Errata for second printing of

Statistical Mechanics: Theory and Molecular Simulation

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The following is a list of the most important corrections to the second printing of the book *Statistical Mechanics: Theory and Molecular Simulation* from Oxford University Press.

Chapter 1

1. In Eq. (1.4.19), there is a factor of 1/2 missing in the second term. The equation should read:

$$\sum_{\beta=1}^{3N} G_{\gamma\beta}(q_1,...,q_{3N})\ddot{q}_\beta + \sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\left[\frac{\partial G_{\gamma\beta}}{\partial q_\alpha} - \frac{1}{2}\frac{\partial G_{\alpha\beta}}{\partial q_\gamma}\right]\dot{q}_\alpha\dot{q}_\beta = -\frac{\partial U}{\partial q_\gamma}.$$

Something interesting happens, however, if we try to restore some symmetry to this equation. Note that $\dot{q}_\alpha\dot{q}_\beta$ is symmetric with respect to α and β. Thus, consider rewriting the equation as follows:

$$\sum_{\beta=1}^{3N} G_{\gamma\beta}(q)\ddot{q}_\beta + \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\left[\frac{\partial G_{\gamma\beta}}{\partial q_\alpha} + \frac{\partial g_{\gamma\alpha}}{\partial q_\beta} - \frac{\partial G_{\alpha\beta}}{\partial q_\gamma}\right]\dot{q}_\alpha\dot{q}_\beta = -\frac{\partial U}{\partial q_\gamma}.$$

where q denotes the full set of generalized coordinates. which is obtained simply by writing

$$\sum_{\alpha,\beta}\frac{\partial G_{\gamma\beta}}{\partial q_\alpha}\dot{q}_\alpha\dot{q}_\beta = \frac{1}{2}\sum_{\alpha,\beta}\left[\frac{\partial G_{\gamma\beta}}{\partial q_\alpha}\dot{q}_\alpha\dot{q}_\beta + \frac{\partial G_{\gamma\beta}}{\partial q_\alpha}\right]\dot{q}_\alpha\dot{q}_\beta$$
$$= \frac{1}{2}\sum_{\alpha,\beta}\left[\frac{\partial G_{\gamma\beta}}{\partial q_\alpha}\dot{q}_\alpha\dot{q}_\beta + \frac{\partial G_{\gamma\alpha}}{\partial q_\beta}\right]\dot{q}_\alpha\dot{q}_\beta$$

where the last line is obtained simply by interchanging the summation indices in the second term. If we do this, then we obtain the affine connection in the generalized coordinates

$$\Gamma_{\gamma\beta\alpha} = \frac{1}{2}\left[\frac{\partial G_{\gamma\beta}}{\partial q_\alpha} + \frac{\partial g_{\gamma\alpha}}{\partial q_\beta} - \frac{\partial G_{\alpha\beta}}{\partial q_\gamma}\right] \equiv \frac{1}{2}\left[G_{\gamma\beta,\alpha} + G_{\gamma\alpha,\beta} - G_{\alpha\beta,\gamma}\right]$$

Finally, if we multiply the equation of motion through by the inverse of the mass-metric tensor, which we will denote here as $G^{\lambda\gamma}$, we obtain the equation of motion in the form (expressed using covariant and contravariant indices) as

$$\ddot{q}^\lambda + \Gamma^\lambda_{\alpha\beta}\dot{q}^\alpha\dot{q}^\beta = -G^{\lambda\gamma}\frac{\partial U}{\partial q^\gamma}$$

When $U = 0$, we see manifestly that this becomes the equation of motion for geodesics in the system of curvilinear coordinates.

2. In problem 1.2, the particle should have unit mass ($m = 1$).

Chapter 3

1. Throughout the chapter, the last name of James Stirling, after whom the Stirling approximation for factorials is named, is misspelled as "Sterling".

2. Page 107: The discussion below eqn. (3.9.15) should more precisely be as given below:

> Eqn. (3.9.15) could be used, for example, to obtain $\delta\tilde{\lambda}_1^{(1)}$ followed immediately by an update of all $\mathbf{r}_i^{(1)}$ involved in the $k = 1$ constraint to obtain positions $\mathbf{r}_i^{(2)}$ for this constraint. Given the updated position, eqn. (3.9.15) is used to obtain $\delta\tilde{\lambda}_1^{(2)}$ immediately followed by an update of all $\mathbf{r}_i^{(2)}$ involved in the $k = 1$ constraint, and we iterate until the $k = 1$ constraint is satisfied. We then proceed to the $k = 2$ constraint and iterate until it is satisfied, which will cause a slight violation of the $k = 1$ constraint. Note that satisfying the kth constraint via this procedure causes all $l < k$ constraints to be slightly violated. Thus, after cycling through all of the constraints in this manner, the procedure must be repeated until the full set of constraints is converged to within a given tolerance.

Chapter 4

1. Page 155: In the text following Eqn. (4.6.11), the function $g^{(1)}(\mathbf{r})$ should be $(V/N)\rho^{(1)}(\mathbf{r})$, and later $\rho^{(1)} = (N/V)g^{(1)}(\mathbf{r})$. Thus, Eqn. (4.6.12), the integral of $\rho^{(1)}(\mathbf{r})$ should integrate to N:

$$\int \mathrm{d}\mathbf{r}\ \rho^{(1)}(\mathbf{r}) = N = \frac{N}{V}\int \mathrm{d}\mathbf{r}\ g^{(1)}(\mathbf{r}).$$

2. Pages 203-205: The K in Eqns. (4.12.3), (4.12.10), (4.12.11), (4.12.14), and (4.12.15) should be $2K$. The same is true in the line just below Eqn. (4.12.10).

3. Page 206: In Eqn. (4.12.23), the position update should be $\mathbf{r}_i \longleftarrow \mathbf{r}_i + \Delta t\mathbf{p}_i/m_i$.

Chapter 5

1. Page 238: In eqn. (5.8.4), the equation of motion for p_V should read:

$$\dot{p}_V = -\frac{\partial \mathcal{H}_{\rm A}}{\partial V} = \frac{1}{3}V^{-5/3}\sum_i \frac{\boldsymbol{\pi}_i^2}{m_i} - \frac{1}{3}V^{-2/3}\sum_i \frac{\partial U}{\partial(V^{1/3}\mathbf{s}_i)}\cdot \mathbf{s}_i - P.$$

2. Page 258: In eqn. (5.13.11), the operators on the right side of the equation are in the reverse order. The equation should read:

$$\hat{\mathcal{O}} = \exp(iL_{\rm NHC-baro}\Delta t/2)\exp(iL_{\rm NHC-part}\Delta t/2)$$

$$\times \exp(iL_{\epsilon,2}\Delta t/2)\exp(iL_2\Delta t/2).$$

Chapter 11

1. Page 422: In Eq. (11.5.26), an exponent is missing in the first expression after the equal sign. This part of the expression should read

$$\rho\lambda^3 = \rho\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}$$

Chapter 12

1. Page 484: In Eq. (12.6.26), x_{l+j} on the right side of the equation should be x_{l+k}, so that the equation reads

$$u_{l+k} = x_{l+k} - \frac{kx_{l+k+1} - x_l}{(k+1)} \qquad k = 1, ..., j.$$

Chapter 13

1. In the second line below Eqn. (13.3.26), the expression $\mathbf{C}_i(\mathbf{p},\mathbf{r}) = 1$ should read $\mathbf{C}_i(\mathbf{p},\mathbf{r}) = 0$.

Appendix B

1. On page 662, eqn. (B.21) should read:

$$U_{\mathrm{corr}}(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_{i,j\in\mathrm{intra}} q_i q_j \chi(r_{ij}, g_{\mathrm{max}}) + \frac{\alpha}{\sqrt{\pi}} \mathrm{erfc}(g_{\mathrm{max}}/2\alpha) \sum_i q_i^2,$$

and $U_{\mathrm{corr}}(\mathbf{r}_1, ..., \mathbf{r}_N)$ should be *added* to $U_{\mathrm{excl}}(\mathbf{r}_1, ..., \mathbf{r}_N)$ in order to correct for the finite truncation of reciprocal space.