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Thermoelectric Energy Conversion Close to a Phase Transition

Ilia Khomchenko[1,2,3,4*] Giuliano Benenti[2,3], Henni Ouerdane[1]

[1]Skolkovo Institute of Science and Technology, [2]University of Insubria,
[3]Istituto Nazionale di Fisica Nucleare, [4]University of Malta, *Current Affiliation

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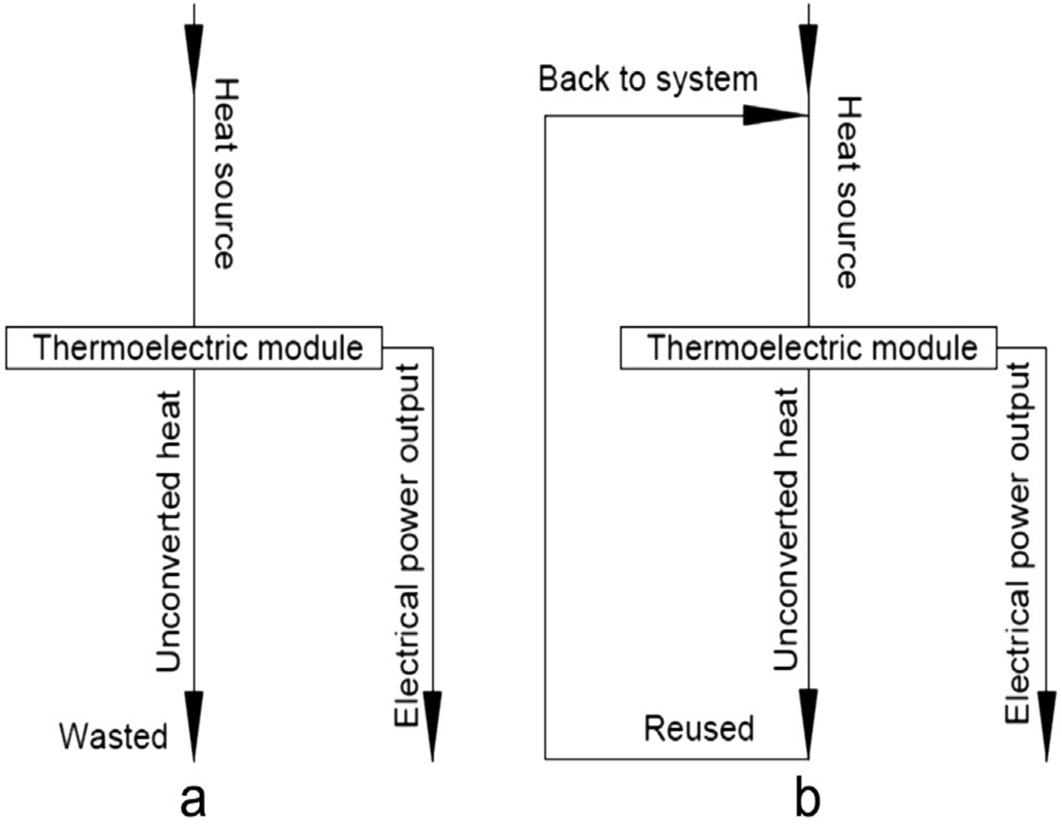
Outline

1. Research Motivation
2. Thermoelectricity & Thermodynamics in a Nutshell
3. Key Results: Numerical Simulations & Experiments
4. Conclusion and Outlook

General Problem

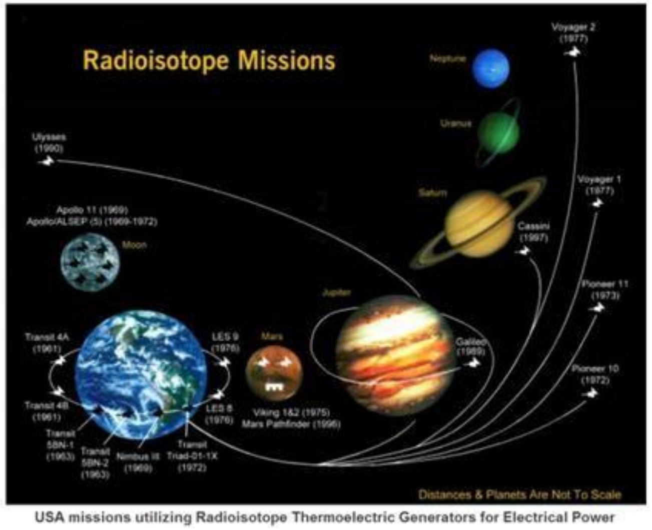
- **Waste heat harvesting** for energy efficiency
- **Thermoelectric solution**:
  - Scalable solid-state technology;
  - No moving parts;
  - Direct heat-to-electrical power conversion;

  Promising technology
  BUT as of yet <u>low-efficiency</u> solution (1-10 % η_c)
- **What are the causes of low-efficiency?**
- **How to remedy this problem?**



[1]X. F. Zheng, C. X. Liu, R. Boukhanouf, Y. Y. Yan, W. Z. Li, "Experimental study of a domestic thermoelectric cogeneration system" *Applied Thermal Energy* **62**, 69 (2014).

Thermoelectricity: Applications



Google pictures

"Thermoelectric energy conversion will never be as efficient as steam engines!"[2]

Why???

[2]C. B. Vining, "An inconvenient truth about thermoelectrics," *Nature materials*, **8**, 83-85 (2009).

Thermoelectricity: Basics

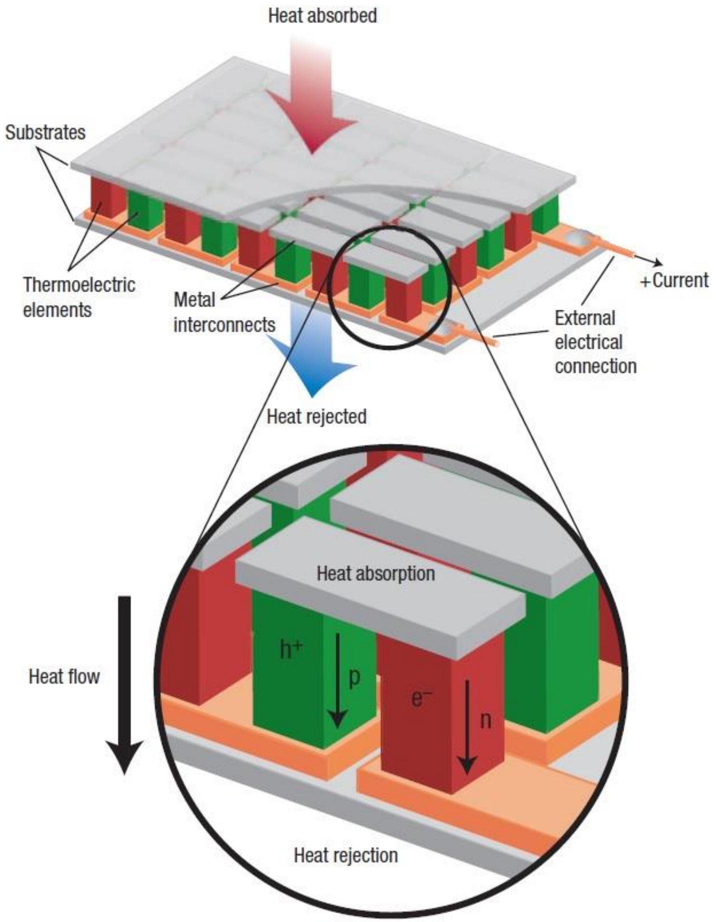


Fig.1. Thermoelectric generator (TEG)[3].

$$\Delta T \to \Delta V$$

$$\alpha = -\frac{\Delta V}{\Delta T}$$

3 main transport coefficients

α is the Seebeck coefficient
σ is the electrical conductivity
κ is the thermal conductivity

$$\kappa = \kappa_e + \kappa_l;$$

$$zT = \frac{\alpha^2\sigma}{\kappa}T$$ is the dimensionless figure of merit

$$\eta_{\max} = \eta_{\mathrm{C}} \frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}}}$$ is the maximum efficiency

$$T = (T_{\mathrm{c}} + T_{\mathrm{h}})/2$$

[3]G. J. Snyder and E. S. Toberer, "Complex Thermoelectric Materials" *Nature Materials* **7**, 105 (2008).

How to Increase Performance?

How to increase performance? Focus on ZT!

$ZT \geq 3$ or 4 **desirable**

$ZT \geq 3?$ **perhaps**

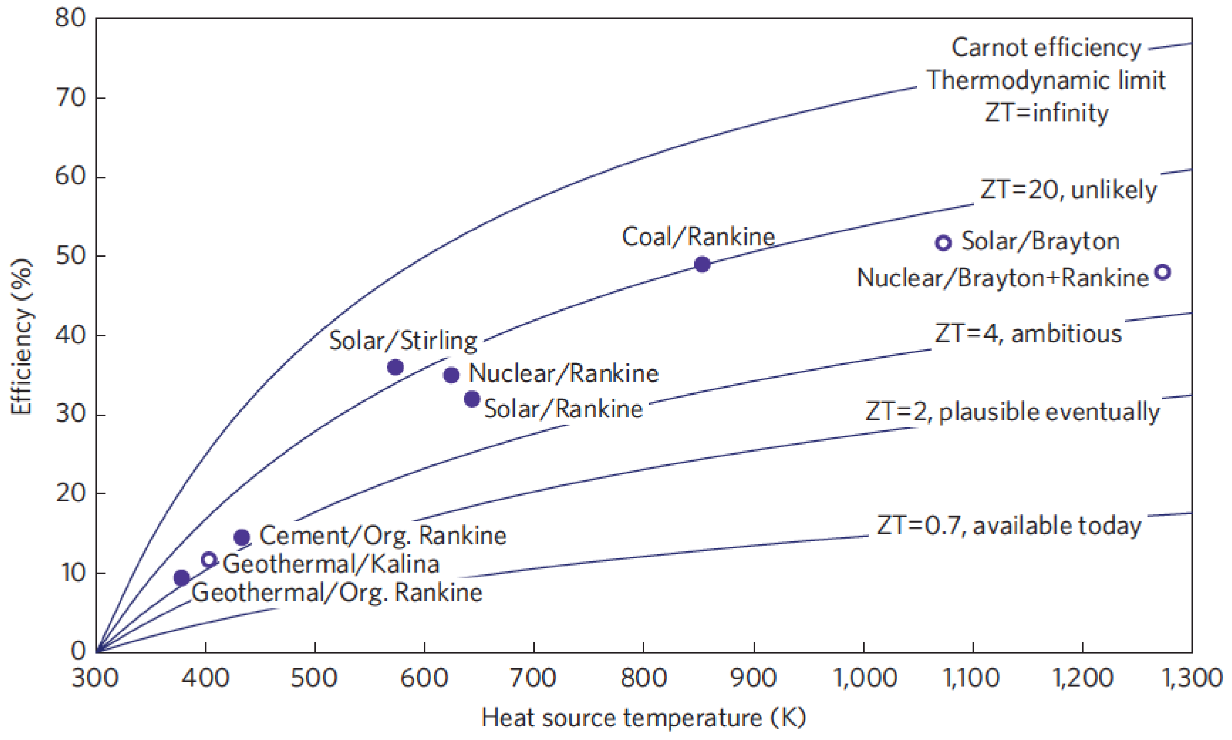
$ZT \approx 2$ **available**

$$\frac{\sigma}{\kappa} \approx const$$

σ *increases*

κ *increases*

κ is the source of dissipation



[2] C. B. Vining, "An inconvenient truth about thermoelectrics," *Nature materials*, **8**, 83-85 (2009).

Available thermoelectric materials[2,4]

Material	T, °C	ZT
SnSe single crystal	1196	2.6
PbTe-SrTe	1188	2.2
$PbTe_{0.85}Se_{0.15}$-2 % Na-4 % SrTe	923	2.3
PbTe-PbS pseudobinary	1196	2.3
Cu_2Se	673	2.3
Na–$Pb_{0.97}Eu_{0.03}Te$	1123	2.2
$PbSe_{0.98}Te_{0.02}$/PbTe	848	3.5
Bi_2Te_3/Sb_2Te_3	573	2.4
$AgPb_{18}SbTe_{20}$	1073	2.2

[2]C. B. Vining, "An inconvenient truth about thermoelectrics," *Nature materials*, **8**, 83-85 (2009).
[4]L. Yang, Zh. Chen, M. S. Dargusch, and J. Zou, "High Performance Thermoelectric Materials: Progress and Their Applications," *Advanced Energy Materials* **1701797**, (2017)

Available Thermoelectric Materials[5]

Material	ΔT, °C	η_{max}, %
p-$Mm_{0.7}Fe_3CoSb_{12}$/n-$Eu_8Ga_{16}Ge_{30}$	250	1-2
TGM-127-1.4-2.5	155	4
p-$Mm_{0.3}Fe_{1.46}Co_{2.54}Sb_{12.05}$/ n-$Yb_{0.09}Ba_{0.05}La_{0.05}Co_4Sb_{12}$	460	7
p-$La_{0.7}Ba_{0.1}Ga_{0.1}Ti_{0.1}Fe_3Co_1Sb_{12}$/ n-$Yb_{0.3}Ca_{0.1}Al_{0.1} - Ga_{0.1}In_{0.1}Co_{3.75}Fe_{0.25}Sb_{12}$	570	8
p-$La_{0.8}Ba_{0.01}Ga_{0.1}Ti_{0.1}Fe_3CoSb_{12}$/ n-$La_{0.3}Ca_{0.1}Al_{0.1} - Ga_{0.1}In_{0.2}Co_{3.75}Fe_{0.25}Sb_{12}$	550	8

[5]LeBlanc, S., Yee, S. K., Scullin, M. L., Dames, C. & Goodson, K. E., “Material and manufacturing cost considerations for thermoelectrics,” *Renewable and Sustainable Energy Reviews* **32**, 313–327 (2014).

Analogy between TEG and heat engine

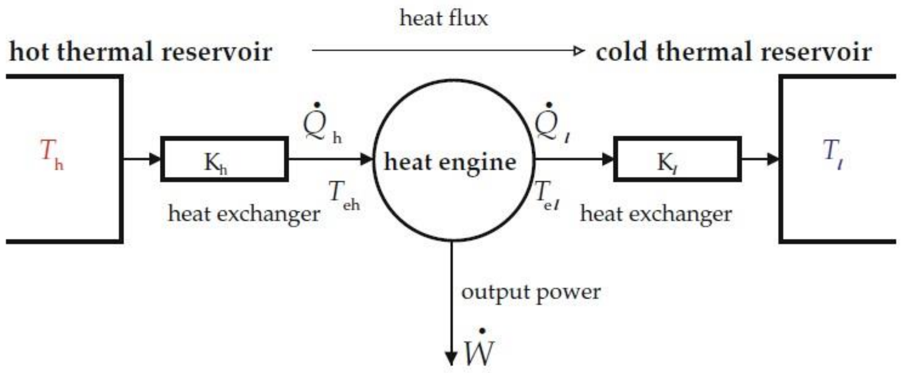


Fig.2. Schematic representation of a heat engine connected to two heat baths through heat exchangers.

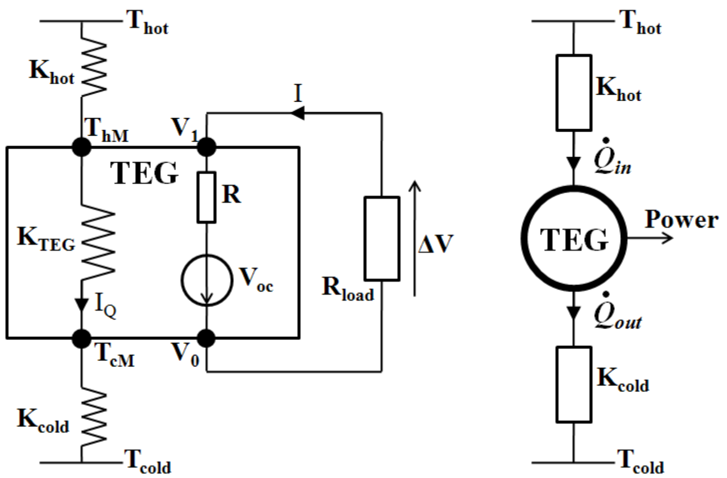


Fig.3. Thermoelectric (left) and thermodynamic (right) TEG pictures[2].

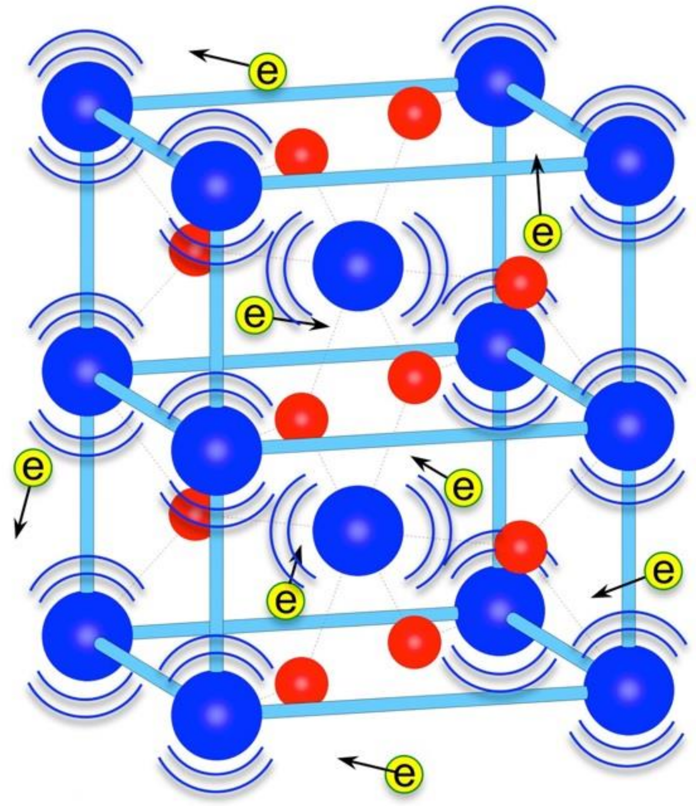


Fig.4. Electrons in a crystal lattice vanadium dioxide (Vanadium is in red color, Oxygen is in blue color).[7]

[7]J. D. Budai et al, *Nature* **515**, 535 (2014), and D. Lindley aps.anl.gov

[6]H. Ouerdane et al., *EPJ ST* **224**, 839 (2015) and Y. Apertet et al., *EPL* **97**, 28001 (2012)

Thermoelastic Properties

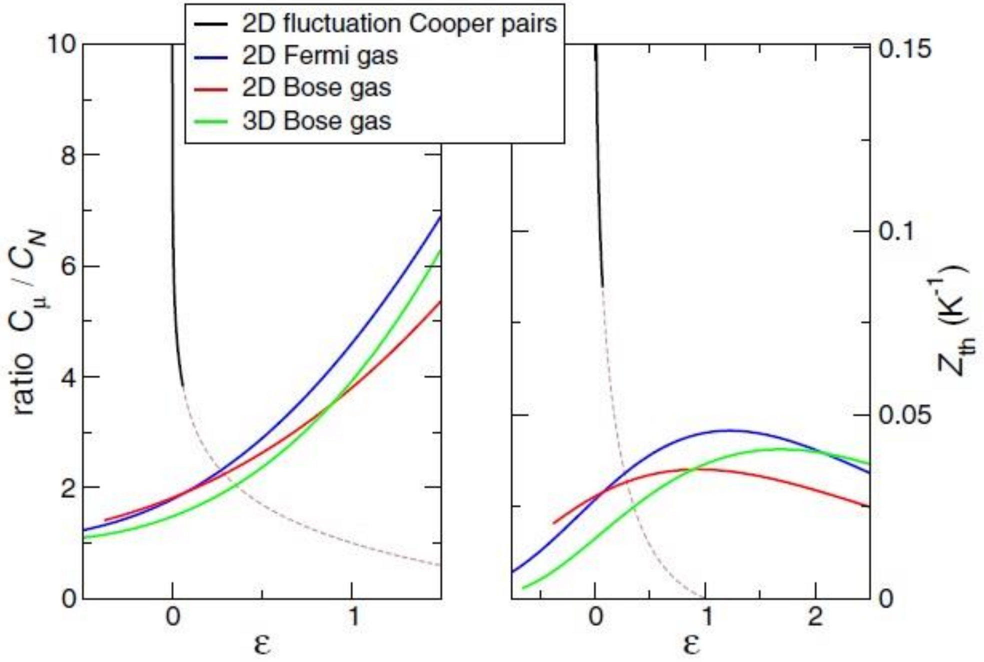


Fig.5. C_μ/C_N and Z_{th} vs ε.[8]

Thermodynamic figure of merit

$$\gamma = \frac{C_\mu}{C_N} = 1 + \frac{\beta^2}{\chi_T C_N} T = 1 + Z_{\mathrm{th}} T,$$

$$Z_{\mathrm{th}} T \neq zT \ ?$$

what is the relationship?

$$\varepsilon = \frac{T - T_c}{T_c}$$

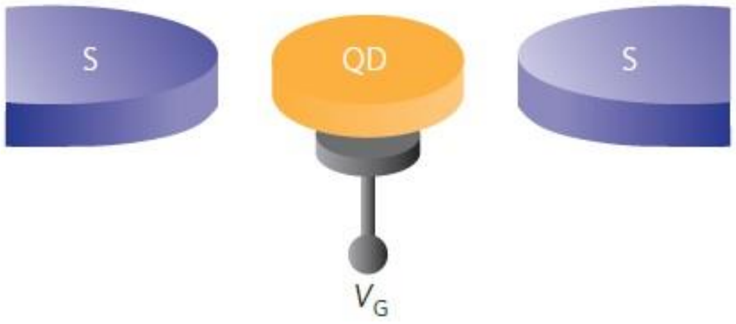
The electron gas' thermoelastic properties limit thermoelectric efficiency!

[8]H. Ouerdane et al., "Enhanced thermoelectric coupling near electronic phase transition: The role of fluctuation Cooper pairs" *Physical Review B* **91**, 100501(R) (2015).

Objectives

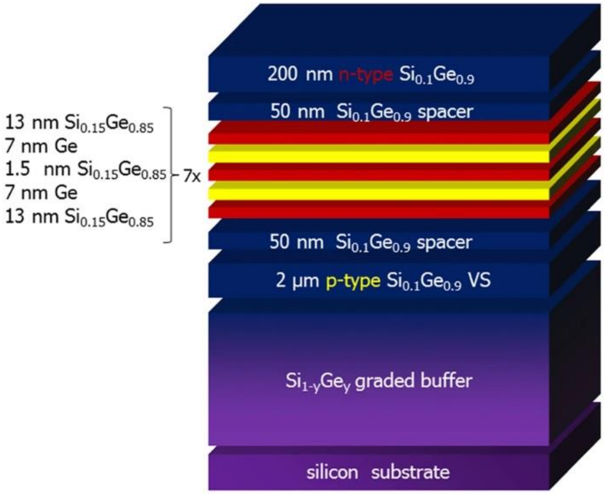
- Better understand the fundamental limits of the thermoelectric conversion efficiency;
- To find a new productive way to significantly increase the thermoelectric conversion efficiency.

Types of Systems



Quantum dot (0D system)

S. De Franceschi et al., Nature Nanotechnology **5**, (2010).

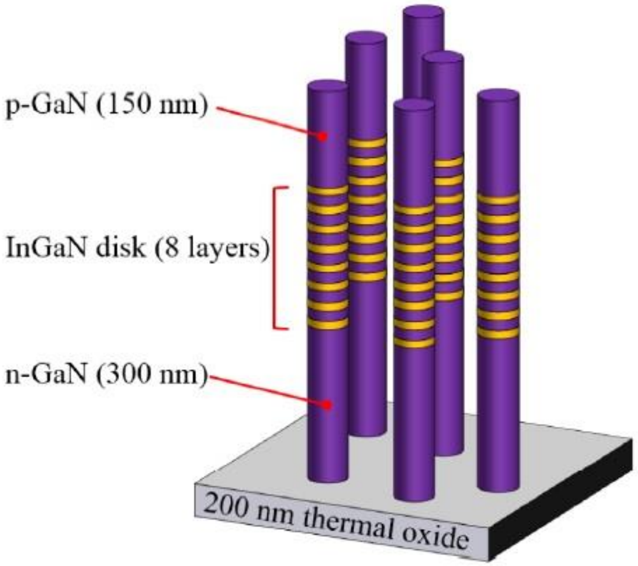


Quantum well (2D system)

J. Frigerio et al., *Sci Rep* **5,** 15398 (2015).

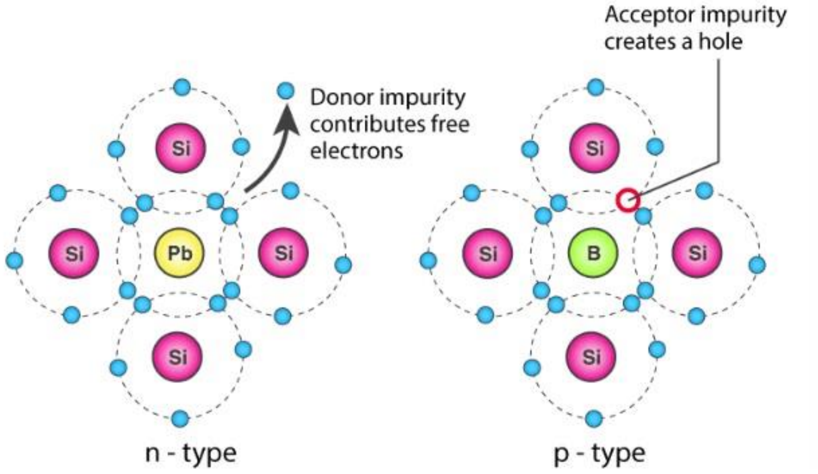
Thin Films(2D-3D system)

Google pictures



Nanowire (1D system)

Y. Park et al., Optic Express **11**, 23 (2015).



Bulk (3D system)

https://byjus.com/jee/semiconductors/.

Thermoelastic Coefficients

Analogy between a classical gas and the electron gas as a working fluid

$$V \to N \qquad -P \to \mu$$

$$\chi_T = \frac{1}{N}\left(\frac{\partial N}{\partial \mu}\right)_T$$ is the "isothermal compressibility";

$$\gamma = \frac{C_\mu}{C_N}$$ is the heat capacity ratio;

$$\beta = \frac{1}{N}\left(\frac{\partial N}{\partial T}\right)_\mu$$ is the "thermal dilatation coefficient";

$$C_\mu = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_\mu$$ is the "specific heat at constant pressure";

$$C_N = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_N$$ is the "specific heat at constant volume".

Transport Coefficients

L_{ij}: solutions of the Boltzmann equation

Seebeck coefficient $\alpha = \dfrac{L_{12}}{L_{11}T}$

electrical conductivity $\sigma = \dfrac{e^2 L_{11}}{T}$

thermal conductivity $\kappa_\mathrm{e} = \dfrac{1}{T^2}\left(\dfrac{L_{21}L_{12} - L_{11}L_{22}}{L_{11}}\right)$

$$z_\mathrm{e}T = \frac{\alpha^2\sigma}{\kappa_\mathrm{e}}T$$

$$L_{11} = \frac{T}{d}\int_0^\infty \mathcal{T}(E)\left(-\frac{\partial f}{\partial E}\right)dE,$$

$$L_{12} = L_{21} = \frac{T}{d}\int_0^\infty (E-\mu)\mathcal{T}(E)\left(-\frac{\partial f}{\partial E}\right)dE,$$

$$L_{22} = \frac{T}{d}\int_0^\infty (E-\mu)^2\mathcal{T}(E)\left(-\frac{\partial f}{\partial E}\right)dE,$$

where d is the system's dimensionality, and $v(E)$ is the velocity of the particle.

$\mathcal{T}(E) = \tau(E)v^2(E)g(E)$ is the transport distribution function.

Thermoelastic Coefficients

$$\chi_T = \int_0^\infty g(E)\left(-\frac{\partial f}{\partial E}\right) dE$$

$$\beta = \frac{1}{T}\int_0^\infty g(E)(E-\mu)\left(-\frac{\partial f}{\partial E}\right) dE$$

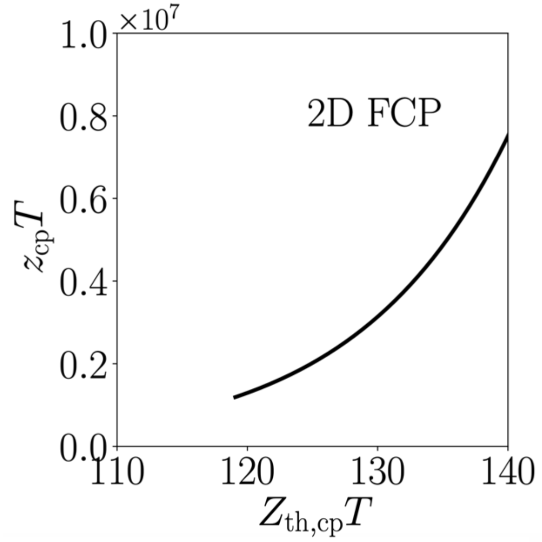
$$C_\mu = \frac{1}{T}\int_0^\infty g(E)(E-\mu)^2\left(-\frac{\partial f}{\partial E}\right) dE$$

where $g(E)$ is the density of states.

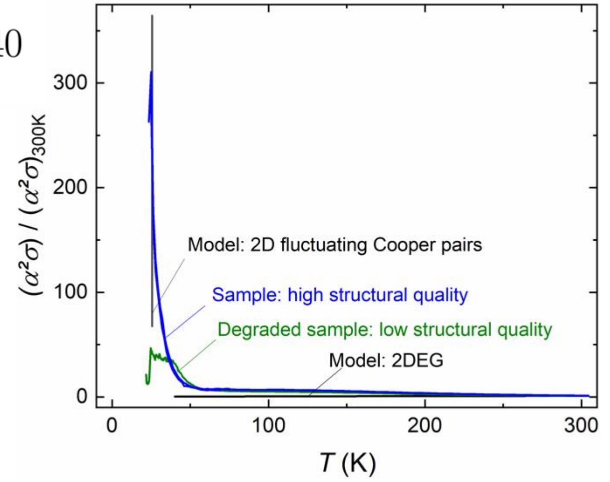
$$Z_{\mathrm{th}}T = \frac{\beta^2}{\chi_T C_N} T$$

Results

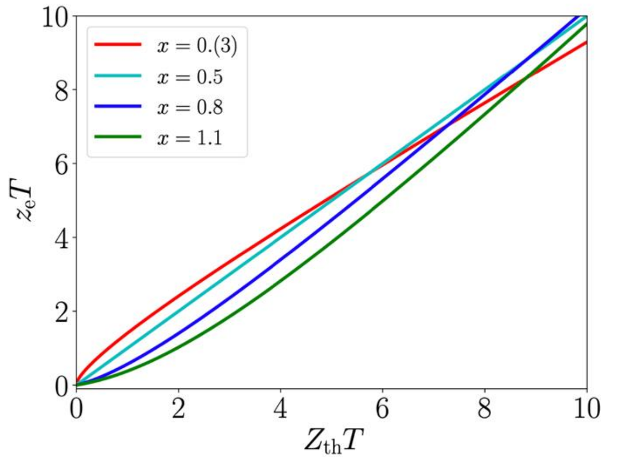
- 2D Fluctuating Cooper Pairs (theory)[9];



$\alpha^2\sigma$ is the power facor



- Nematic fluctuations (experiment)[9];



- Anderson transition (theory)[10].

[9]**I. Khomchenko** et al., "The thermoelectric conversion efficiency problem: Insights from the electron gas thermodynamics close to a phase transition" SciPost Physics Core, **8** 015, (2025).

[10]**I. Khomchenko**, H. Ouerdane, G. Benenti , "Influence of the Anderson Transition on Thermoelectric Energy Conversion in Disordered Electronic Systems", *IOP Journal of Physics: Conference Series*, **2701**, 012018 (2024).

Theory vs Experiment

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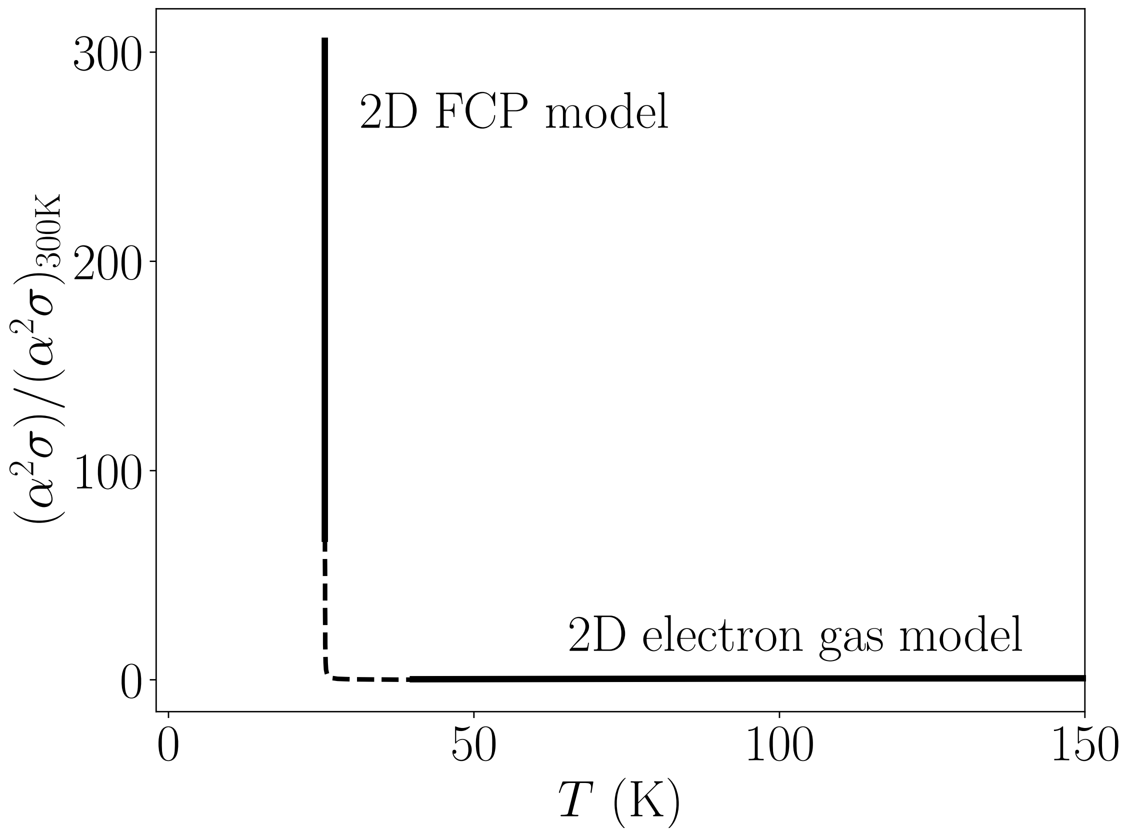

Fig.6. Relative change of the power factor α^2/ρ, plotted as a fucntion of temperture for 2D flucttutation of Cooper pairs and 2D electron gas.

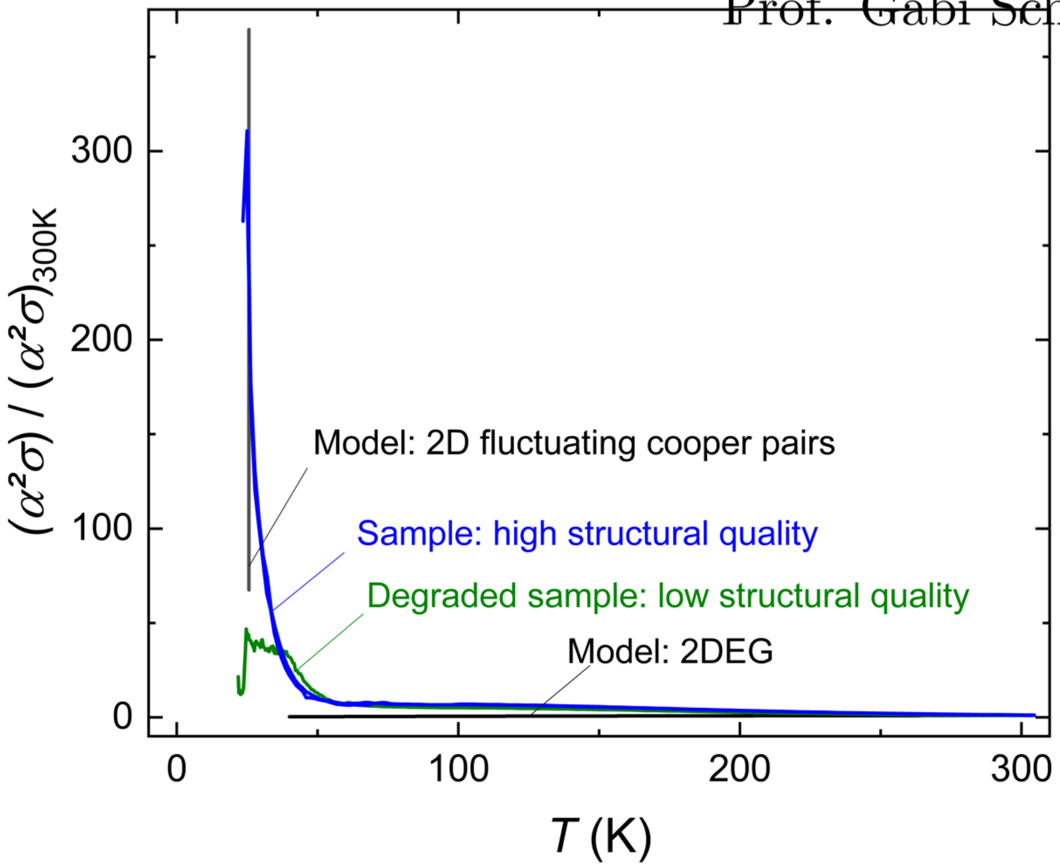

Fig.7. Relative change of the power factor α^2/σ, normalized to its value at 300 K for a 100 nm $Ba(Fe_{0.90}Co_{0.10})_2As_2$ thin film.

[9]**I. Khomchenko** et al., "The thermoelectric conversion efficiency problem: Insights from the electron gas thermodynamics close to a phase transition" SciPost Physics Core, **8** 015, (2025).

Efficiency of Energy Conversion

$$\eta_{\max}^{\text{th}} = \frac{\sqrt{1+Z_{\text{th}}T}-1}{\sqrt{1+Z_{\text{th}}T}+1}\eta_{\text{C}} \qquad \eta_{\max}^{\text{tr}} = \frac{\sqrt{1+z_{\text{e}}T}-1}{\sqrt{1+z_{\text{e}}T}+1}\eta_{\text{C}}$$

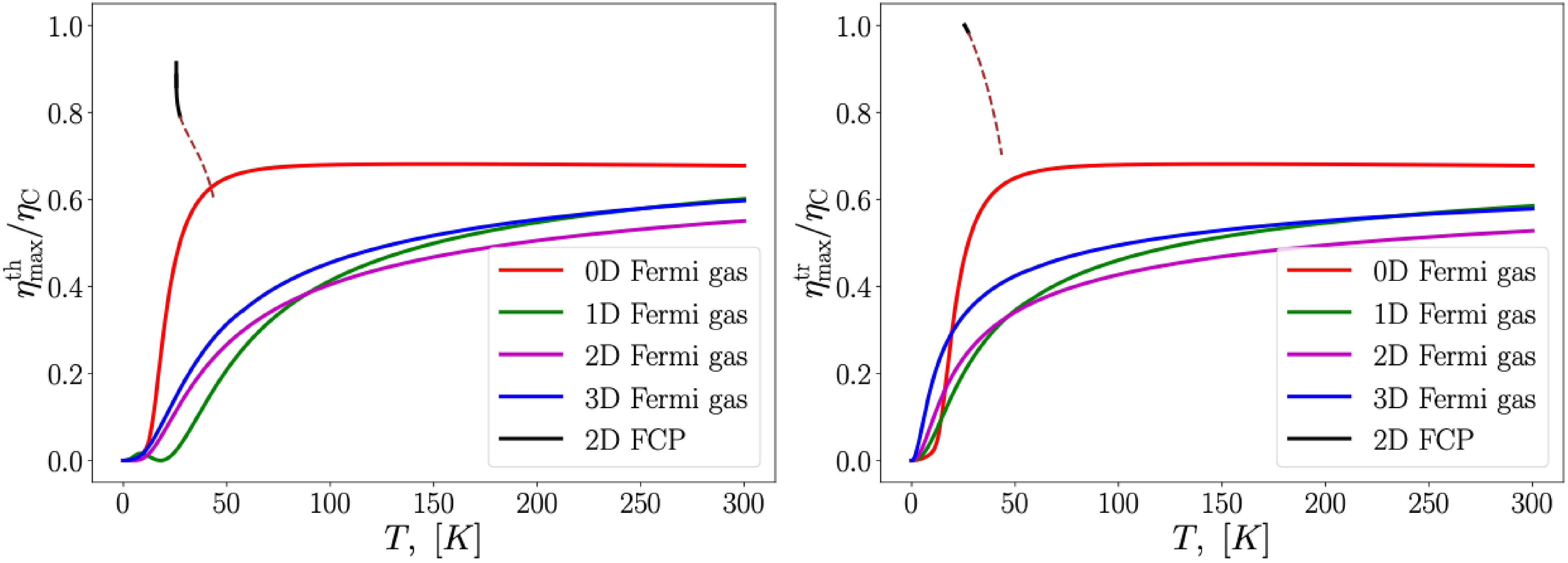

Fig.8. Maximum thermoelectric conversion efficiencies $\eta_{\max}^{\text{th}}$ and $\eta_{\max}^{\text{tr}}$ scaled to Carnot efficiency vs. temperature[9].

[9] **I. Khomchenko** et al., "The thermoelectric conversion efficiency problem: Insights from the electron gas thermodynamics close to a phase transition" SciPost Physics Core, **8** 015, (2025).

Discussion of the results

- The thermoelectric conversion efficiency η is directly related to the heat capacity ratio γ.
- We established relationships between the two figures of merit z_eT (resp. z_e) (transport) and $Z_{\mathrm{th}}T$ (resp. Z_{th}) (thermodynamic);
- New concepts in thermoelectricity have been developed.
- The thermoelectric conversion efficiency η can be greatly enhanced:

➢ For systems with high heat capacity ratio;

➢ For systems with thermal fluctuations and phase transitions.

Innovative implementation

Possible extension of our research: Nanoscale thermometer based on thermoelectric transport.

We are here.

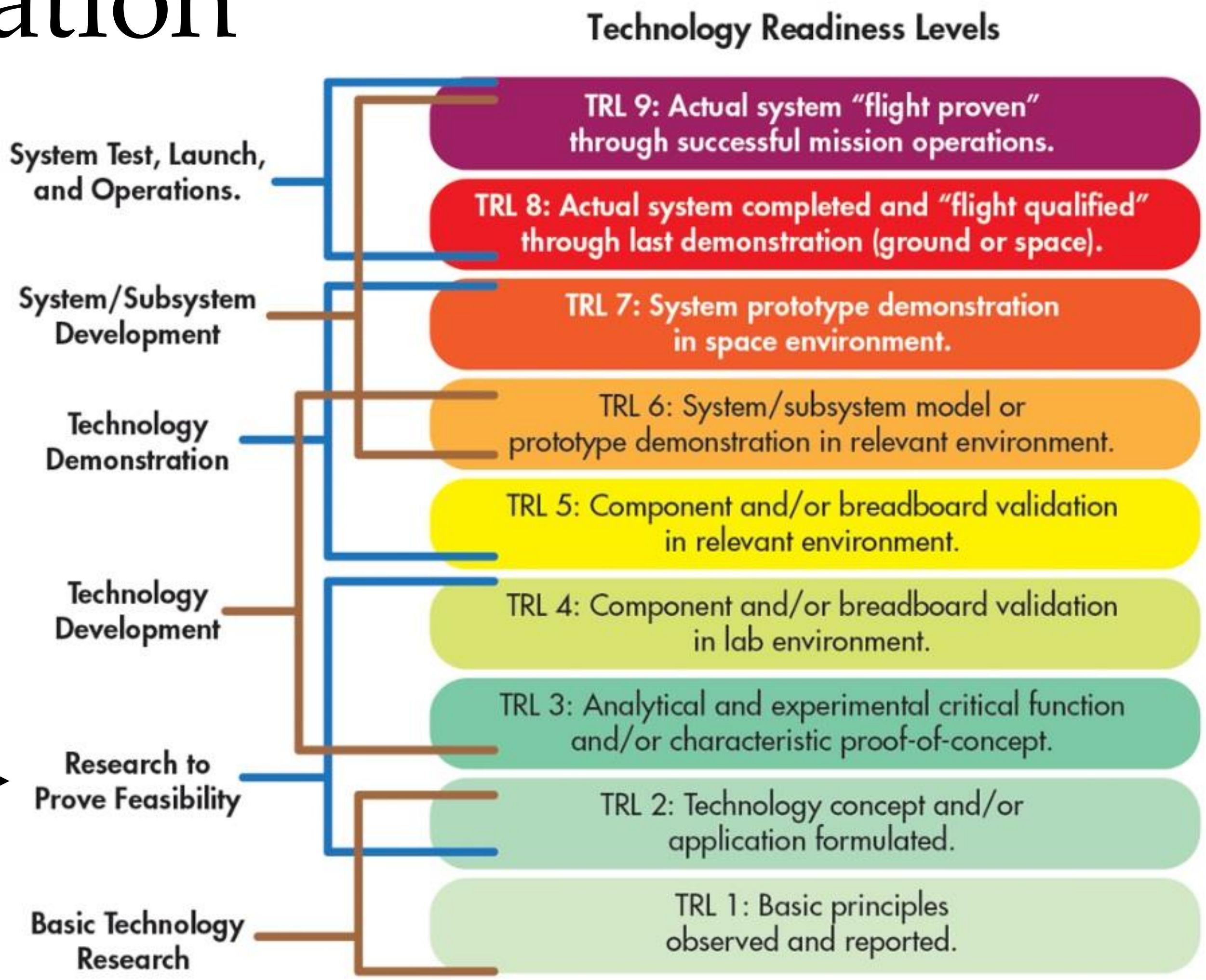

Fig.9. Technology Readiness Levels with a brief explanation of each level[11].

[11] B. Goldense, Technology readiness levels are widely adopted. MachineDesign 89, **64** (2017).

Conclusion

1. A thermodynamic approach allowed us to gain a deep insight into better control conditions for the increased efficiency of energy conversion.

2. Phase transitions provide an approximate 30 % enhancement of energy conversion efficiency in the fluctuating regime compared to the electron gas.

3. Our approach predicts the increase the size of thermoelectric market from $ 460 million/annum in 2019 to $ 741 million/annum in 2025.[12]

[12] S. Singh, Thermoelectric Generators Market by Application (Waste Heat Recovery, Energy Harvesting, Direct Power Generation, Co-generation), Wattage (< 10 W, 10-1kW, >1kW), Temperature (<80°C, 80°- 500°C, >500°C, Material, Vertical, Component, Region - Global Forecast to 2025 , MarketsandMarkets™, (2019).

Acknowledgements

I thank

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- Prof. Giuliano Benenti, University of Insubria, Italy

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Thank you for your attention!

ilia.khomchenko@um.edu.mt

Ilia Khomchenko: LinkedIn/Facebook/Telegram

I. Khomchenko et al., ”The thermoelectric conversion efficiency problem: Insights from the electron gas thermodynamics close to a phase transition”
SciPost Physics Core, **8** 015, (2025).

Appendix: Experimental Data

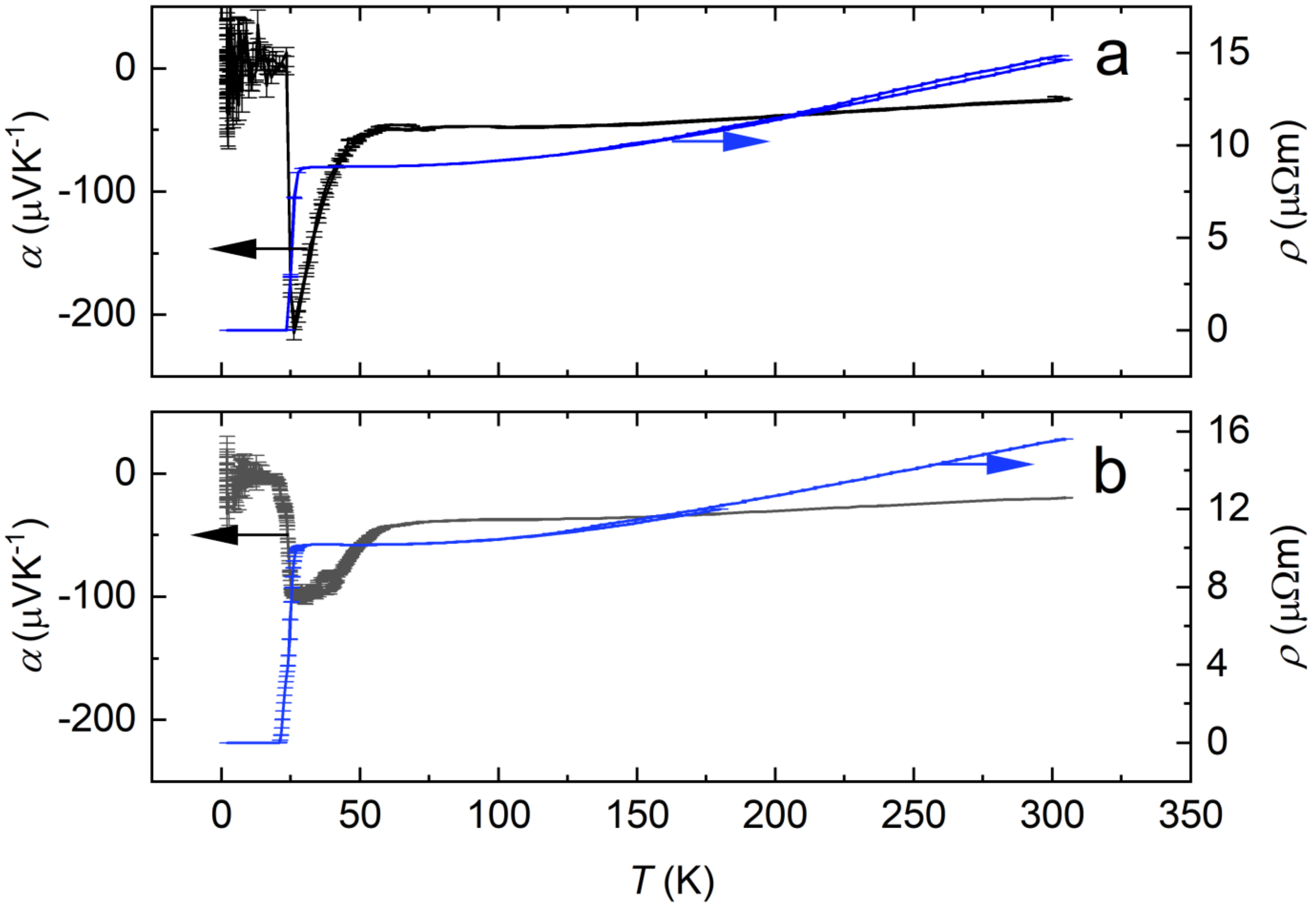


Fig.10. Thermoelectric transport characterization of the 100 nm $Ba(Fe_{0.90}Co_{0.10})_2As_2$ thin film showing the Seebeck coefficient α and electrical resistivity ρ:
a) high structural quality before ion bombardment, and b) low structural quality after ion bombardment.

Universität Bielefeld

Prof. Gabi Schierning

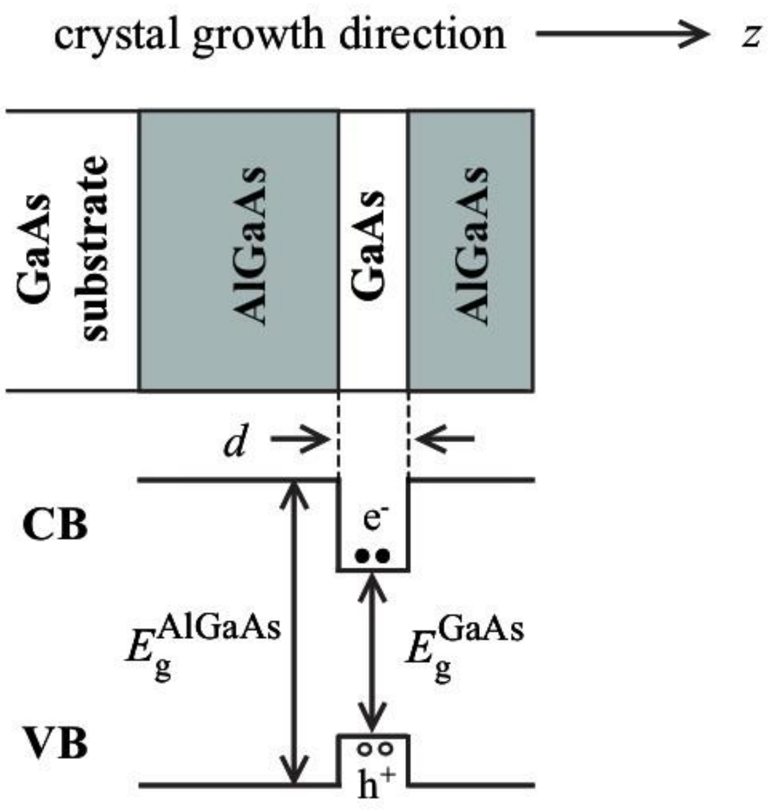
IFW Leibniz Institute for Solid State and Materials Research Dresden

Prof. Fritz Kurth, Prof. Ruben Hühne

UNIVERSITÄT DUISBURG ESSEN

Prof. Marika Schleberger, Dr. Franziska Maculewicz

Appendix: Quantum well structure



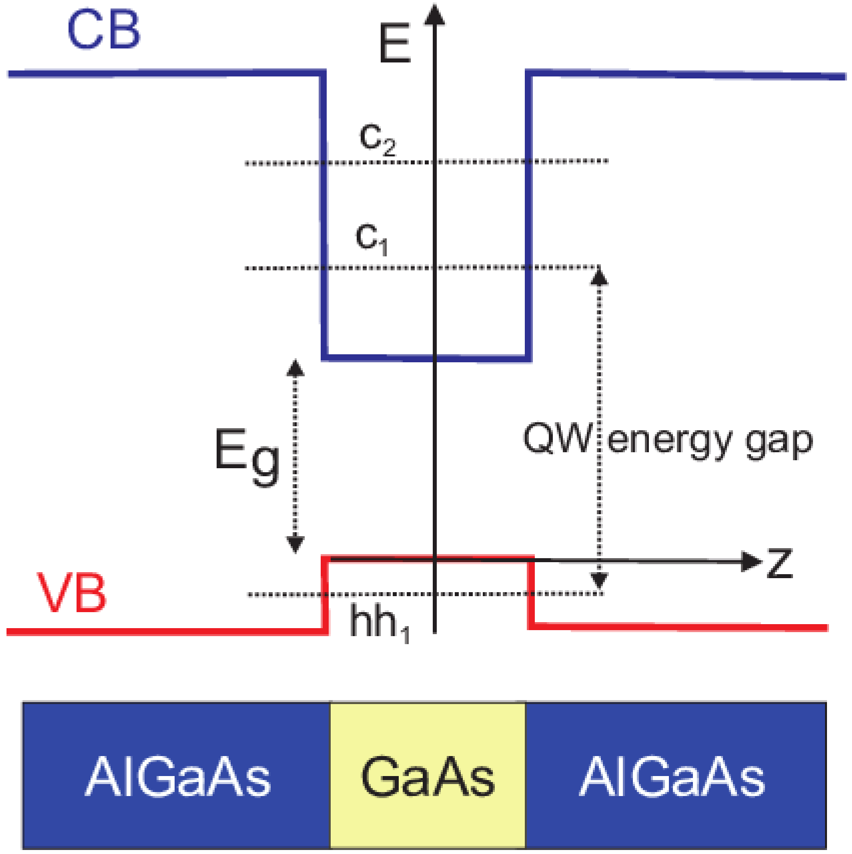


Fig.11. Quantum well: Scematic Picture.

M. Fox, Oxford University press, (2010).

D. Neilson et al. Journal of Physics: Conference Series 012008, **702** (2016).

Appendix: Available thermoelectric materials[5]

Applications Scenario temperature	Thermoelectric cooling (Cooling)	Low temperature recovery **Scenario #1** Low	Solar thermal generator **Scenario #2** Medium-Low	Automotive exhaust heat recovery **Scenario #3** Medium-High	Industrial furnace heat recovery **Scenario #4** High
Hot side temperature, T_H (°C)	15	100	250	500	800
Cold side temperature, T_C (°C)	5	20	20	50	50
Average temperature, T_m (°C)	10	60	135	275	425
Hot side *U*-value, U_H (W/m^2 K)	∞	102	102	120	120
Cold side *U*-value, U_C (W/m^2 K)	∞	105	105	105	105
HX & Plate Costs ($/(W/K))	–	18.48	18.48	18.48	18.48

[5]LeBlanc, S., Yee, S. K., Scullin, M. L., Dames, C. & Goodson, K. E., "Material and manufacturing cost considerations for thermoelectrics," *Renewable and Sustainable Energy Reviews* **32**, 313–327 (2014).

Appendix: Available thermoelectric materials[5]

Material type	ID #	Material name	Manufacturing type	Material cost ($/kg)	Evaluated for low or high temp. scenario				Ref.
					ZT_m material	F_{opt}	L_{opt} (mm)	Scenario Temp.	
Chalcogenides and SiGe	1	Bi_2Te_3	Bulk	110	0.74	0.18	4.53	Low	[35,36]
	2	$Bi_{0.52}Sb_{1.48}Te_3$	Bulk	125	1.05	0.21	4.41	Low	[37]
	3	$Bi_{0.52}Sb_{1.48}Te_3$	Nanobulk	125	1.52	0.29	3.47	Low	[37]
	4	$Bi_{0.54}Te_{0.46}$	Nanowire	84	0.02	0.07	1.10	Low	[38]
	5	$(Na_{0.0283}Pb_{0.945}Te_{0.9733})(Ag_{1.11}Te_{0.555})$	Nanobulk	81	1.45	0.34	3.01	High	[39]
	6	Bi-doped $PbSe_{0.98}Te_{0.02}$/PbTe	Superlattice	55	1.96	0.02	0.31	Low	[40]
	7	$AgPb_{18}SbTe_{20}$	Bulk	84	1.31	0.26	3.59	High	[41]
	8	SiGe	Bulk	679	0.30	0.07	2.66	High	[42]
	9	$Si_{80}Ge_{20}$	Nanobulk	371	0.53	0.13	3.39	High	[42]
	10	SiGe	Nanowire	679	0.22	0.06	1.59	Low	[43]
Silicides	11	$Mg_2Si_{0.85}Bi_{0.15}$	Nanobulk	6.67	0.67	0.74	29.5	High	[44]
	12	$Mg_2Si_{0.6}Sn_{0.4}$	Bulk	4.04	1.05	~1	45.5	High	[45]
	13	Si	Nanobulk	3.09	0.21	0.71	94.5	High	[46]
	14	Si	Nanowire	3.09	0.72	0.09	3.38	Low	[47]
	15	$MnSi_{1.75}$	Bulk	1.46	0.05	~1	37.5	Low	[48]
	16	$Mn_{15}Si_{28}$	Nanobulk	1.51	0.07	~1	35.7	Low	[48]
Clathrates	17	$Ba_8Ga_{16}Ge_{28}Zn_2$	Bulk	615	0.48	0.13	1.50	High	[49]
	18	$Ba_8Ga_{16}Ge_{30}$	Bulk	644	0.36	0.11	1.65	High	[50]
	19	$Ba_7Sr_1Al_{16}Si_{30}$	Bulk	1.64	0.09	~1	38.6	High	[51]
Skutterudites	20	$CeFe_4Sb_{12}$	Bulk	37	0.77	0.28	8.34	High	[52]
	21	$Yb_{0.2}In_{0.2}Co_4Sb_{12}$	Bulk	24	0.93	0.31	10.6	High	[53]
	22	$Ca_{0.18}Co_{3.97}Ni_{0.03}Sb_{12.40}$	Bulk	13	0.77	0.39	17.6	High	[54]
Oxides	23	$(Zn_{0.98}Al_{0.02})O$	Bulk	2.30	0.08	0.48	58.6	High	[55]
	24	$Ca_{2.4}Bi_{0.3}Na_{0.3}Co_4O_9$	Bulk	30	0.13	0.43	7.17	High	[56]
	25	InGaZnO	Nanowire	511	0.07	0.04	1.59	Low	[39]
	26	$Na_{0.7}CoO_{2-\delta}$	Bulk	36	0.52	0.22	12.7	High	[57]
Half Heuslers	27	$Zr_{0.25}Hf_{0.25}Ti_{0.5}NiSn_{0.994}Sb_{0.006}$	Bulk	9.71	1.38	0.49	19.6	High	[58]
	28	$Zr_{0.5}Hf_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$	Bulk	8.51	0.69	0.46	15.4	High	[59]
	29	$Ti_{0.8}Hf_{0.2}NiSn$	Bulk	10.70	0.41	0.41	16.5	High	[60]
Other	30	PEDOT:PSS	Polymer	0.34	0.01	~8	101	Low	[61]

[5]LeBlanc, S., Yee, S. K., Scullin, M. L., Dames, C. & Goodson, K. E., "Material and manufacturing cost considerations for thermoelectrics," *Renewable and Sustainable Energy Reviews* **32**, 313–327 (2014).

Appendix: Thermoelastic & Transport coefficients: FCP

$$\sigma_{\rm cp} = \frac{e^2}{16\hbar}\frac{1}{\varepsilon},$$

$$\alpha_{\rm cp} = \frac{\alpha_{\rm GL} k_{\rm B}}{2e} \ln\ \varepsilon,$$

$$\kappa_{\rm cp} = \frac{k_{\rm B}^2 \alpha_{\rm GL}^2}{64\hbar} T_{\rm c}\ \varepsilon\ \ln\frac{1}{\varepsilon}.$$

$$\varepsilon = \ln T/T_{\rm c} \approx (T - T_{\rm c})/T_{\rm c}$$

$$\mathcal{F}_{\rm cp} = -\frac{A}{4\pi\xi^2} k_{\rm B} T_{\rm c} \varepsilon \ln \varepsilon$$

$$\mu_{\rm cp} = \frac{\mathcal{F}_{\rm cp}}{\partial \varepsilon} \times \left(\frac{\partial N_{\rm cp}}{\partial \varepsilon}\right)^{-1}$$

$$\chi_T = \frac{1}{N_{\rm cp}} \left(\frac{\partial N_{\rm cp}}{\partial \mu_{\rm cp}}\right)_T \quad C_N = -\frac{T}{N_{\rm cp}}\frac{\partial^2 \mathcal{F}_{\rm cp}}{\partial T^2}$$

ξ – coherence length, A – surface area of 2D system, and $T_{\rm c}$ – critical temperature.

$\alpha_{\rm GL}$ – dimensionless parameter in the Ginzburg-Landau free energy functional.

[9]**I. Khomchenko** et al., "The thermoelectric conversion efficiency problem: Insights from the electron gas thermodynamics close to a phase transition" SciPost Physics Core, **8** 015, (2025).

Appendix: Additional $z_e T$ vs. $Z_{th} T$ curves

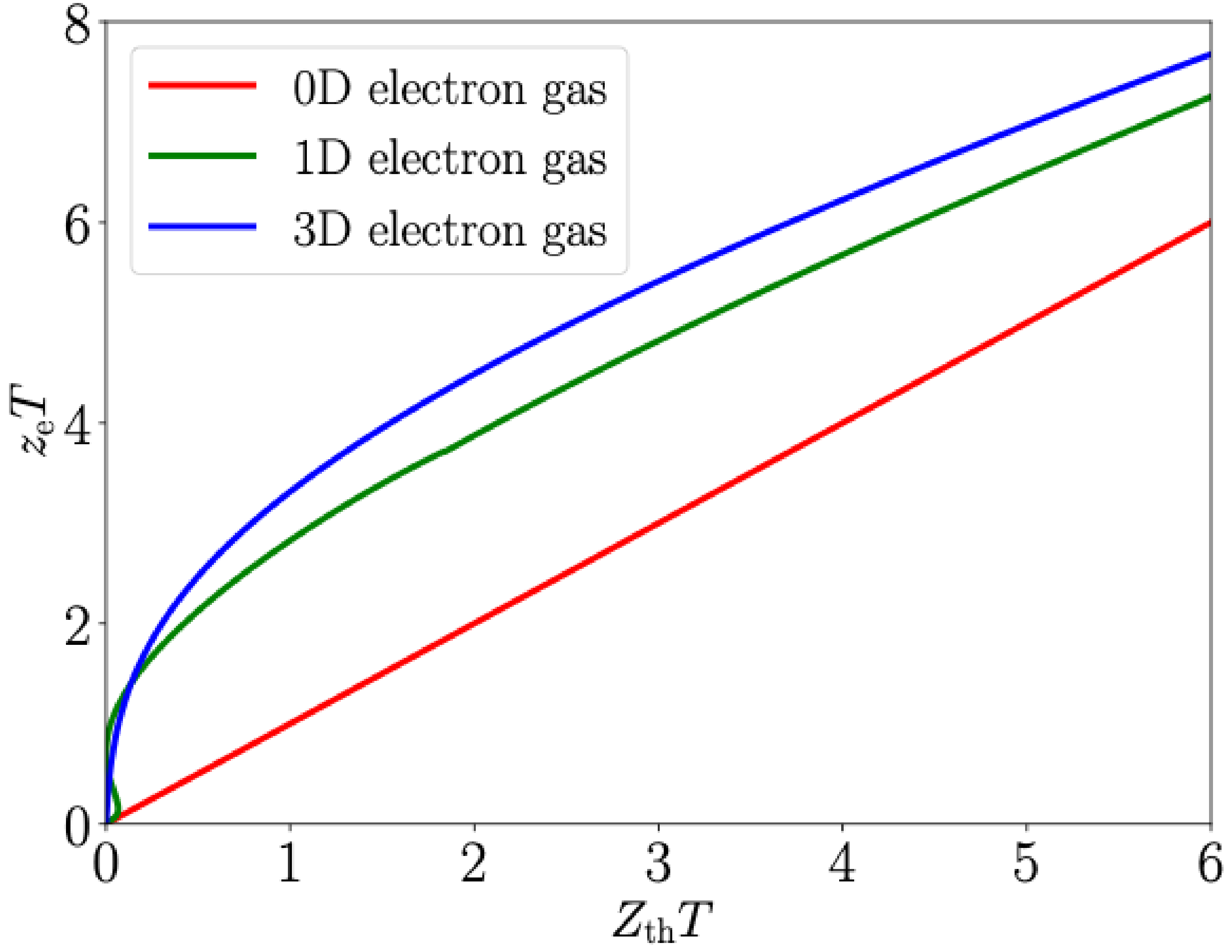


Fig.12. $z_e T$ vs $Z_{th} T$ for the 0D, 1D and 3D electron gases.

[9] **I. Khomchenko** et al., "The thermoelectric conversion efficiency problem: Insights from the electron gas thermodynamics close to a phase transition" SciPost Physics Core, **8** 015, (2025).