

统计力学及应用作业 4

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根据教材的 (15.8) 有

$$S = - \left(\frac{\partial G}{\partial T} \right)_P, \quad V = \left(\frac{\partial G}{\partial P} \right)_T. \quad (1.1)$$

又根据

$$G = E - TS + PV, \quad (1.2)$$

$$G = F + PV, \quad (1.3)$$

$$G = H - TS. \quad (1.4)$$

得

$$E = G - T \left(\frac{\partial G}{\partial T} \right)_P + P \left(\frac{\partial G}{\partial P} \right)_T, \quad (1.5)$$

$$F = G - P \left(\frac{\partial G}{\partial P} \right)_T, \quad (1.6)$$

$$H = G - T \left(\frac{\partial G}{\partial T} \right)_P. \quad (1.7)$$

又

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial \left(G - T \left(\frac{\partial G}{\partial T} \right)_P \right)}{\partial T} \right)_P. \quad (1.8)$$

$$C_v = C_p + T \frac{\left(\frac{\partial V}{\partial T} \right)_P^2}{\left(\frac{\partial V}{\partial P} \right)_T} = \left(\frac{\partial \left(G - T \left(\frac{\partial G}{\partial T} \right)_P \right)}{\partial T} \right)_P + T \frac{\left(\frac{\partial \left(\frac{\partial G}{\partial P} \right)_T}{\partial T} \right)_P^2}{\left(\frac{\partial \left(\frac{\partial G}{\partial P} \right)_T}{\partial P} \right)_T}. \quad (1.9)$$

□

2

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_P = T \frac{\partial(S, P)}{\partial(T, P)} = T \frac{\partial(S, P)/\partial(T, V)}{\partial(T, P)/\partial(T, V)} \quad (2.1)$$

$$= T \frac{\left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial P}{\partial V} \right)_T - \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial P}{\partial T} \right)_V}{\left(\frac{\partial P}{\partial V} \right)_T} \quad (2.2)$$

$$= C_v - T \frac{\left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial P}{\partial T} \right)_V}{\left(\frac{\partial P}{\partial V} \right)_T} \quad (2.3)$$

$$= C_v - T \frac{\left(\frac{\partial P}{\partial T} \right)_V^2}{\left(\frac{\partial P}{\partial V} \right)_T}, \quad (2.4)$$

即

$$C_p - C_v = -T \frac{\left(\frac{\partial P}{\partial T} \right)_V^2}{\left(\frac{\partial P}{\partial V} \right)_T}. \quad \square \quad (2.5)$$

3

1

不能, 只能通过状态方程求出 C_p , C_v 的差.

2

通过测量 C_p 或 C_v , 然后积分

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_V \quad (3.1)$$

得 S , 然后通过积分

$$dE = T dS - P dV, \quad (3.2)$$

得 E , 然后可得

$$G = E - TS + PV, \quad (3.3)$$

$$F = E - TS, \quad (3.4)$$

$$H = E + PV. \quad (3.5)$$

3

在 V 不变的情况下

$$E = \int_0^T C_v(\tau) \tau d\tau, \quad (3.6)$$

$$S = \int_0^T C_v(\tau) / \tau d\tau. \quad (3.7)$$

$$G = \int_0^T C_v(\tau) \tau d\tau - T \int_0^T C_v(\tau) / \tau d\tau + PV, \quad (3.8)$$

$$F = \int_0^T C_v(\tau) \tau d\tau - T \int_0^T C_v(\tau) / \tau d\tau, \quad (3.9)$$

$$H = \int_0^T C_v(\tau) \tau d\tau + PV. \quad (3.10)$$

4

一个一维简谐振子与一个温度为 τ 的热库相互作用, 简谐振子 $H = \frac{p^2}{2} + \frac{x^2}{2}$, $\tau = 1.5$ (无量纲单位). 用 Metropolis 方法求相空间分布 $\rho(x, p)$.

1. 相点初始位置为 $(0, 0)$.

2. 若相点在某一点 x_1 , 则在两个方向都产生一个位移, 步长为 $[0, 6]$ 中的一个随机数, 到达点 x_2 .

3. 根据

$$E = e^{-H/\tau} \quad (4.1)$$

来计算其概率密度.

(a) 若 $E_2 < E_1$, 则相点移动到 x_2 .

(b) 若 $E_2 > E_1$, 则产生一个 $[0, 1]$ 中的随机数 ξ , 若 $\xi < e^{-(H_2-H_1)/\tau}$ 则相点移动到 x_2 . 否则不移动.

4. 重复 2,3, 直到给定的停止条件.

图 4.1 为散点分布图, 可以发现粒子处于原点的概率最大. 图 4.2 为二维概率密度分布图, 即 $\rho(x, p)$.

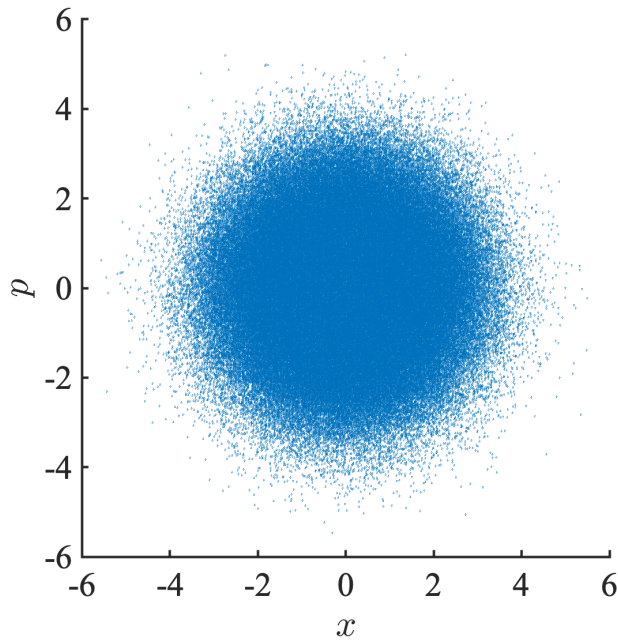


图 4.1. 散点图.

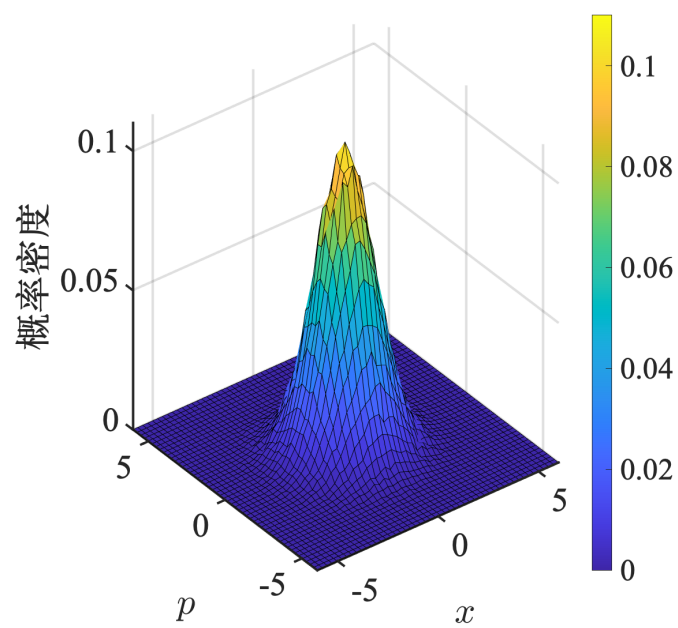


图 4.2. 概率密度图.