Ideal Quantum Gases I: Bosons [tsc14]

In the previous module [tsc13] we have set the stage for the thermodynamic analysis of a gas massive bosons. We assume the particles have nonrelativistic energies and no spin.

Equation of state:

The thermodynamic equation of state of an ideal gas is a relation between pressure, volume per particle (or mole), and temperature.

For the classical ideal gas it reads[1] $pV = \mathcal{N} k_B T$.

For the ideal boson gas we use (from [tsc13]) two sums over 1-particle states,

$$pV = -\Omega = -k_B T \sum_{k=1}^{\infty} \ln\left(1 - z e^{-\beta\epsilon_k}\right), \quad \mathcal{N} = \sum_{k=1}^{\infty} \frac{1}{z^{-1} e^{\beta\epsilon_k} - 1},$$

and the density 1-particle states, $D(\epsilon) = \dfrac{V}{\Gamma(\mathcal{D}/2)} \left(\dfrac{2\pi m}{h^2}\right)^{\mathcal{D}/2} \epsilon^{\mathcal{D}/2-1}$.

This allows us to convert the sums into integrals [tex113]:[2]

$$\frac{pV}{k_B T} = -\int_0^{\infty} d\epsilon\, D(\epsilon) \ln\left(1 - z e^{-\beta\epsilon}\right) = \frac{V}{\lambda_T^{\mathcal{D}}} g_{\mathcal{D}/2+1}(z),$$

$$\mathcal{N} = \int_0^{\infty} d\epsilon\, \frac{D(\epsilon)}{z^{-1} e^{\beta\epsilon} - 1} = \frac{V}{\lambda_T^{\mathcal{D}}} g_{\mathcal{D}/2}(z),$$

where we have introduced the polylogarithmic Bose-Einstein functions,

$$g_n(z) = \mathrm{Li}_n(z) \doteq \frac{1}{\Gamma(n)} \int_0^{\infty} \frac{dx\, x^{n-1}}{z^{-1} e^x - 1}, \qquad 0 \leq z \leq 1,$$

whose properties are elucidated in [tsl36].

Note the limited range of fugacity, $0 \leq z \leq 1$. The limit $z \to 1$ from below signals criticality and the onset of condensation. At $z = 1$, the lowest energy level (at $\epsilon = 0$) may be populated by a macroscopic number of particles.

Parametric representation of the thermodynamic equation of state:

$$\frac{pV}{\mathcal{N} k_B T} = \frac{g_{\mathcal{D}/2+1}(z)}{g_{\mathcal{D}/2}(z)}, \quad 0 \leq z \leq 1.$$

---

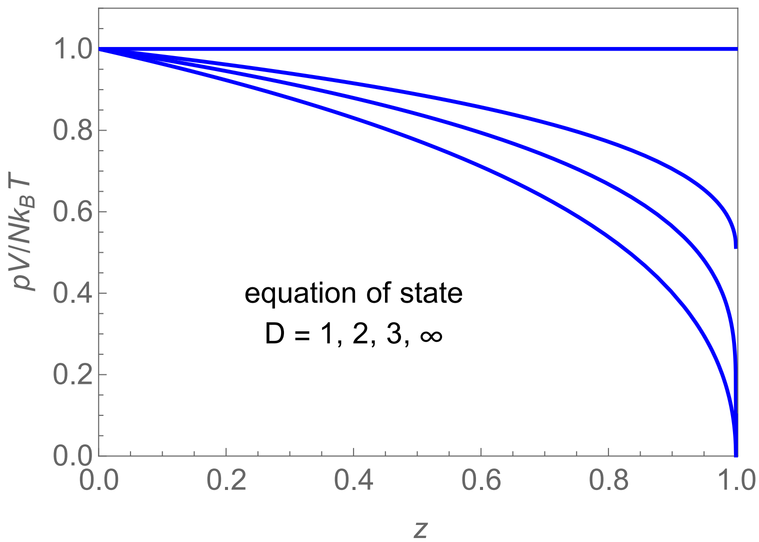
[1] In the grandcanonical ensemble, $\mathcal{N}$ is the average number of particles in an open system, controlled by the chemical potential μ or the fugacity $z = e^{\beta\mu}$.

[2] The expression for $\mathcal{N}$ requires a more subtle interpretation for $z = 1$ (see later).

Low fugacity, $z \ll 1$, means high temperature and/or low density. Here the boson equation of state deviates little from that of the classical ideal gas.

At lower temperature and/or higher density, the pressure of bosons is lower than that of classical particles. The deviations are stronger in low dimensions.

The horizontal line indicates that the boson gas in $\mathcal{D} = \infty$ dimensions behaves like a classical ideal gas. It does so only if $z < 1$.



Additional insight into the equation of state is gained by a look at isochores, isotherms, and isobars. For that purpose we introduce scaled variables.

Here we switch to the canonical ensemble. We keep the number of particles fixed ($N =$ const) and treat the fugacity (now a dependent thermodynamic variable) as a convenient parameter.

Reference values:

The reference values for T, $v \doteq V/N$, and p introduced here are based on

– the thermal wavelength: $\lambda_T \doteq \sqrt{\frac{h^2}{2\pi m k_B T}} = \sqrt{\frac{\Lambda}{k_B T}}, \quad \Lambda = \frac{h^2}{2\pi m},$

– the MB equation of state: $pv = k_B T$.

We construct p_v, T_v for isochores, v_T, p_T for isotherms, and T_p, v_p for isobars from the two ingredients as follows:

▷ $p_v v = k_B T_v, \quad v = \left(\frac{\Lambda}{k_B T_v}\right)^{\mathcal{D}/2} \qquad (v = \text{const.})$

▷ $p_T v_T = k_B T, \quad v_T = \left(\frac{\Lambda}{k_B T}\right)^{\mathcal{D}/2} \qquad (T = \text{const.})$

▷ $p v_p = k_B T_p, \quad v_p = \left(\frac{\Lambda}{k_B T_p}\right)^{\mathcal{D}/2} \qquad (p = \text{const.})$

The results are listed in the following:

$$k_B T_v = \frac{\Lambda}{v^{2/\mathcal{D}}} \qquad p_v = \frac{\Lambda}{v^{2/\mathcal{D}+1}} \qquad (v = \text{const.})$$

$$v_T = \left(\frac{\Lambda}{k_B T}\right)^{\mathcal{D}/2} \qquad p_T = \Lambda \left(\frac{k_B T}{\Lambda}\right)^{\mathcal{D}/2+1} \qquad (T = \text{const.})$$

$$k_B T_p = \Lambda \left(\frac{p}{\Lambda}\right)^{2/(\mathcal{D}+2)} \qquad v_p = \left(\frac{\Lambda}{p}\right)^{\mathcal{D}/(\mathcal{D}+2)} \qquad (p = \text{const.})$$

The use of scaled variables with these reference values allows us to construct universal curves for isochores, isotherms, and isobars:

▷ p/p_v versus T/T_v at $v = \text{const.}$
▷ p/p_T versus v/v_T at $T = \text{const.}$
▷ v/v_p versus T/T_p at $p = \text{const.}$

The shape of these curves is independent of the number of particles and of the value of the variable kept constant.

Isochores:

Universal isochore inferred from expressions for pV/k_BT and $\mathcal{N}$ [tex114]:

$$\frac{p}{p_v} = \frac{g_{\mathcal{D}/2+1}(z)}{\left[g_{\mathcal{D}/2}(z)\right]^{2/\mathcal{D}+1}}, \quad \frac{T}{T_v} = \left[g_{\mathcal{D}/2}(z)\right]^{-2/\mathcal{D}} \quad : \ 0 \leq z \leq 1.$$

This parametric expression holds for $T \geq T_c$.

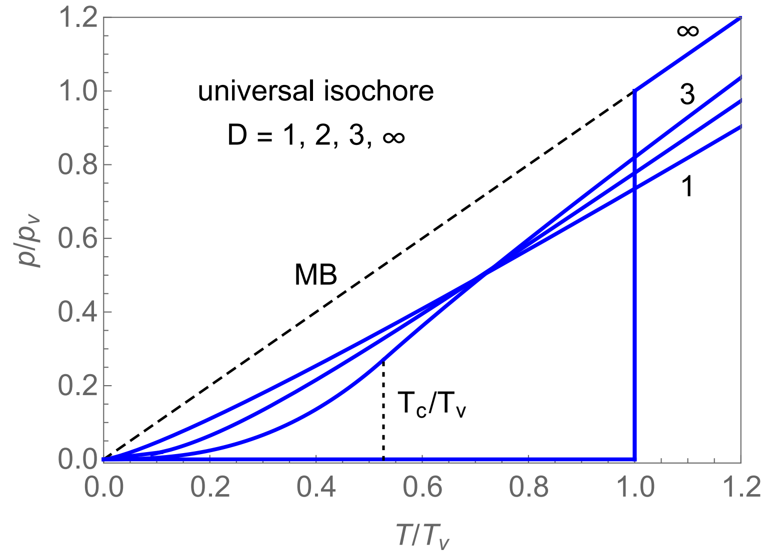
Critical temperature is approached from above as $z \to 1$:

$$\Rightarrow \ \frac{T_c}{T_v} = [\zeta(\mathcal{D}/2)]^{-2/\mathcal{D}} = \begin{cases} 0 & : \ \mathcal{D} = 1, 2 \\ 0.527 & : \ \mathcal{D} = 3 \\ 1 & : \ \mathcal{D} = \infty \end{cases}$$

At $T \leq T_c$, the fugacity is locked into the value $z = 1$ [tex114].

Isochore at $T \leq T_c$: $\dfrac{p}{p_v} = \left(\dfrac{T}{T_v}\right)^{\mathcal{D}/2+1} \zeta(\mathcal{D}/2+1)$.

This expression also holds asymptotically for $T \ll T_v$ in $\mathcal{D} \leq 2$.



– The isochore of the MB gas is a straight line with unit slope and no intercept (dashed line).

– The boson isochores approach zero faster, $\sim T^{\mathcal{D}/2+1}$, in the low-T limit.

– The critical temperature T_c is nonzero only for $\mathcal{D} > 2$.

– At $T < T_c$, the isochore is a pure power law. Bosons in the Bose-Einstein condensate (BEC) do not contribute to the pressure.[3]

– In the limit $\mathcal{D} \to \infty$, the isochore becomes discontinuous. Bosons behave classically at $T > T_c$ and are all condensed at $T < T_c$.

– The high-temperature asymptotics of the boson isochore is [tex114]

$$\frac{p}{p_v} \sim \frac{T}{T_v}\left[1 - \frac{1}{2^{\mathcal{D}/2+1}}\left(\frac{T_v}{T}\right)^{\mathcal{D}/2}\right].$$

At high T, lower $\mathcal{D}$ means lower pressure. At low T the trend is opposite.

[3]This is only true in the framework of ideal gases. Real condensates have an extension albeit tiny compared to the gas.

Coexistence of gas and condensate:

It is convenient to introduce phase coexistence in the context of isochores, where it is realized at $T < T_c$. The original (grandcanonical) expression for $\mathcal{N}$ must be adapted to the case $N = \text{const}$ as follows:

$$N = \begin{cases} N_{\text{gas}} = \dfrac{V}{\lambda_T^{\mathcal{D}}} g_{\mathcal{D}/2}(z) & : \; T \geq T_c, \\ N_{\text{gas}} + N_{\text{BEC}} = \dfrac{V}{\lambda_T^{\mathcal{D}}} \zeta(\mathcal{D}/2) + N_{\text{BEC}} & : \; T \leq T_c. \end{cases}$$

– The two expressions are consistent at $T = T_c$: $N_{\text{gas}} = N$, $N_{\text{BEC}} = 0$.

– The first expression determines z for given $N = N_{\text{gas}}$, V, and T.

– The second expression determines N_{gas} and N_{BEC} for given N, $z = 1$, and $T < T_c$.

– For the regime of coexistence, we can write.

$$\frac{N_{\text{gas}}}{N} = 1 - \frac{N_{\text{BEC}}}{N} = \frac{[V/\lambda_T^{\mathcal{D}}]\zeta(\mathcal{D}/2)}{[V/\lambda_{T_c}^{\mathcal{D}}]\zeta(\mathcal{D}/2)} = \left(\frac{T}{T_c}\right)^{\mathcal{D}/2} \quad : \; T \leq T_c.$$

– If $T_c > 0$, N_{gas} vanishes in a power-law cusp as $T \to 0$.

– If $T_c = 0$, N_{gas} stays constant for any $T > 0$.

Isotherms:

Universal isotherm inferred from expressions for pV/k_BT and $\mathcal{N}$ [tex115]:

$$\frac{p}{p_T} = g_{\mathcal{D}/2+1}(z), \qquad \frac{v}{v_T} = [g_{\mathcal{D}/2}(z)]^{-1}.$$

This parametric expression holds for $v \geq v_c$.

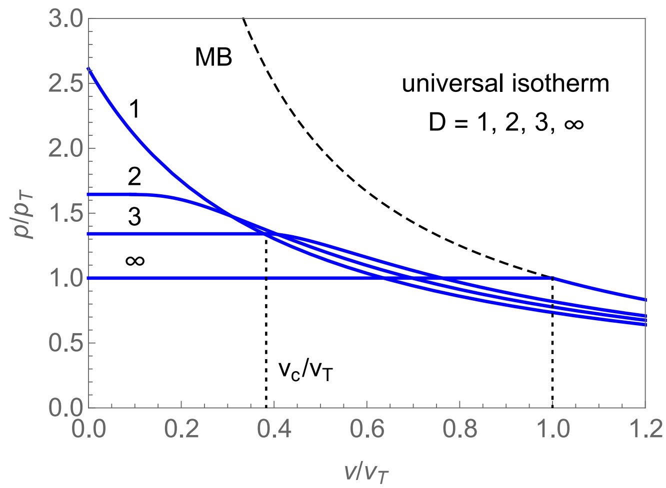
Critical volume is approached from above as $z \to 1$:

$$\frac{v_c}{v_T} = [\zeta(\mathcal{D}/2)]^{-1} = \begin{cases} 0 & : \; \mathcal{D} = 1, 2 \\ 0.383 & : \; \mathcal{D} = 3 \\ 1 & : \; \mathcal{D} = \infty \end{cases}$$

Constant pressure p_c at $v \leq v_c$:

$$\frac{p}{p_T} = \frac{p_c}{p_T} = \zeta(\mathcal{D}/2 + 1) = \begin{cases} 2.612 & : \; \mathcal{D} = 1 \\ 1.645 & : \; \mathcal{D} = 2 \\ 1.341 & : \; \mathcal{D} = 3 \\ 1 & : \; \mathcal{D} = \infty \end{cases}$$

Out[1415]=



– The isotherm of the MB gas (shown dashed) reflects Boyle's law.

– If $v_c = 0$, realized in $\mathcal{D} \leq 2$, the isochores are strictly monotonically decreasing, but the pressure is significantly lower than in the BE gas.

– If $v_c > 0$, realized in $\mathcal{D} > 2$, the pressure levels off to a constant at $v < v_c$. Only the particles in the gas phase contribute.

– In the limit $\mathcal{D} \to \infty$, the particles in the gas phase uphold Boyle's law.

– The large volume asymptotics of the boson isotherm is [tex115]

$$\frac{p}{p_T} \sim \frac{v_T}{v}\left[1 - 2^{-\mathcal{D}/2-1}\left(\frac{v_T}{v}\right)\right].$$

The deviations are strongest in low $\mathcal{D}$. By contrast, for small v the deviations from Boyle's law are largest in high $\mathcal{D}$.

Isobars:

Universal isobar inferred from expressions for pV/k_BT and $\mathcal{N}$ [tex115]:

$$\frac{v}{v_p} = \frac{\left[g_{\mathcal{D}/2+1}(z)\right]^{\mathcal{D}/(\mathcal{D}+2)}}{g_{\mathcal{D}/2}(z)}, \qquad \frac{T}{T_p} = \left[g_{\mathcal{D}/2+1}(z)\right]^{-2/(\mathcal{D}+2)}.$$

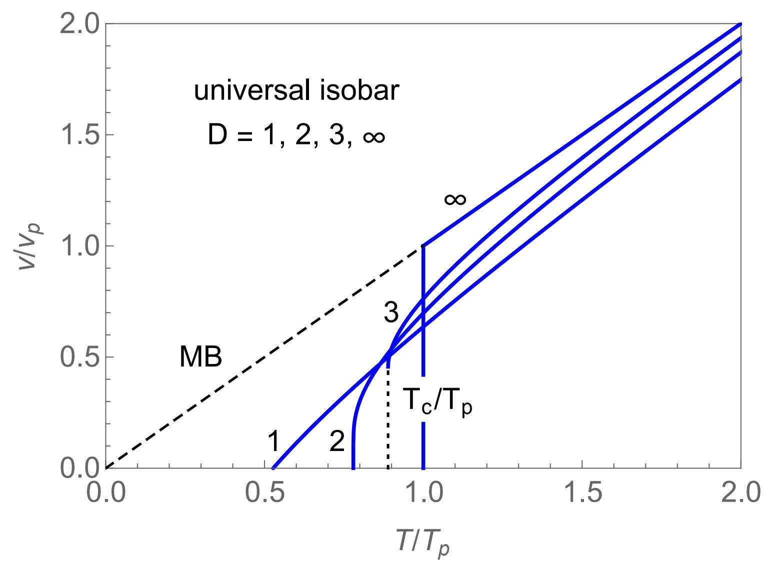
This parametric expression holds for $T \geq T_c$.

Critical temperature is approached from above as $z \to 1$:

$$\frac{T_c}{T_p} = \left[\zeta(\mathcal{D}/2+1)\right]^{-2/(\mathcal{D}+2)} = \begin{cases} 0.527 & : \mathcal{D} = 1 \\ 0.780 & : \mathcal{D} = 2 \\ 0.889 & : \mathcal{D} = 3 \\ 1 & : \mathcal{D} = \infty \end{cases}$$

Critical volume:

$$\frac{v_c}{v_p} = \frac{[\zeta(\mathcal{D}/2+1)]^{\mathcal{D}/(\mathcal{D}+2)}}{\zeta(\mathcal{D}/2)} = \begin{cases} 0 & : \ \mathcal{D} = 1, 2 \\ 0.457 & : \ \mathcal{D} = 3 \\ 1 & : \ \mathcal{D} = \infty \end{cases}$$



– The MB isobar (shown dashed) is linear with no intercept.

– Boson isobars in any $\mathcal{D}$ reach $v = 0$ at a nonzero T_c. Bosons can only support a gas phase at given pressure if the temperature exceeds the threshold value T_c.

– The critical volume v_c vanishes in $\mathcal{D} \leq 2$. The isobars bend down to $v = 0$ continuously.

– In $2 < \mathcal{D} < \infty$, the isobars bend down to a nonzero v_c and then drop to $v = 0$ in a discontinuity.

– In the limits $\mathcal{D} \to \infty$ the boson gas behaves classically at $T > T_c$ and collapses with no warning.

– The high-temperature asymptotics of the boson isobar is [tex115]

$$\frac{v}{v_p} \sim \frac{T}{T_p}\left[1 - 2^{-\mathcal{D}/2-1}\left(\frac{T_p}{T}\right)^{\mathcal{D}/2+1}\right].$$

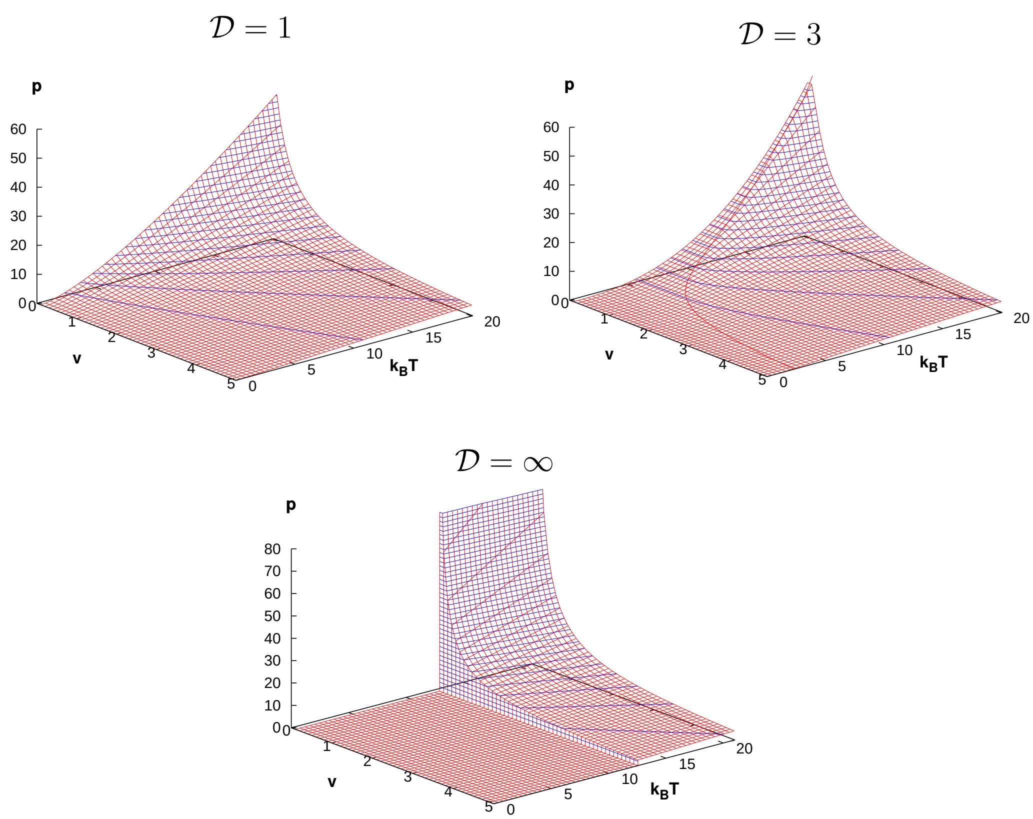
As already observed in isochores and isotherms, the deviations of the boson asymptotics from the MB results are highest in low $\mathcal{D}$ and vanish as $\mathcal{D} \to \infty$.

Phase diagrams:

The thermodynamic equation of state of the ideal BE gas describes a surface in pvT-space. For the MB gas that surface is described by $pv = k_B T$.

The onset of condensation in the BE gas is described by a transition line on that surface.

- ▷ $\mathcal{D} = 1$: The transition is at $v = 0$ and forms an edge of the surface. It is a particular isochore. The same is the case in $\mathcal{D} = 2$ (not shown).
- ▷ $\mathcal{D} = 3$: The transition line runs through the surface and causes a sharp edge in it. The same is the case in $3 < \mathcal{D} < \infty$ (not shown).
- ▷ $\mathcal{D} = \infty$: The transition line is at $k_B T_c = h^2/2\pi m$. It is an isotherm and causes a discontinuity in the sureface.



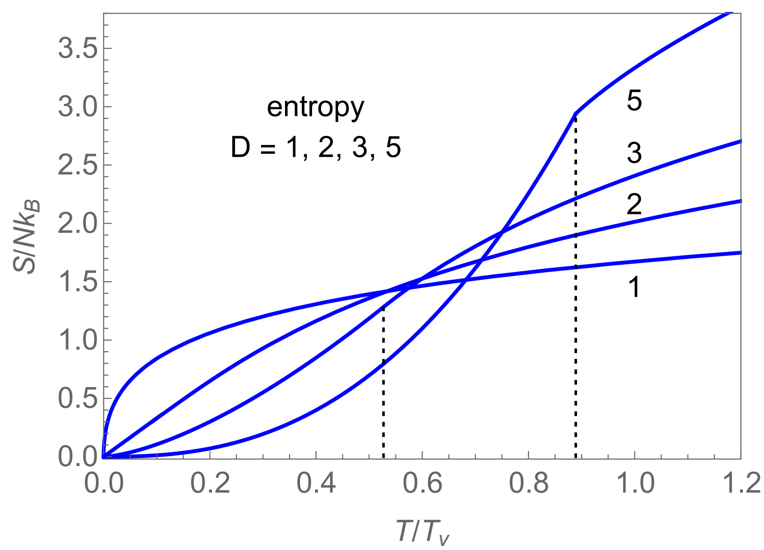
Entropy:

For the derivation of the entropy we recall the expression for the grand potential stated at the beginning of this module and its relation to the entropy:

$$\Omega = -\frac{V k_B T}{\lambda_T^{\mathcal{D}}} g_{\mathcal{D}/2+1}(z), \quad S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}.$$

The result is worked out in [tex179] for N particles confined to a rigid box:

$$\frac{S}{N k_B} = \begin{cases} \left(\frac{\mathcal{D}}{2}+1\right)\frac{g_{\mathcal{D}/2+1}(z)}{g_{\mathcal{D}/2}(z)} - \ln z, & T \geq T_c, \\ \left(\frac{\mathcal{D}}{2}+1\right)\zeta(\mathcal{D}/2+1)\left(\frac{T}{T_v}\right)^{\mathcal{D}/2}, & T \leq T_c. \end{cases}$$



– The values of T_c/T_v in $\mathcal{D} > 2$ were derived for the isochores.

– The expression for $T < T_c$, which is exact in $\mathcal{D} > 2$, is also accurate in $\mathcal{D} \leq 2$ asymptotically for $T \ll T_v$.

– At high temperature, all curve rise logarithmically – an attribute shared with the MB gas.

– In the low-temperature limit all curves approach zero – an attribute not shared with the MB gas.

– At T_c, the curve for $\mathcal{D} = 5$ has a discontinuity on slope, which the curve for $\mathcal{D} = 3$ does not have.

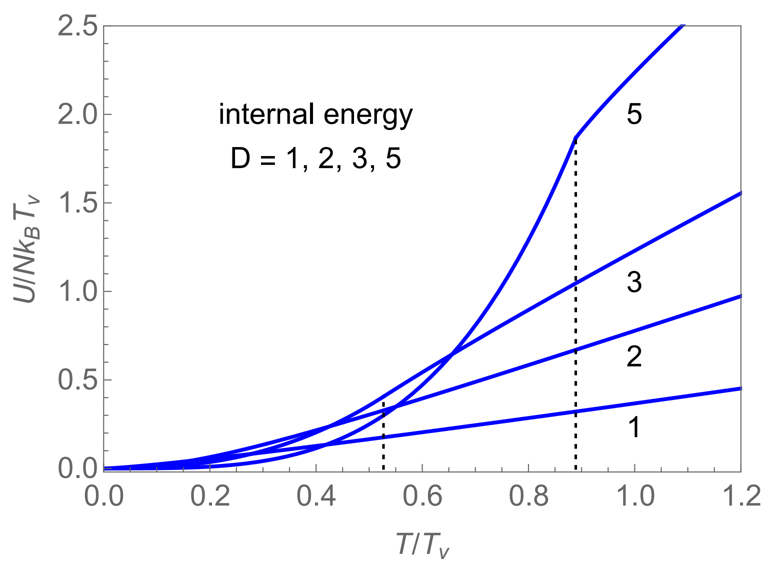
Internal energy:

Given the explicit expressions for Ω, S, N derived earlier, we can calculate the internal energy from the relation,

$$U = \Omega + TS + \mu N.$$

The result is worked out in [tex179] for N particles confined to a rigid box:

$$\frac{U}{Nk_BT_v} = \begin{cases} \dfrac{\mathcal{D}}{2}\dfrac{g_{\mathcal{D}/2+1}(z)}{g_{\mathcal{D}/2}(z)}\dfrac{T}{T_v}, & T \geq T_c, \\ \dfrac{\mathcal{D}}{2}\zeta(\mathcal{D}/2+1)\left(\dfrac{T}{T_v}\right)^{\mathcal{D}/2+1}, & T \leq T_c. \end{cases}$$



- The values of T_c/T_v in $\mathcal{D} > 2$ were derived for the isochores.
- The expression for $T < T_c$, which is exact in $\mathcal{D} > 2$, is also accurate in $\mathcal{D} \leq 2$ asymptotically for $T \ll T_v$.
- At high temperature, all curve rise linearly – an attribute shared with the MB gas.
- In the low-temperature limit all curves approach zero faster than linearly – an attribute not shared with the MB gas, which exhibits a linear approach.
- At T_c, the curve for $\mathcal{D} = 5$ has a discontinuity on slope, which the curve for $\mathcal{D} = 3$ does not have.

Heat capacity:

Given the explicit expressions for U and S derived earlier, we can calculate the heat capacity from either result as follows:

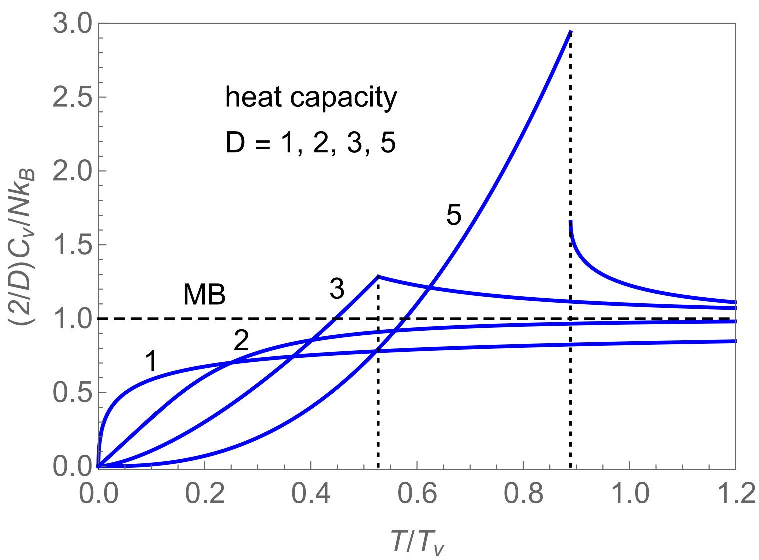
$$C_v = \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}.$$

The derivatives carried out for $T \geq T_c$ yield the expression [tex97],

$$\frac{C_V}{\mathcal{N}k_B} = \left(\frac{\mathcal{D}}{2} + \frac{\mathcal{D}^2}{4}\right)\frac{g_{\mathcal{D}/2+1}(z)}{g_{\mathcal{D}/2}(z)} - \frac{\mathcal{D}^2}{4}\frac{g_{\mathcal{D}/2}(z)}{g_{\mathcal{D}/2-1}(z)}.$$

The result for $T \leq T_c$ represents a pure power-law [tex116]:

$$\frac{C_V}{\mathcal{N}k_B} = \left(\frac{\mathcal{D}}{2}+\frac{\mathcal{D}^2}{4}\right)\zeta\left(\frac{\mathcal{D}}{2}+1\right)\left(\frac{T}{T_v}\right)^{\mathcal{D}/2} = \left(\frac{\mathcal{D}}{2} + \frac{\mathcal{D}^2}{4}\right)\frac{\zeta\left(\frac{\mathcal{D}}{2}+1\right)}{\zeta\left(\frac{\mathcal{D}}{2}\right)}\left(\frac{T}{T_c}\right)^{\mathcal{D}/2}.$$



– All BE curves are approach zero in the low-T limit as required by the third law of thermodynamics. The MB result violates that law.

– All BE curves approach the MB result in the high-T limit, but from different sides. The switch is reflected in the high-T asymptotics,

$$\frac{C_V}{\mathcal{N}k_B} \sim \frac{\mathcal{D}}{2}\left[1 + \frac{\mathcal{D}/2-1}{2^{\mathcal{D}/2+1}}\left(\frac{T_v}{T}\right)^{\mathcal{D}/2}\right].$$

– The expression for $T < T_c$ is exact to leading order in $\mathcal{D} = 1$ asymptotically for $T \ll T_v$, but misses logarithmic corrections in $\mathcal{D} = 2$.

– The heat capacity is smooth for $\mathcal{D} < 2$, remains continuous for $\mathcal{D} \leq 4$, and becomes discontinuous for $\mathcal{D} > 4$.

Exercises:

▷ Fundamental relations [tex113]

▷ Isochores [tex114]

▷ Isotherms and isobars [tex115]

▷ Entropy and internal energy [tex179]

▷ Heat capacity at high temperature [tex97]

▷ Heat capacity at low temperature [tex116]

▷ Isothermal compressibility [tex128]

▷ Isobaric expnasivity [tex129]

▷ Speed of sound [tex130]

▷ Ultrarelativistic Bose-Einstein gas [tex98]

▷ Statistical mechanics of blackbody radiation [tex105]