MIT Course X PhD Qualifying Exam Study Guide

April 22, 2016

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Chapter 1

Multiscale Analysis

1.1 Basic Physics (1-1)

Physics (Box 1-1)

Descriptions of Matter, Energy, and Moments

Macro- and Micro- Views

Types of work interactions

$\delta W = F \cdot d\underline{x}$

Type of work	$F \cdot \mathrm{d}\underline{x}$
Pressure-Volume	$-P \cdot \mathrm{d}\underline{V}$
Frictional	$F_f \cdot \mathrm{d}\underline{x}$
Surface Deformation	$\sigma \cdot \mathrm{d}\underline{a}$
Electrical Charge Transport	$\epsilon \cdot \mathrm{d}\underline{q}$
Electric Polarization	$E \cdot \mathrm{d}\underline{D}$
Magnetic Polarization	$H \cdot \mathrm{d}\underline{B}$
Stress-Strain	$\underline{V}_0({}^{F_x}/_{\underline{a}})\mathrm{d}\Omega = \underline{V}_0({}^{F_x}/_{\underline{a}})^{\mathrm{d}x}/_{x_0}$

1.2 Quantum

1.3 Single Molecule (7-2 – 7-4)

Potential Fundamentals (Box 7-2)

$F = \frac{\mathrm{d}u}{\mathrm{d}r}$

Coulombic interaction: $u \sim \frac{q_i q_j}{r}$

Dipole-Dipole: $u_{d-d} \sim \frac{-\epsilon_{dipole}}{r^6 kT}$

Dispersion-Attraction: $u_{att} \sim \frac{-\epsilon_{att}}{r^6}$

Repulsion: $u_{rep} \sim \frac{-\epsilon_{rep}}{r^{12}}$

Mixing for Potential Functions (Box 7-3)

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$
$$\epsilon_{ij} = \left(\epsilon_{ii}\epsilon_{jj}\right)^{1/2}$$

Potential (Box 7-4)

Ideal

- $\Phi(r) = 0$
- Parameters: none

Hard Sphere

- $$\Phi(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$
- Parameters: σ

Square well

- $$\Phi(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon & \sigma < r \leq R\sigma \\ 0 & r > R\sigma \end{cases}$$
- Parameters: σ, ϵ, R

Lennard-Jones

- $$\Phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$
- Parameters: σ, ϵ

Kihara

- $$\Phi(r) = 4\epsilon\left[\left(\frac{\sigma - 2a}{r - 2a}\right)^{12} - \left(\frac{\sigma - 2a}{r - 2a}\right)^{6}\right]$$
- Parameters: σ, ϵ, a

Sutherland (νdW)

- $$\Phi(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon\left(\frac{\sigma}{r}\right)^{6} & r > \sigma \end{cases}$$
- Parameters: σ, ϵ

1.4 Molecular Ensemble (2-1)

Statistical Mechanics (Box 2-1)

Goal: Connect quantum state of matter (microscopic) to classical thermodynamics (macroscopic).

Postulates

- Ergodic
  - Time averaging equivalent to ensemble averaging
- Equal A Priori Probabilites
  - States with equal N,V,E are equally likely

$$\beta = \frac{1}{kT},\ \langle B \rangle = \sum P_i B_i,\ \ln N! \approx N \ln N - N,\ P_i = \frac{\exp(-\beta \underline{E}_i)}{\sum \exp(-\beta \underline{E}_i)}$$

1.5 Continuum

1.6 Macroscopic Analysis

Chapter 2

Thermodynamics

2.1 Statistical Mechanics and Calculus

2.1.1 Ensembles and Averaging (2-2 - 2-5, 3-1)

Microcanonical (Box 2-2)

Constant: N, $\underline{\text{V}}$, $\underline{\text{E}}$

Constraint Equations: $\sum n_i = \tilde{N}$

Partition Function:

$\Omega \equiv \omega(\underline{E})$

Natural Function: $S = k \ln \Omega$

Canonical (Box 2-3)

Constant: N, $\underline{\text{V}}$, T

Constraint Equations: $\sum n_i = \tilde{N}, \;\; \sum n_i \underline{E}_i = \underline{E}^{total}$

Partition Function:

$$Q_N \equiv \sum_{\underline{E}_i} \Omega \exp(-\beta \underline{E}_i) = \sum_{\underline{E}_i} \omega(\underline{E}_i) \exp(-\beta \underline{E}_i)$$

$$Q_N \equiv \sum_{i} \exp(-\beta \underline{E}_i)$$

Natural Function: $A = -kT \ln Q_N$

Grand Canonical (Box 2-4)

Constant: $\mu, \underline{V}, T$

Constraint Equations: $\sum n_i = \tilde{N}, \;\; \sum n_i \underline{E}_i = \underline{E}^{total}, \;\; \sum n_i N = N^{total}$

Partition Function:

$$\Xi \equiv \sum_{N} \sum_{\underline{E}_i} Q_N \exp(\beta \mu N) = \sum_{N} \sum_{\underline{E}_i} \omega(\underline{E}_i) \exp(-\beta \underline{E}_i) \exp(\beta \mu N)$$

$$\Xi \equiv \sum_{N} \sum_{i} \exp(-\beta \underline{E}_i) \exp(\beta \mu N)$$

Natural Function: $P\underline{V} = kT \ln \Xi$

Isobaric/Isothermal (Box 2-5)

Constant: N, P, T

Constraint Equations: $\sum n_i = \tilde{N}, \sum n_i \underline{E}_i = \underline{E}^{total}, \sum n_i \underline{V}_i = \underline{V}^{total}$

Partition Function:

$$\Delta \equiv \sum_{\underline{V}} \sum_{\underline{E}_i} Q_N \exp(-\beta P\underline{V}) = \sum_{\underline{V}} \sum_{\underline{E}_i} \omega(\underline{E}_i) \exp(-\beta \underline{E}_i) \exp(-\beta P\underline{V})$$

$$\Delta \equiv \sum_{\underline{V}} \sum_{i} \exp(-\beta \underline{E}_i) \exp(-\beta P\underline{V})$$

Natural Function: $\underline{G} = -kT \ln \Delta$

2.1.2 Applied Statistical Mechanics (4-1 - 6-2)

Classical Approach (Box 6-1)

Criteria: ${}^{\Delta E}/_{kT} \ll 1$

$Q_{cl} = Q_{int} Q_{cm} = Q_{int} Q_{trans} Z = \dfrac{Z Q_{int}}{\Lambda^{3N} N!}$, classical partition coefficient

- $\Lambda \equiv \left(\dfrac{h^2}{2\pi m k T}\right)^{1/2}$, thermal DeBroglie wavelength
- $Q_{int} = \dfrac{{q_{int}}^N}{N!}$, internal partition coefficient
  - $q_{int} = q_{elec} q_{nuc} q_{vib} q_{rot}$, molecular partition coefficient
- $Z^* \equiv \int \dots \int \exp\left[-\dfrac{\Phi(\underline{r}^N)}{kT}\right] \mathrm{d}\underline{r}^N$, configurational integral

Mean Field Theory (Box 6-2)

$$Z^* = \exp\left[-\frac{\left\langle \Phi(\underline{r}^N) \right\rangle}{2kT}\right]^N \left[\underline{V}_f\right]^N$$

- $\left\langle \Phi(\underline{r}^N) \right\rangle = \dfrac{N \langle \rho \rangle}{2} \int\limits_0^\infty \Phi_{ij}(r) g(r) 4\pi r^2 \mathrm{d}r$

- $g(r)$, radial distribution function
- $\Phi_{ij}(r)$, potential function

2.1.3 Property Frameworks

2.1.3.1 Fundamental Surface (13-1 - 13-6)

2.1.3.2 Legendre Transform (14-3)

2.1.3.3 EOS (7-1)

Virial (Box 7-1)

Form

– $p = \rho kT + kT\sum\limits_{n=2}^{\infty} B_n(T)\rho^n = \rho kT(1 + B_2\rho + ...)$

– $B_2(T) = -2\pi N_A \int\limits_0^{\infty} \Big[\exp[-\beta\Phi(r)] - 1\Big] r^2 \mathrm{d}r$

- Quantifies the two-body interaction
  - McMillan-Mayer TM 471
- Hard sphere: $B_2 = \dfrac{2\pi\sigma^3}{3}$
- Square well: $B_2 = \dfrac{2\pi\sigma}{3}\Big[1 + (1 - exp(\beta\epsilon))(R^3 - 1)\Big]$
- Lennard-Jones: $B_2(T) = -2\pi N_A \int\limits_0^{\infty} \left[\exp\left[-\beta\left(4\epsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right]\right)\right] - 1\right] r^2 \mathrm{d}r$

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Osmotic Pressure (Box 8-1)

Vant Hoff Formulation (ideal)

- $\Pi = C_s RT$
- Parallel to Ideal Gas Law ($Cs = {}^{N}/_{V}$)

Equilibrium Approach

- $\mu_w(T, 1bar + \Pi, x_s) = \mu_w(T, 1bar, pure) + RT \ln \gamma_w x_w + \int_1^{1+\Pi} \overline{V}_w \, \mathrm{d}P$
  - For incompressible

- $\ln(\gamma_w) \approx -\ln(x_w) - \frac{\Pi\overline{V}_w}{RT}$ *with* $x_w = 1 - x_s$

Statistical Mechanics Approach

- McMillan-Mayer Theory
  - Grand Canonical Function as natural variable
    - $\ln(\Xi) = \frac{(P+\Pi)\underline{V}}{kT}$
  - Under dilute solution limit,
    - $\frac{\Pi}{kT} = \rho_2 + B_2{\rho_2}^2 + ...$
    - $\frac{\Pi}{C} = \frac{RT}{M_W} + \frac{B_2NRT}{(M_W)^2}C + ...$
      - Graph of $(^{\Pi}/_{C})$ v. C
        - Intercept: $M_W = \frac{RT}{(^{\Pi}/_{C})_{C\to 0}}$
  - Assuming Pairwise additivity
    - $B_2 = -2\pi \int\limits_0^{\infty} \left(\exp\left[\frac{-\langle\Phi_{12}\rangle}{kT}\right] - 1\right) r^2 \mathrm{d}r$
    - For Hard Sphere Interactions
      - $B_2 = \frac{16}{3}\pi {b_0}^3,\ B_3 = \frac{5}{8}{B_2}^2$
  - Using a ΔG^{EX} function
    - $-\overline{V}_1\Pi = RT\ln a_1$
      - Flory-Huggins (11-66)

- $\dfrac{\partial \Delta G^{EX}}{\partial N_1} = RT \ln a_1$

Flory Huggins Theory (Box 8-2)

$\Delta G_{mix} = RT\big[N\phi_1\phi_2\chi + \big(x_1 \ln \phi_1 + x_2 \ln \phi_2\big)\big]$

$\dfrac{\partial \Delta G_{mix}}{\partial x_1} = \mu_1,\ \dfrac{\partial \Delta G_{mix}}{\partial x_2} = \mu_2$

$N_1 = V\phi_1 \ and \ \phi_2 = \dfrac{nN_2}{N_1 + nN_2}$

Binodal

- $\mu_1 - \mu_1^0 = RT\left[\ln\big(1-\phi_2\big) + \left(1 - \dfrac{1}{n}\right) + \chi\phi_2^2\right]$
- $\mu_2 - \mu_2^0 = RT\left[\ln\phi_2 + \big(1-\phi_2\big)\big(1-n\big) + \chi\big(1-\phi_2\big)^2\right]$

Spinodal

- $\dfrac{\partial^2 \Delta G_{mix}}{\partial x_2^2} = 0 = \dfrac{\partial \Delta\mu_1}{\partial \phi_2} = -\dfrac{1}{1-\phi_2} + 1 - \dfrac{1}{n} + 2\chi\phi_2$

Critical Point

- $\dfrac{\partial^3 \Delta G_{mix}}{\partial x_2^3} = 0 = \dfrac{\partial^2 \Delta\mu_1}{\partial \phi_2^2} = -\dfrac{1}{\big(1-\phi_{c,2}\big)^2} + 2\chi_c$
- $\chi_c = \dfrac{1}{2\phi_{1,c}} + 1 - \dfrac{1}{n} + \dfrac{1-\phi_{1,c}}{{\phi_{1,c}}^2} = 0$
- $\chi_c = \dfrac{1}{2}\big(1 + n^{-1/2}\big)^2$

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a
A
B
B
B_i
Bi
Br
c_D
C
C_P
C_V
D
D_{ij}
D_i
Da
D_e
D_0
$\underline{e}_i$
$\underline{e}$
E
E
f
$\widehat{f}$
$f_{\underline{e}_i}$
F
F_B
$g(r)$
G
Gr
h
H
$\mathcal{H}$
H
$\mathcal{H}_i$
H_V
i
I
J_i
k
$k_{c,i}$
K
K
$\mathcal{K}_i$

K_a
K_P
K_y
K_γ
K_ϕ
L
m
M_W
$\underline{n}$
N
N_i
Nu
P
P
Pe
Pr
q_i
q
q_{elec}
q_{int}
q_{nuc}
q_{rot}
q_{trans}
q_{vib}
$q^{(x)}$
Q
Q_{int}
Q_{cl}
Q_{cm}
Q_N
r
R_V
Ra
Re
S
S_A
$\underline{S}$
Sc
Sh
Sr
t
T
u
U
U

v
V
V_f
$\underline{w}$
$\underline{\underline{w}}$
W
x
x_i
x_i
z
z_i
Z
Z^*
α
β
β
β_i
γ_i
γ
$\underline{\underline{\Gamma}}$
δ
Δ
$\epsilon_M, \epsilon_i, \epsilon_E$
ϵ
η
η
Θ
Θ_ν
Θ_n
κ
λ
λ
λ
Λ
μ
μ
ν
ν
ν_{ij}
ν_i
ξ
ξ
Ξ
Π
ρ

σ
σ
$\underline{\underline{\sigma}}$
τ
τ_{ij}
ϕ_i
ϕ
ϕ
Φ
Φ
$\Phi_{ij}(r)$
Φ_n
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Ψ
Ψ
ω
ω
ω_e
Ω
Ω_{mix}
$\Im$
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$\mathcal{R}$
c
e
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$\mathcal{F}$
h
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R
k_B
π
x
$\underline{x}$
$\underline{\underline{x}}$
$\tilde{x}$
$\mathbf{X}$
$\widehat{x}$
$\overline{x}$
$\dot{x}$
$\underline{\nabla}$
$\underline{\nabla}_s$
E^4
0
i

mix
$atherm$
σ
c
EX
id
sat

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5.6 Temporary Appendix - undeclared quantities

box number	undeclared symbol/s	uncertain symbol/s
1-1	none	F_f (force + fugacity) σ (boundary) $\underline{q}$ (heat flux) $\underline{V}_0$ (volume + initial) F_x (force + displacement) x_0 (displacement + initial)
2-1	none	B_i (nth virial coefficient) $\underline{E}_i$ (energy)
2-2	n_i	$\tilde{N}$ (number of moles)
2-3	n_i	$\tilde{N}$ (number of moles)
2-4	n_i	$\tilde{N}$ (number of moles)
2-5	n_i	$\tilde{N}$ (number of moles)
6-1	n	Q_{trans} (heat flow) $\Phi(\underline{r}^N)$ (potential + position + number of moles)
6-2	n	$\underline{V}_f$ (volume + fugacity)
7-1	p	N_A (mass species flux of i, + Helmholtz energy) $\Phi(r)$ (potential + position) σ (molecular radius)
7-2	none	$u_{d-d}, u_{att}, u_{rep}$ (force potential) $\epsilon_{dipole}, \epsilon_{att}, \epsilon_{rep}$ (dielectric)
7-3	none	σ_{ij} (molecular radius) ϵ_{ij} (dielectric constant)
7-4	none	σ (molecular radius) R (ideal gas constant); $\Phi(r)$ (potential + position)
8-1	w, s,$bar, pure, b_0$	C_s, Cs (concentration) x_s, x_w (fraction of species i) μ_w (chemical potential) γ_w (surface tension) $\overline{V}_w, \underline{V}$ (volume) B_2, B_3 (nth virial coefficient) N_i (mass species flux of i); Φ_{12} (potential) a_1 (activity)
8-2	n	μ_i (chemical potential) x_i (fraction of species i)