphi(0,t) - \varphi(L,t) = \left[C_1\left(1 - e^{(1+i)\sqrt{\frac{\omega}{2\alpha}}L}\right) + C_2\left(1 - e^{-(1+i)\sqrt{\frac{\omega}{2\alpha}}L}\right)\right] e^{i\omega t} \tag{21}$$

For small ω (i.e., $L_p \gg L$), the Taylor expansion of the form $e^v = 1 + v + v^2/2! + v^3/3!...$ can be used to replace the exponential terms in eqn. (21) as,

$$\omega \to 0 \Rightarrow e^{(1+i)\sqrt{\frac{\omega}{2\alpha}}L} \cong 1+(1+i)\sqrt{\frac{\omega}{2\alpha}}L \tag{22}$$

Hence, $\Delta\varphi$ simplifies to,

$$\Delta\varphi = (C_2 - C_1)(1+i)\sqrt{\frac{\omega}{2\alpha}}Le^{i\omega t} \tag{23}$$

Substitution of eqn. (22) into the boundary condition at $x=0$ results in,

$$(C_1 - C_2)(1+i)\sqrt{\frac{\omega}{2\alpha}} - \left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right)(C_1+C_2) - \frac{2I_{ss}^2R\alpha i}{AkL\omega}\left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right) = -\left(q_1 - \frac{ST_{hss}I_{ss}}{A}\right)\Big/k \tag{24}$$

and at $x=L$ results in,

$$\begin{aligned}&(C_1 - C_2)(1+i)\sqrt{\frac{\omega}{2\alpha}}\left[1-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)L\right] \\ &\quad +(C_1+C_2)\left[\frac{\omega Li}{\alpha}-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\right] - \frac{2I_{ss}^2R\alpha i}{AkL\omega}\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right) = \frac{ST_{css}I_{ss}}{Ak}\end{aligned} \tag{25}$$

To isolate $(C_1$-$C_2)$ so that it can be substituted for in eqn. (23) we begin by multiplying eqn. (24) by $\left[\frac{\omega Li}{\alpha}-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\right]$,

$$\begin{aligned}&(C_1 - C_2)(1+i)\sqrt{\frac{\omega}{2\alpha}}\left[\frac{\omega Li}{\alpha}-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\right] - \left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right)(C_1+C_2)\left[\frac{\omega Li}{\alpha}-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\right] \\ &-\frac{2I_{ss}^2R\alpha i}{AkL\omega}\left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right)\left[\frac{\omega Li}{\alpha}-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\right] = \left[\frac{\omega Li}{\alpha}-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\right]\left(\frac{ST_{hss}I_{ss}}{kA}-\frac{q_1}{k}\right)\end{aligned} \tag{26}$$

and eqn. (25) by $\left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right)$,

$$\begin{aligned}&(C_1 - C_2)(1+i)\sqrt{\frac{\omega}{2\alpha}}\left[1-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)L\right]\left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right) + (C_1+C_2)\left[\frac{\omega Li}{\alpha}-\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\right]\left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right) \\ &-\frac{2I_{ss}^2R\alpha i}{AkL\omega}\left(\frac{SI_{ss}}{Ak}-\frac{h_2}{k}\right)\left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right) = \frac{ST_{css}I_{ss}}{Ak}\left(\frac{SI_{ss}}{kA}+\frac{h_1}{k}\right)\end{aligned} \tag{27}$$

then add eqn. (26) and (27) together to get,

$$C_2 - C_1 = \frac{\left(\frac{q_1}{k} - \frac{ST_{hss}I_{ss}}{kA}\right)\left[\frac{\omega Li}{\alpha} - \left(\frac{SI_{ss}}{Ak} - \frac{h_2}{k}\right)\right] - \frac{ST_{css}I_{ss}}{Ak}\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right) + \frac{2I_{ss}^2R}{Ak}\left[\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right)\right]}{(1+i)\sqrt{\frac{\omega}{2\alpha}}\left\{\frac{\omega Li}{\alpha} - \frac{SI_{ss}}{Ak} + \frac{h_2}{k} + \left[1 - \left(\frac{SI_{ss}}{Ak} - \frac{h_2}{k}\right)L\right]\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right)\right\}} \tag{28}$$

Such that the expression for $\Delta\varphi$ from eqn. (23) is,

$$\Delta\varphi = \frac{\left(\frac{q_1}{k} - \frac{ST_{hss}I_{ss}}{kA}\right)\left[\frac{\omega Li}{\alpha} - \left(\frac{SI_{ss}}{Ak} - \frac{h_2}{k}\right)\right] - \frac{ST_{css}I_{ss}}{Ak}\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right) + \frac{2I_{ss}^2R}{Ak}\left[\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right)\right]}{\left\{\frac{\omega Li}{\alpha} - \frac{SI_{ss}}{Ak} + \frac{h_2}{k} + \left[1 - \left(\frac{SI_{ss}}{Ak} - \frac{h_2}{k}\right)L\right]\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right)\right\}} Le^{i\omega t} \tag{29}$$

We now assume that $\omega \Rightarrow 0$, such that eqn. (29) simplifies to,

$$\Delta\varphi = \frac{\left(\frac{q_1}{k} - \frac{ST_{hss}I_{ss}}{Ak}\right)\left(\frac{h_2}{k} - \frac{SI_{ss}}{Ak}\right) - \frac{ST_{css}I_{ss}}{Ak}\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right) + \frac{2I_{ss}^2R\alpha}{AkL}\left[\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right)\frac{L}{\alpha}\right]}{\left\{-\frac{SI_{ss}}{Ak} + \frac{h_2}{k} + \left[1 - \left(\frac{SI_{ss}}{Ak} - \frac{h_2}{k}\right)L\right]\left(\frac{SI_{ss}}{kA} + \frac{h_1}{k}\right)\right\}} Le^{i\omega t} \tag{30}$$

Where the amplitude is independent of *ω*. Given the fact that conversion efficiency $\eta = \frac{1}{Q}\int_0^\tau I^2 R_l dt \propto (\Delta T)^2$, it is clear that it will asymptote to a constant value at low frequency, as our results in Figures 4 and 5 demonstrate.

In an ideal TPG no heat is lost by convection from the hot side, such that $h_1 \cong 0$ and effective convection on the cold side such that $h_2 \to \infty$. This simplifies eqn. (30) and the amplitude of $\Delta\varphi$ is,

$$|\Delta\varphi| = \frac{q_1 L - ST_{hss}I_{ss}L/A}{k + SI_{ss}L/A} \tag{31}$$

It is our assumption that $q_1 = q_0$, and from eqn. (6),

$$q_1 = q_0 = \frac{SI_{ss}T_{hss}}{A} + \frac{k}{L}\Delta T_{ss} - \frac{I_{ss}^2 R}{2A} \tag{32}$$

where $\Delta T_{ss} = T_h - T_c$. Substitution of eqn. (32) into eqn. (31) yields,

$$|\Delta\varphi| = \frac{k\Delta T_{ss} - I_{ss}^2 RL/2A}{k + SI_{ss}L/A} \tag{33}$$

which can be written in terms of Z and $\beta = \sqrt{1+Z\overline{T}}$ based on,

$$\frac{SI_{ss}L}{A} = \frac{S^2\Delta T_{ss}L}{(1+\beta)RA} = \frac{S^2\sigma\Delta T_{ss}L}{L(1+\beta)} = \frac{Zk\Delta T_{ss}}{(1+\beta)} \tag{34}$$

and

$$\frac{I^2RL}{2A} = \frac{S^2\Delta T_{ss}^2 L}{2(1+\beta)^2 RA} = \frac{S^2\sigma\Delta T_{ss}^2 L}{2(1+\beta)^2 L} = \frac{Zk\Delta T_{ss}^2}{2(1+\beta)^2} \tag{35}$$

which are substituted into eqn. (33) to yield,

$$|\Delta\varphi| = \frac{\Delta T_{ss}(1+\beta) - Z\Delta T_{ss}^2/2(1+\beta)}{(1+\beta) + Z\Delta T_{ss}} \tag{36}$$

If Z=0, and hence β=1, this results in $|\Delta\varphi| = \Delta T_{ss}$.

The conversion efficiency is then written as,

$$\eta = \frac{I^2R_L}{Q} = \frac{S^2\Delta T^2 R_L}{Q(R+R_L)^2} = \frac{S^2R_L}{A(R+R_L)^2}\frac{\int_0^{\tau=2\pi/\omega}\left(\Delta T_{ss}^2 + 2\Delta T_{ss}|\Delta\varphi|\sin\omega t + |\Delta\varphi|^2\sin^2\omega t\right)dt}{\int_0^{\tau=2\pi/\omega}(q_0 + q_1\sin\omega t)dt} \tag{37}$$

where the integrals have been taken over one period ($2\pi/\omega$). The $\sin\omega t$ terms integrate to zero over these limits, and eqn. (37) is simplified to,

$$\eta = \frac{S^2R_L\Delta T_{ss}^2}{A(R+R_L)^2 q_0}\left\{1 + \frac{\left[(1+\beta) - Z\Delta T_{ss}/2(1+\beta)\right]^2}{2(1+\beta+Z\Delta T_{ss})^2}\right\} \tag{38}$$

Finally, we can express the periodic efficiency in terms of η_{ss} as,

$$\eta = \eta_{ss}\left\{1 + \frac{\left[(1+\beta) - Z\Delta T_{ss}/2(1+\beta)\right]^2}{2(1+\beta+Z\Delta T_{ss})^2}\right\} \tag{39}$$

Numerical solution to periodic heating of a TPG

For a more accurate solution, presented in Figures 3-6, we have also solved the problem numerically. Our numerical approach uses a central difference approximation to $\frac{\partial^2 T(x,t)}{\partial x^2}$ and explicit time marching, as shown in Figure S1. The procedure yields

$$\frac{\partial^2 T_{m,j}}{\partial x^2} = \frac{T_{m-1,j} - 2T_{m,j} + T_{m+1,j}}{\Delta x^2} \tag{40}$$

and,

$$\frac{\partial T_{m,j+1}}{\partial t} = \frac{T_{m,j+1} - T_{m,j}}{\Delta t} \tag{41}$$

where m is the spatial index and j is the temporal index. The heat conduction equation becomes,

$$\frac{T_{m-1,j} - 2T_{m,j} + T_{m+1,j}}{\Delta x^2} + \frac{q'''}{k} = \frac{1}{\alpha}\frac{T_{m,j+1} - T_{m,j}}{\Delta t} \tag{42}$$

Comparison of analytical and numerical solutions to periodic heating of a TPG

A comparison of the numerical and analytical solutions (eqn. (4)) under constant heat flux, with the TPG properties in Table 1, are shown in Figure S2. Numerical and analytical solutions match. In the case of periodic heating, we first compare the numerical result against the exact analytical solution (eqn. (20)) when $q_{p1} = q_{p2} = q''' = 0$. Figure S3a shows the amplitude of temperature vs. x-position for the analytical approach and the numerical under these conditions. The difference between the hot and cold side is accurately predicted by eqn. (36) to be ΔT_{ss} in this low frequency limit. In this plot, angular velocity is very low, $\omega = 0.01 Hz$. Agreement between these solutions validates the numerical model.

The amplitude of temperature vs. x-position when Joule and Peltier terms are considered is shown in Figure S3b. The analytical estimate from eqn. (20) is compared with the numerical solution. Reasonable agreement indicates that our simple analytical model can provide reasonable accuracy at low frequency.

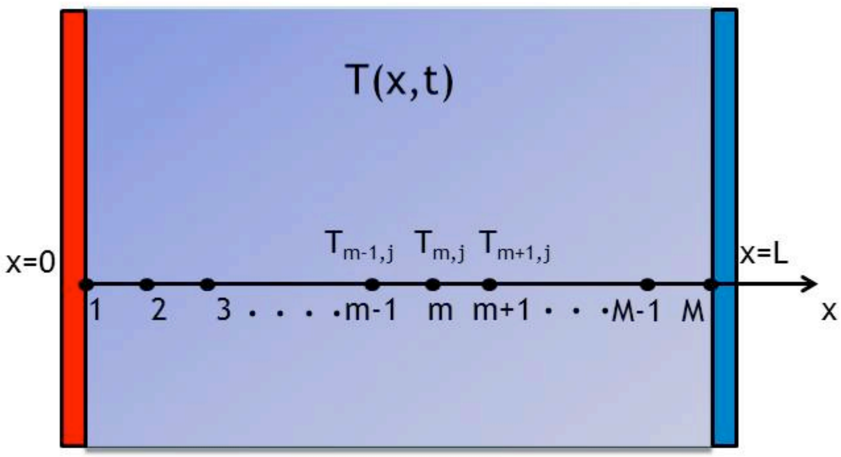

FIG S1. Numerical Model

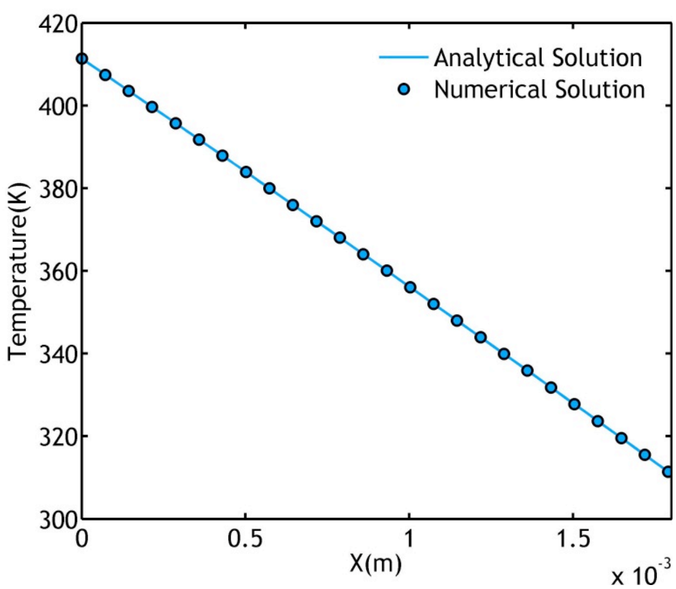

FIG S2. Comparison of temperature distribution from analytical solution and numerical solution

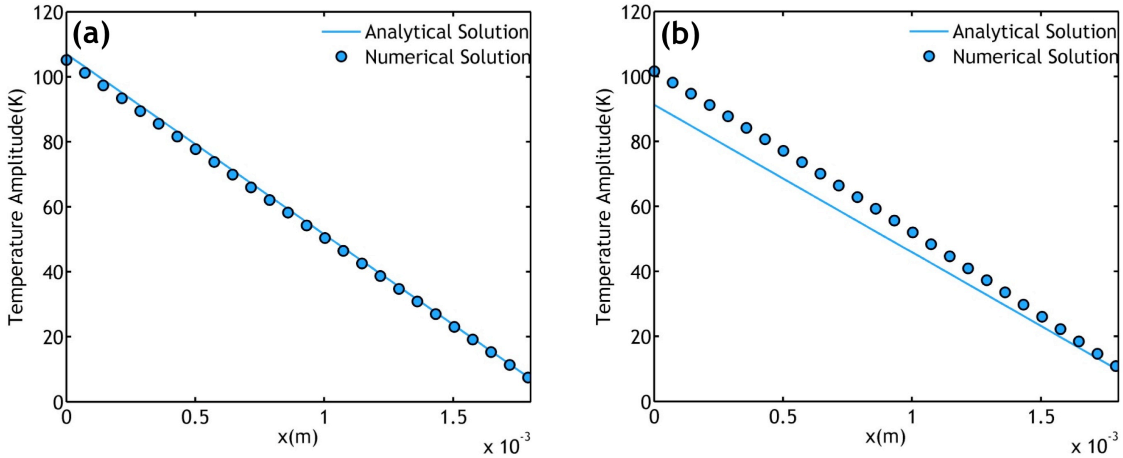

FIG S3. Temperature amplitude from numerical and analytical approaches with (a) no thermoelectric effects, and (b) with thermoelectric effects.

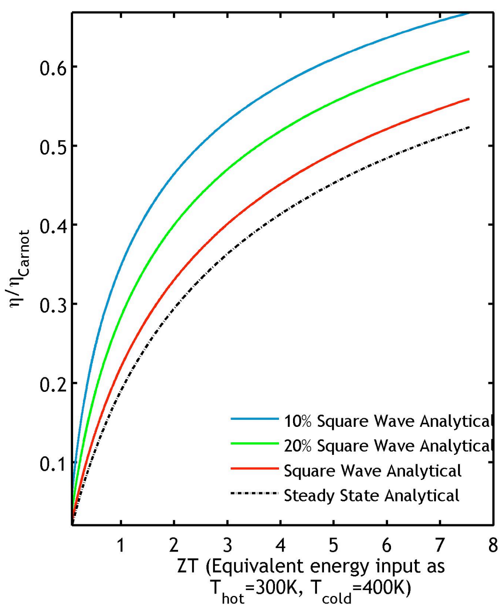

FIG S4. Ratio of the periodic efficiency to the Carnot efficiency (η/η_{Carnot}) vs. ZT where η_{Carnot} is based on the actual ΔT for the given duty cycle. All approximations are based on the quasi-steady limit for rectangular (square) wave heating.

1. G. Chen, *Nanoscale energy transport and conversion : a parallel treatment of electrons, molecules, phonons, and photons*, Oxford, Oxford ; New York, 2005.