

What good is the thermodynamic limit?

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Statistical mechanics applies to large systems: technically, its results are exact only for infinitely large systems in “the thermodynamic limit.” The importance of this proviso is often minimized in undergraduate courses. This paper presents six paradoxes in statistical mechanics that can be resolved only by acknowledging the thermodynamic limit. For example, it demonstrates that the widely used microcanonical “thin phase space limit” must be taken *after* taking the thermodynamic limit. © 2004 American Association of Physics Teachers.
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Statistical mechanics is the study of matter in bulk. Whereas undergraduate courses in subjects like classical or quantum mechanics are loath to approach the three-body problem, statistical mechanics courses routinely deal with the 6.02×10^{23} -body problem. How can one subject be so generous with particle number while others are so parsimonious?

The answer has two facets: First, statistical mechanics asks different questions from, say, classical mechanics. Instead of trying to trace all the particle trajectories for all time, statistical mechanics is content to ask, for example, how the mean energy varies with temperature and pressure. Second, statistical mechanics turns the difficulty of bigness into a blessing by insisting on treating only very large systems, in which many of the details of system size fade into insignificance. The formal, mathematical term for this bigness condition is “the thermodynamic limit.”

For example, in a fluid system specified by the temperature T , volume V , and particle number N , statistical mechanics can calculate the Helmholtz free energy $F(T, V, N)$, but usually finds that function interesting only in the limit that $V \rightarrow \infty$ and $N \rightarrow \infty$ in such a way that their ratio $\rho = N/V$ approaches a finite quantity. In this so-called thermodynamic limit, the free energy F itself grows to infinity, but the free energy per particle $f_N(T, \rho) = F(T, V, N)/N$ is expected to approach a finite value.

Alternatively, in the microcanonical ensemble, this fluid system would be specified by energy E , volume V , and particle number N . The function of interest is now the entropy $S(E, V, N)$, and one expects that a doubling of E , V , and N will result in a doubling of S . However, we shall soon see that this expectation—the expectation of extensivity—is not exact for any finite system. The expectation holds with increasing accuracy for larger and larger systems, but is exactly true only in the thermodynamic limit.

Why should anyone care about results in the thermodynamic limit, when every real system is finite? Because real bulk systems have so many particles that they can be considered to exist in the thermodynamic limit. As the system size increases, the free energy density $f_N = F/N$ approaches the limiting value f_∞ , and typically the difference between $f_{10^{23}}$ and f_∞ is smaller than experimental error.

Undergraduate statistical mechanics texts usually have little to say directly about the thermodynamic limit. Instead of an explicit mention, they vaguely invoke a “large system.” Of the four well-known texts by Reif,¹ Kittel and

Kroemer,² Baierlein,³ and Schroeder,⁴ only the last one mentions the thermodynamic limit at all. This is a pity, because any student trained to ask questions and to delve into the meanings behind equations will find confusing situations in statistical mechanics, and these confusions will vanish only when the thermodynamic limit is invoked. This paper introduces six such cases and shows how the resulting paradoxes are resolved in the thermodynamic limit. Those desiring a more systematic treatment of the thermodynamic limit should consult Thompson,⁵ or Fisher,⁶ or the definitive formal treatment by Ruelle.⁷

I. THE LIMIT OF THIN PHASE SPACE

Here is a story of statistical mechanics in the microcanonical ensemble: The system consists of N identical, classical particles (perhaps interacting, perhaps independent) confined to a container of volume V . The energy is known to have some value between E and $E + \Delta E$. The volume of phase space corresponding to this energy range is called $W(E, \Delta E, V, N)$, and the entropy is given by

$$S(E, V, N) = k_B \ln\{W(E, \Delta E, V, N)/h^{3N}N!\}, \quad (1)$$

where h is Planck’s constant. The use of an energy range ΔE is, of course, nothing but a mathematical convenience. At the end of any calculation, we will take the “thin phase space limit,” namely $\Delta E \rightarrow 0$.

Really? Why wait for the end of the calculation? In the limit $\Delta E \rightarrow 0$, the phase-space volume W vanishes, so $S = k_B \ln(0) = -\infty$. This holds true for any system, whether gas, liquid, or solid. We have just completed all possible statistical mechanical calculations, and found that the result is necessarily trivial!

Obviously something is wrong with the above analysis, but what? Rather than resolve the paradox in the most general case, we look to the simplest special case, namely the monatomic ideal gas. For this system, phase space consists of $3N$ position-space dimensions and $3N$ momentum-space dimensions. Because the particles are restricted to positions within the box, the position-space dimensions contribute a factor of V^N to W . The total energy is

$$\frac{1}{2m}(p_{1,x}^2 + p_{1,y}^2 + p_{1,z}^2 + \cdots + p_{N,x}^2 + p_{N,y}^2 + p_{N,z}^2), \quad (2)$$

where m is the mass of each particle, so the energy restriction implies that the accessible region in momentum space is

a spherical shell with inner radius $\sqrt{2mE}$ and outer radius $\sqrt{2m(E+\Delta E)}$. The volume of a d -dimensional sphere is⁸

$$V_d(r) = \frac{\pi^{d/2}}{(d/2)!} r^d, \quad (3)$$

so the volume of this $3N$ -dimensional shell is

$$\frac{\pi^{3N/2}}{(3N/2)!} [(2m(E+\Delta E))^{3N/2} - (2mE)^{3N/2}], \quad (4)$$

whence

$$W(E, \Delta E, V, N) = V^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!} \left[\left(1 + \frac{\Delta E}{E} \right)^{3N/2} - 1 \right]. \quad (5)$$

(I have rearranged the expressions to make the dimensions more apparent: The quantity in square brackets is dimensionless.)

The entropy follows immediately. It is

$$\begin{aligned} S &= k_B \ln \left\{ \frac{W}{N! h^{3N}} \right\} \\ &= k_B \ln \left\{ \left(\frac{2\pi mE V^{2/3}}{h^2} \right)^{3N/2} \frac{1}{N! (3N/2)!} \right. \\ &\quad \left. \times \left[\left(1 + \frac{\Delta E}{E} \right)^{3N/2} - 1 \right] \right\}, \end{aligned} \quad (6)$$

so

$$\begin{aligned} \frac{S}{k_B} &= \frac{3}{2} N \ln \left(\frac{2\pi mE V^{2/3}}{h^2} \right) - \ln N! - \ln \left(\frac{3}{2} N \right)! \\ &\quad + \ln \left[\left(1 + \frac{\Delta E}{E} \right)^{3N/2} - 1 \right]. \end{aligned} \quad (7)$$

What happens when we take the limit $\Delta E \rightarrow 0$? As demanded by the paradox, the entropy approaches $\ln(0) = -\infty$.

The problem with this result for the entropy is that it attempts to hold for systems of any size. In justifying the definition of the entropy one relies upon the assumption of a ‘‘large’’ system, but in deriving the above expression we never made use of that assumption. In fact, our expectation that we could let $\Delta E \rightarrow 0$ and obtain a sensible result holds only approximately for finite systems: the expectation holds to higher and higher accuracy for larger and larger systems, but it holds exactly only for infinite systems, that is, for systems in the thermodynamic limit.

The thermodynamic limit, in the microcanonical case, consists of allowing the system’s particle number, volume, energy, and energy spread all to grow without bound, but to do so in such a way that the intensive ratios remain finite. That is, we allow

$$\begin{aligned} N \rightarrow \infty \text{ in such a way that } V/N \rightarrow v, \quad E/N \rightarrow e, \\ \text{and } \Delta E/N \rightarrow \delta e. \end{aligned} \quad (8)$$

In this limit we expect that the entropy will grow linearly with system size, that is,

$$S(E, \Delta E, V, N) \rightarrow Ns(e, v, \delta e). \quad (9)$$

To prepare for taking the thermodynamic limit of Eq. (7), write V as vN , E as eN , and ΔE as δeN , so that the only extensive variable is N . This results in

$$\begin{aligned} \frac{S}{k_B} &= \frac{3}{2} N \ln \left(\frac{2\pi m e v^{2/3} N^{5/3}}{h^2} \right) - \ln N! - \ln \left(\frac{3}{2} N \right)! \\ &\quad + \ln \left[\left(1 + \frac{\delta e}{e} \right)^{3N/2} - 1 \right] \\ &= \frac{3}{2} N \ln \left(\frac{2\pi m e v^{2/3}}{h^2} \right) \\ &\quad + \frac{3}{2} N \ln N^{5/3} - \ln N! - \ln \left(\frac{3}{2} N \right)! + \ln \left[\left(1 + \frac{\delta e}{e} \right)^{3N/2} - 1 \right]. \end{aligned} \quad (10)$$

Now use Stirling’s approximation,

$$\ln n! \approx n \ln n - n \quad \text{for } n \gg 1, \quad (11)$$

to simplify the expressions like $\ln(\frac{3}{2}N)!$ above. The middle three terms are approximately (in an approximation that becomes exact as $N \rightarrow \infty$)

$$\begin{aligned} \frac{3}{2} N \ln N^{5/3} - \ln N! - \ln \left(\frac{3}{2} N \right)! &\approx \frac{5}{2} N \ln N - N \ln N + N \\ &\quad - \left(\frac{3}{2} N \right) \ln \left(\frac{3}{2} N \right) + \frac{3}{2} N \\ &= N \left[\frac{5}{2} - \frac{3}{2} \ln \left(\frac{3}{2} \right) \right]. \end{aligned} \quad (12)$$

After this manipulation, we have

$$\begin{aligned} \frac{S}{k_B} &\approx \frac{3}{2} N \ln \left(\frac{2\pi m e v^{2/3}}{h^2} \right) + N \left[\frac{5}{2} - \frac{3}{2} \ln \left(\frac{3}{2} \right) \right] \\ &\quad + \ln \left[\left(1 + \frac{\delta e}{e} \right)^{3N/2} - 1 \right]. \end{aligned} \quad (13)$$

All the pieces grow linearly with N except for the rightmost one—the piece related to ΔE ! In this rightmost piece, as N grows, the term $(1 + \delta e/e)^{3N/2}$ completely dominates 1 as $N \rightarrow \infty$ (so long as $\delta e/e$ is positive, no matter how small). Thus

$$\begin{aligned} \ln \left[\left(1 + \frac{\delta e}{e} \right)^{3N/2} - 1 \right] &\approx \ln \left(1 + \frac{\delta e}{e} \right)^{3N/2} \\ &= \frac{3}{2} N \ln \left(1 + \frac{\delta e}{e} \right). \end{aligned} \quad (14)$$

This term is not only linear with N in the thermodynamic limit, it also has a well-behaved limit (it vanishes) when $\delta e \rightarrow 0$!

This special case, the ideal gas, illustrates the general principle that resolves our paradox: One must first take the thermodynamic limit $N \rightarrow \infty$, and only then take the ‘‘thin phase space’’ limit $\delta e \equiv \Delta E/N \rightarrow 0$.

With this understanding in place, we find that the entropy is finite when $\Delta E \rightarrow 0$, that it does indeed grow linearly with N , and that it is given by the well-known Sackur–Tetrode formula

$$S(E, V, N) = k_B N \left[\frac{3}{2} \ln \left(\frac{4\pi m e v^{2/3}}{3h^2} \right) + \frac{5}{2} \right]. \quad (15)$$

II. EXTENSIVITY

The expression (7) for the entropy of a finite system is not extensive: If you double E , V , and N , you will not exactly

Table I. The entropy of a finite system is not extensive. (The “error” column lists the percentage difference between, for example, S_{20} and $2S_{10}$. If the entropy were extensive, all the entries in this column would be zero.)

N	S_N	$2S_{N/2}$	Error
10	52.99		
20	110.14	105.98	-3.8%
40	224.75	220.28	-2.0%

double S . Only the Sackur–Tetrode formula (15), which holds in the thermodynamic limit, produces an exactly extensive entropy. The lack of extensivity can be demonstrated through the following concrete illustration. Because we need a purely mathematical result, we ignore dimensions and arbitrarily select $k_B=1$, $E=3N$, $V=8N$, $\Delta E=0.3N$, and $2\pi m/h^2=1$. Evaluating expression (7) for selected values of N produces the results in Table I. Clearly, this expression for the entropy is *not* extensive. (The Appendix presents a problem that can help underscore this point for students.)

III. EQUIVALENCE OF ENSEMBLES

The microcanonical and canonical ensembles are conceptually quite distinct. The microcanonical ensemble—characterized by E , V , and N —is a collection of microstates Γ with energies $H(\Gamma)$ ranging from E to $E+\Delta E$, and with equal probability of encountering any such microstate. The canonical ensemble—characterized by T , V , and N —is a collection of microstates Γ with any possible energy, and with probability

$$\frac{e^{-H(\Gamma)/k_B T}}{Z(T, V, N)} \quad (16)$$

of encountering microstate Γ . (Here Z is the partition function.)

In addition, the microcanonical and canonical ensembles are operationally quite distinct. For example, described below are the two procedures for finding $E(T, V, N)$.

Using the microcanonical ensemble, the procedure is to (1) find the number of accessible microstates $\Omega(E, V, N)$, (2) calculate the thermodynamic entropy function $S(E, V, N) = k_B \ln(\Omega)$, (3) calculate the temperature through the thermodynamic relation

$$\frac{1}{T(E, V, N)} = \left(\frac{\partial S}{\partial E} \right)_{V, N}, \quad (17)$$

and finally (4) solve this expression for E to produce the desired function $E(T, V, N)$.

In contrast, using the canonical ensemble one must (1) find the partition function $Z(T, V, N)$, (2) calculate the thermodynamic free energy function $F(T, V, N) = -k_B T \ln(Z)$, and then (3) use the Gibbs–Helmholtz relation

$$E(T, V, N) = \left(\frac{\partial(F/T)}{\partial(1/T)} \right)_{V, N} = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{V, N} \quad (18)$$

to produce the desired function $E(T, V, N)$.

Despite these vast conceptual and operational differences, the principle of “equivalence of ensembles” guarantees that

the two functions $E(T, V, N)$ produced through these two very different procedures will be exactly the same! Surely, this remarkable result requires explication.

Rather than provide a detailed proof, undergraduate texts typically give plausibility arguments.⁹ This is the correct pedagogical choice, because the detailed proofs (which hold even for interacting particles) are excruciatingly difficult.^{6,7} Yet any student trained to expect rigor will find this strategy inadequate.

A reasonable approach is to discuss the equivalence of ensembles, refer to the plausibility arguments in the text, and then prove the result in the ideal gas case by having the student actually execute both procedures. [Suggested wording for this problem is given in the appendix. Alternatively, the student could calculate the entropy $S(E, V, N)$ using the canonical ensemble, and compare it to the result previously obtained using the microcanonical ensemble.] The student will find that the results of the two different procedures are indeed identical, *but only in the thermodynamic limit!*

IV. PHASE TRANSITIONS

Iced tea, boiling water, and other aspects of two-phase coexistence are familiar features of daily life. Yet we will soon see that phase transitions do not exist at all in finite systems! They appear only in the thermodynamic limit.

A phase transition is marked by a singularity (usually a discontinuity) in the entropy function $S(T)$. How can such a singularity appear? The Boltzmann factor $e^{-H(\Gamma)/k_B T}$ is an analytic function of T except at $T=0$. For $T>0$ the partition function,

$$Z(T) = \sum_{\text{microstates } \Gamma} e^{-H(\Gamma)/k_B T}, \quad (19)$$

is a sum of positive, analytic functions of T , so it is a positive, analytic function of T . The free energy,

$$F(T) = -k_B T \ln(Z(T)), \quad (20)$$

will have a singularity whenever $Z=0$, but Z is never equal to zero, so $F(T)$ is likewise analytic for $T>0$. The entropy,

$$S(T) = - \frac{\partial F}{\partial T}, \quad (21)$$

is of course analytic again. Thus there is no mechanism to produce a phase transition except at zero temperature.

The analysis of the above paragraph is absolutely correct for finite systems. Phase transitions arise when an additional mathematical step is introduced: the thermodynamic limit. For any finite system, the curve of S as a function of T might be very steep, but it is never discontinuous. The “growth of a phase transition” as N approaches infinity is insightfully discussed in the lectures by Fisher.¹⁰ A specific example, with graphs, is given in Ref. 11.

V. DENSITY OF LEVELS IN k -SPACE

Sooner or later, every statistical mechanics text introduces the energy eigenstates of a single independent particle in a cube of volume $V=L^3$, usually with periodic boundary conditions.¹² These so-called levels are characterized by wave vectors¹³

$$\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \quad \text{where } n_i = 0, \pm 1, \pm 2, \dots \quad (22)$$

And sooner or later, in the process of executing sums over these levels, every text replaces these sums with volume integrals in k -space.

It is clear that a sum is not an integral, so why can we get away with this replacement? Because the distance between adjacent “allowed wavevectors” is $2\pi/L$. In the thermodynamic limit, $L \rightarrow \infty$ so the allowed wave vectors become densely packed in k space. In all but the rarest situations (see the next section) this limit permits the sums to be replaced by integrals.

VI. BOSE CONDENSATION

The argument for Bose condensation can be outlined as follows:¹⁴ The chemical potential $\mu(T, V, N)$ is determined by demanding that

$$N = \sum_r \frac{1}{e^{(\epsilon_r - \mu)/k_B T} - 1}, \quad (23)$$

where the one-particle level r has energy eigenvalue ϵ_r . To carry out this process, it is convenient to approximate this sum by an integral which, with full consideration for degeneracy, turns out to be

$$N = V \left[\frac{\sqrt{2m^3}}{2\pi^2 \hbar^3} \right] \int_0^\infty \frac{\sqrt{\mathcal{E}}}{e^{(\mathcal{E} - \mu)/k_B T} - 1} d\mathcal{E}. \quad (24)$$

The integral on the right cannot be evaluated in closed form, but one can establish an upper bound, namely

$$N < V \left[\frac{2\pi m k_B T}{h^2} \right]^{3/2} (2.612\dots). \quad (25)$$

For a system with a given N and V , this condition will be violated when the temperature is low enough. This violation marks the Bose condensation.

Anyone approaching this argument critically will find it extremely suspect. “You approximated a sum by an integral, and when that approximation proved untenable, you should have gone back to evaluate the sum more accurately. Instead, you threw your hands into the air and invented a phase transition!” Indeed, arguments¹⁵ similar to those of Sec. IV show rigorously that the exact summation (22) cannot admit a phase transition, suggesting that the so-called “Bose condensation” is nothing but a failure of the approximation with no physical significance.

The resolution of this paradox would require more pages than are in this paper.^{15,16} Suffice it to say that when the thermodynamic limit is taken with exquisite care (and it is so taken in the papers cited), then the crossover behavior at the Bose condensation point is no mere breakdown in an approximation, but a true physical effect. (The thermodynamic limit also plays an interesting, although less central, role in Fermi–Dirac statistics.¹⁷ Also of interest is the Bose condensation of particles that are independent but not free.¹⁸)

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2000. During the 13 years that Professor Romer edited this journal, he has often suggested improvements in my papers—ranging from deep physics issues to spelling corrections—but he never allowed me to acknowledge these suggestions. “I’m just doing my job,” he would say, and then use his power as editor to excise any sentence of acknowledgment that I had included. Now that Professor Romer is no longer editor, I am at last able to acknowledge his help not only in this paper, but also in all the other papers that I have published in AJP. In grateful acknowledgment I dedicate this paper to him.

APPENDIX

Here are two problems that can be assigned to students to help drive home the ideas presented in this paper.

(1) *The extensivity of entropy*: For the classical monatomic ideal gas, plot the entropy as a function of particle number using both the “finite size” form (7) and the Sackur–Tetrode form (15). All other things being equal, is the thermodynamic limit approached more rapidly for atoms of high mass or for atoms of low mass?

(2) *Equivalence of canonical and microcanonical ensembles*: For the classical monatomic ideal gas, the canonical partition function is

$$Z(T, V, N) = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}. \quad (A1)$$

Carry out the procedure described in Sec. III to show that the energy calculated in the canonical ensemble is

$$E = \frac{3}{2} N k_B T. \quad (A2)$$

In addition, start with the “finite size” microcanonical entropy equation (7) and carry out the microcanonical procedure described in Sec. III to find

$$E = \frac{3}{2} N k_B T \left[1 - \frac{\delta e}{e} \left(1 + \frac{\delta e}{e} \right)^{(3N/2)-1} \left[\left(1 + \frac{\delta e}{e} \right)^{(3N/2)} - 1 \right]^{-1} \right]. \quad (A3)$$

Under what conditions are these two expressions for E identical?

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¹F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).

²Charles Kittel and Herbert Kroemer, *Thermal Physics*, 2nd ed. (W. H. Freeman, New York, 1980).

³Ralph Baierlein, *Thermal Physics* (Cambridge University Press, Cambridge, UK, 1999).

⁴Daniel V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, San Francisco, 2000).

⁵Colin J. Thompson, *Classical Equilibrium Statistical Mechanics* (Clarendon, Oxford, UK, 1988), Chap. 3.

⁶Michael E. Fisher, “The free energy of a macroscopic system,” *Arch. Ration. Mech. Anal.* **17**, 377–410 (1964).

⁷David Ruelle, *Statistical Mechanics: Rigorous Results* (W. A. Benjamin, Reading, MA, 1969).

⁸*Standard Mathematical Tables and Formulae*, edited by Daniel Zwillinger (CRC Press, Boca Raton, FL, 1996), Eq. (4.18.2).

⁹See, for example, Ref. 1, pp. 205–206 and 219–232.

¹⁰Michael E. Fisher, “The nature of critical points,” *Lectures in Theoretical Physics* (University of Colorado Press, Boulder, Colorado, 1965), Vol. 7, Part C, pp. 1–159. See particularly Secs. 12 and 13.

¹¹Arthur E. Ferdinand and Michael E. Fisher, “Bounded and inhomogeneous Ising models. I. Specific-heat anomaly of a finite lattice,” *Phys. Rev.* **185**, 832–846 (1969).

¹²See Ref. 1, pp. 353–360; Ref. 2, pp. 72–73; Ref. 3, pp. 75–80; or Ref. 4, pp. 251–255.

¹³Professor W. Bruce Richards of the Oberlin College Physics Department calls these “allowed wavevectors” the “special ks.”

¹⁴For details, see Ref. 2, pp. 199–206; Ref. 3, pp. 199–209; or Ref. 4, pp. 315–319.

¹⁵Robert M. Ziff, George E. Uhlenbeck, and Mark Kac, “The ideal Bose–Einstein gas, revisited,” *Phys. Rep.* **32**, 169–248 (1977), especially pp. 172–173.

¹⁶G. Scharf, “On Bose–Einstein condensation,” *Am. J. Phys.* **61**, 843–845 (1993); William J. Mullin, “The loop-gas approach to Bose–Einstein condensation for trapped particles,” *ibid.* **68**, 120–128 (2000).

¹⁷K. Schönhammer, “Thermodynamics and occupation numbers of a Fermi gas in the canonical ensemble,” *Am. J. Phys.* **68**, 1032–1037 (2000).

¹⁸Martin Ligare, “Numerical analysis of Bose–Einstein condensation in a three-dimensional harmonic oscillator potential,” *Am. J. Phys.* **66**, 185–190 (1998).



Bottle Bursting Apparatus. This apparatus at Denison University was bought from the Central Scientific Company of Chicago ca. 1905. In the 1927 catalogue it is listed at \$3.25, including two extra 175 cc bottles. It demonstrates the incompressibility of water. The bottle is filled completely with water, and the top is clamped down firmly. The piston rod is then pushed down, highly incompressible water pushes against the sides of the glass bottle, and the bottle breaks. Today, safety precautions would be taken when doing the demonstration! (Photograph and notes by Thomas B. Greenslade, Jr., Kenyon College)