Bibliography

1. The problematic cases are mostly those where the number of particles is too small for the approximations made in the statistical approach.↩

2. As the distributions are vectors and all combinations have to be considered, an outer product must be taken.↩

3. The solution of the second task can be found in .↩

4. Here, each individual spin is considered as a system and the N spins as an ensemble of identical systems↩

5. Thanks to Takuya Segawa for pointing out a mistake in this expression in ↩

6. If the individual random numbers are not identically distributed, the theorem will still apply, if Lyapunov's condition or Lindeberg's condition is fulfilled. See the very useful and detailed Wikipedia article on the Central limit theorem for more information and proofs.↩

7. This one-liner may cause efficiency problems if computational effort per trial besides random number generation is small.↩

8. It is more tricky to argue that it will *only* vanish if ρ is uniform. However, as the individual particles follow random phase space trajectories, it is hard to imagine that the right-hand side could be stationary zero unless ρ is uniform.↩

9. Where g_e is the g value of the free electron and μ_{B} the Bohr magneton.↩

10. The dependence on N and V arises, because these parameters influence the energy levels↩

11. The condition of a quadratic contribution arises from an assumption that is made when integrating over the corresponding coordinate.↩

12. Boltzmann was thinking in terms of discrete probability theory. As we want to use continuous probability theory here, we have made the transition from probability to probability density.↩

13. The theorem relies on uniform distribution in this volume at some point in time, but it applies here, as we have seen before that such uniform distribution in an energy shell is a feature of the equilibrium state of an isolated system.↩

14. Purists of statistical thermodynamics will shudder, as we now rely on the entropy definition of phenomenological thermodynamics. We hide the fact that we are incapable of a strict general derivation and just relate the new concepts of statistical thermodynamics to the concepts of phenomenological thermodynamics. In effect, we show how state functions of phenomenological thermodynamics must be computed if both Boltzmann's and Clausius' entropy definitions apply.↩

15. This thought experiment was suggested to me by Roland Riek.↩

16. One can speculate on philosophical interpretations. Irreversibility could be a consequence of partitioning the universe into an observer and all the rest, a notion that resonates with intuitions of some mystical thinkers across different religious traditions. Although the idea is appealing, it cannot be rationally proved. Rational thought already implies that an observer exists.↩

17. This is more a matter of taste than of substance. As long as $Be^{\epsilon_i/k_{\mathrm{N}}T} \gg 1$, we can approximate any type of quantum statistics by Maxwell-Boltzmann statistics before solving for B. We are thus permitted to freely mix Maxwell-Boltzmann statistics with quantum-mechanical equations of motion.↩

18. The shift does not influence the denominator, as it merely removes the first factor on the right-hand side of Equation ???).↩

19. We neglect nuclear quadrupole coupling, which averages in gases.↩

20. The zero-point vibrational energy is an exception from this principle with respect to internal energy, but not heat capacity.↩

21. There is a misprint in ↩

22. This separation of the terms is mathematically somewhat awkward, since in the last two terms the argument of the logarithm has a unit. However, if the two terms are combined the logarithm of the unit cancels.↩