

PHY831 Statistical Mechanics  
Chapter 2: 2.6 - 2.7 (Conceptual)

Mason Boles and Teh, Chi En

Presented on November 29, 2017

1. (2.6 Grand Canonical vs. Canonical)

Suppose you are studying an open system with many moles in number count. Is it reasonable to approximate a canonical ensemble as a grand canonical ensemble in this case? Why?

Solution: Yes. Although the grand canonical ensemble assumes a spread of particle number around an average  $\bar{N}$ , the fluctuation goes as

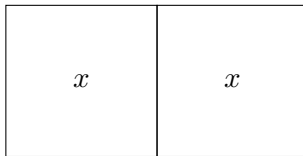
$$\frac{(\Delta\bar{N})}{\bar{N}} = \frac{1}{\sqrt{\bar{N}}}$$

which goes to 0 as  $\bar{N} \rightarrow \infty$ . For an open single mole system where  $\bar{N}$  is on the order of  $10^{24}$ , the fluctuation of particle number is around  $10^{-12}$  and the ensemble can be thought of as canonical, i.e., has constant particle count.

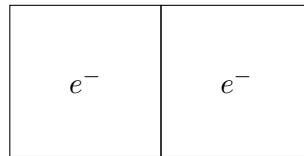
2. (2.7 Gibb's Paradox)

Consider three equally parted boxes that are kept under constant temperature, with each partition containing  $N/2$  number of the following particles:

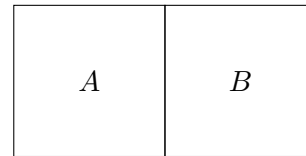
- (a) identical spinless particles  $x$  in both sides;
- (b) electrons in both sides;
- (c) 2 types of identical spinless particles  $A$  and  $B$  in each side.



(a)



(b)



(c)

After removing the partitions from all these boxes, which of the following relation correctly describes their respective changes in entropy?

- (A)  $0 = \Delta S_a < \Delta S_b < \Delta S_c$
- (B)  $0 < \Delta S_a = \Delta S_b < \Delta S_c$
- (C)  $0 < \Delta S_a < \Delta S_b = \Delta S_c$
- (D)  $0 = \Delta S_a = \Delta S_b < \Delta S_c$
- (E) None of the above.

Solution: Both (a) and (b) have zero change in entropy (recall Gibb's paradox). For (c), after removal of the partition, the box will evolve into a mixed system, increasing the entropy. Hence, (D)  $0 = \Delta S_a = \Delta S_b < \Delta S_c$ .